



Flow Control Division



Refinery Processes Industry Guide

Valtek Control Products

Refinery Processes Industry Guide

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Refining Industry

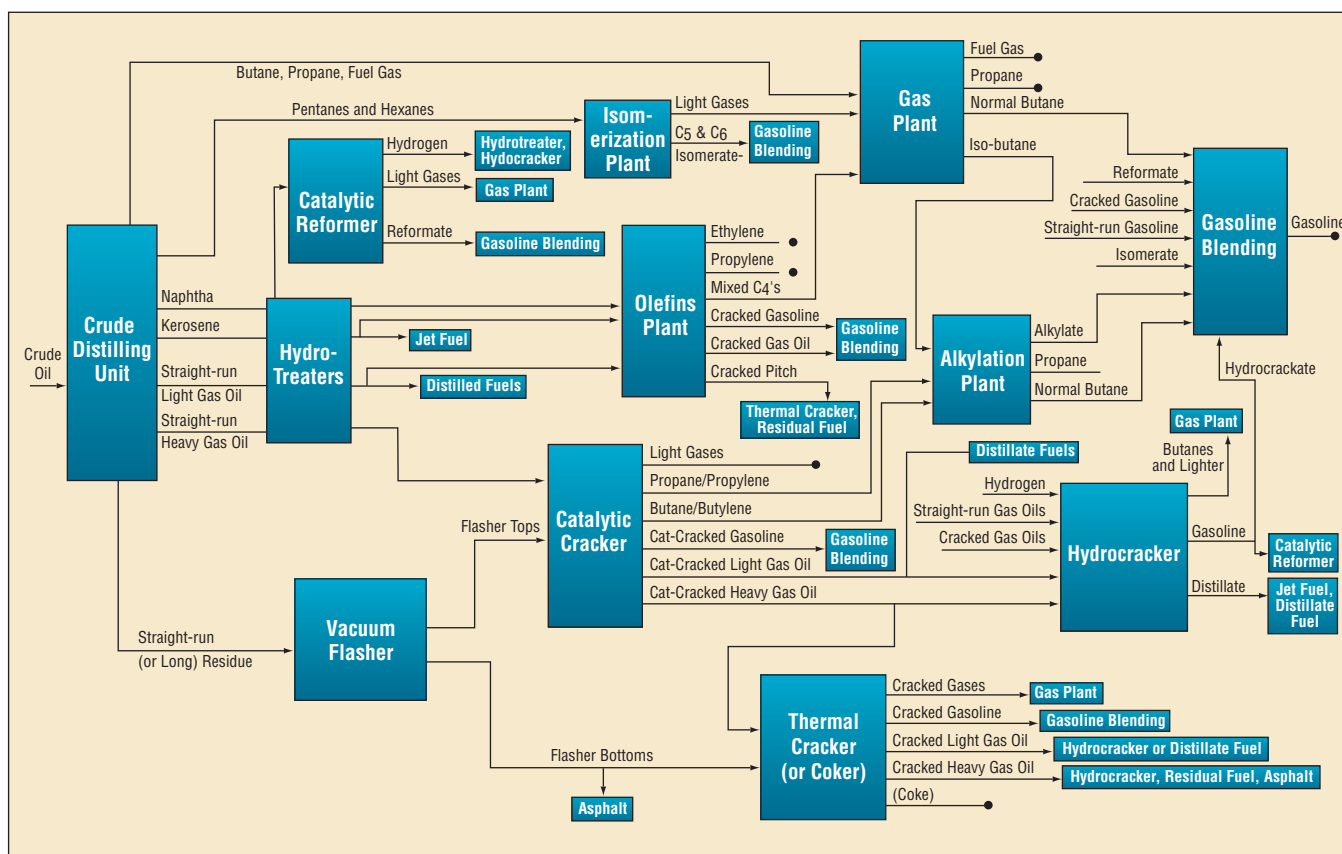


Figure 1: Refining Process Flow Diagram

Introduction to Refining

The modern crude oil *refinery* is designed to convert basic raw crude oil into various useful products through a series of separation and chemical processes. For example, the refinery process is used to produce gasoline, kerosene, light oils, lubricating oils, and gases.

By nature, many refining applications are severe services characterized by extreme temperatures, erosion, corrosion, and high pressure drops. With strict environ-

mental requirements, process equipment must also restrict fugitive emissions to acceptable limits.

The purpose of this guide is to outline these processes, while offering selection guidelines for choosing the correct control valve for a particular refining application.

As shown in Figure 1, a typical refinery is divided into several subprocesses or plants.



Crude Distilling Unit

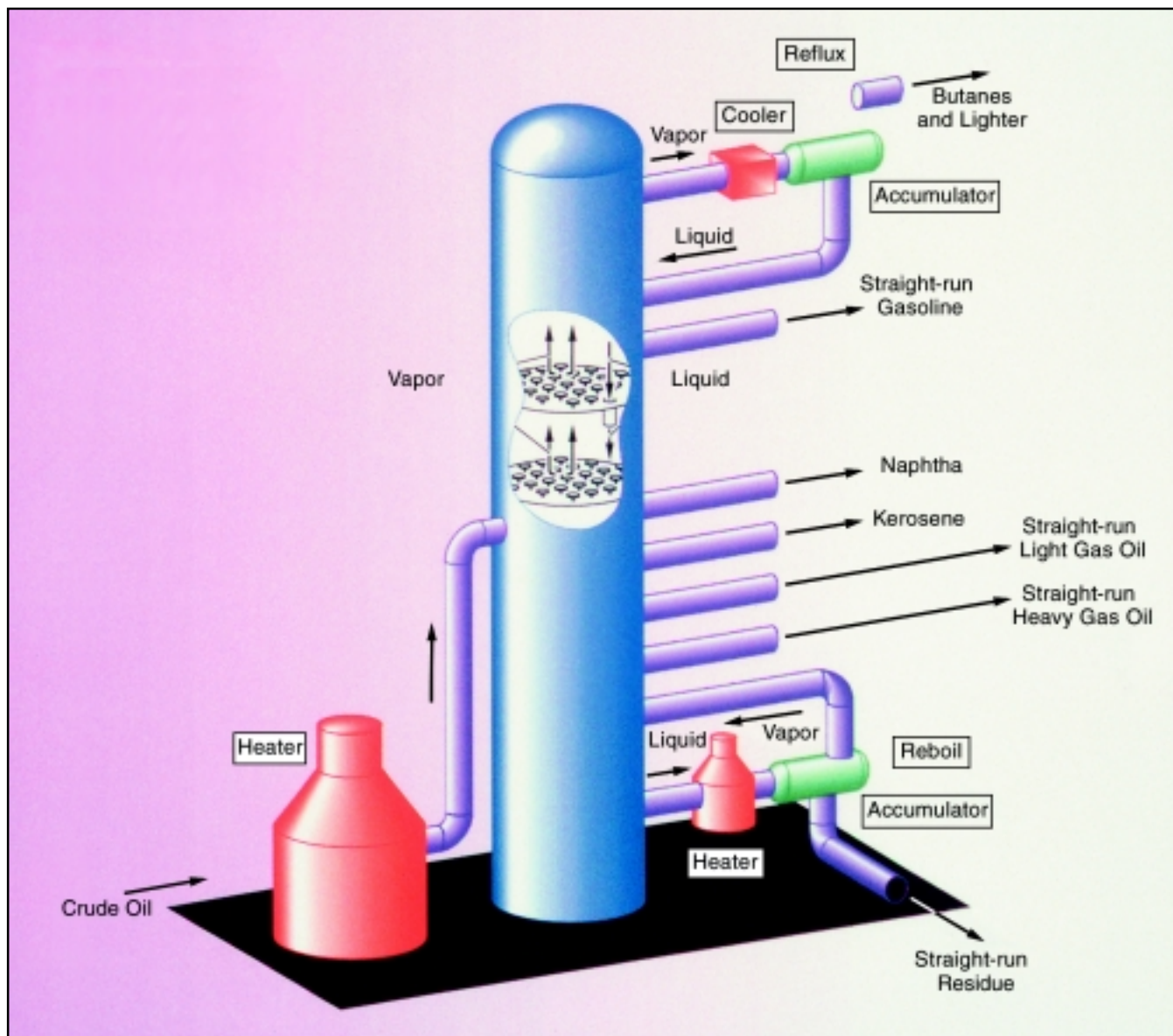


Figure 2: Crude Distilling Unit

Crude Oil Characteristics

Crude oil is a carbon- and hydrogen-based natural resource liquid used to produce petroleum products. It is not just one chemical compound; rather, it is a mixture of chemical compounds. This becomes apparent when the crude oil is heated. When heated to its boiling point, crude oil does not completely evaporate and leaves a residue. In contrast, if water (which is a pure compound) is heated to its boiling point and left at that temperature, it would continue to boil until no water remained. A thermometer would indicate that the water stayed at its boiling point 212° F at 14.7 psia (100° C at 1 bar) throughout the process.

Unlike water, crude is not a single chemical compound, but rather thousands of different chemical compounds. Some of these compounds are as simple as methane (CH_4) or more complex such as isooctane (C_8H_{18}). The important point to remember is that each one of these compounds has its own boiling temperature. For example, if a vessel filled with a medium weight crude is heated until it reaches a temperature of about 150° F (66° C), the oil will begin to boil. If enough heat is applied to keep the vessel at 150° F (66° C), soon the vessel will stop boiling. If the heat is applied to raise the temperature to 350° F (177° C), the vessel will begin to boil again and stop after a period of time.

This process can be repeated many times, boiling off more crude with each step and increase in temperature. The compounds that boil at a temperature below 150° F (66° C), vaporized in the first step, while the compounds that boil at a temperature between 150° F and 350° F (66° and 177° C) vaporized in the second step, and so forth. With this process, a distillation curve can be developed, which is a plot of temperature on one scale and the percent evaporated on the other. Each type of crude oil has a unique distillation curve that determines what kinds of chemical compounds are in the crude (Figure 3).

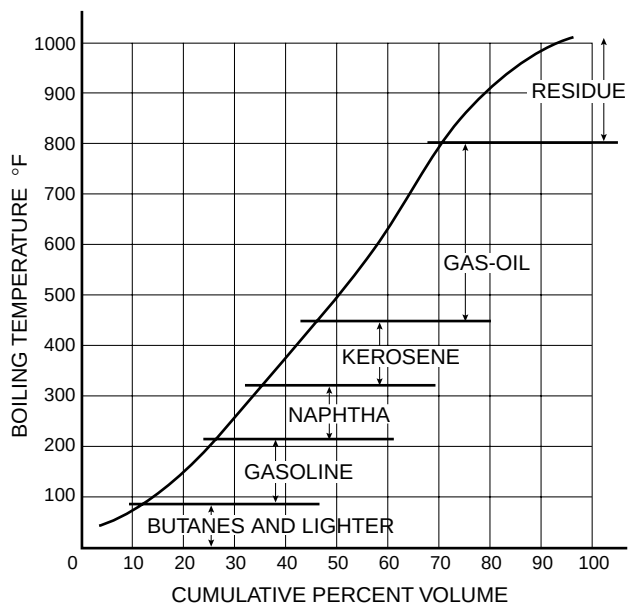


Figure 3: Crude Oil Distillation Curve and Fractions

When further specifying the character of crude oil, grouping certain compounds in fractions or cuts is useful. The typical crude oil has the following fractions:

Table I: Crude Oil Temperatures/Fractions

Temperatures	Fraction
Less than 90° F (32° C)	butanes and lighter
90 - 220° F (32 - 104° C)	gasoline
220 - 315° F (104 - 157° C)	naphtha
315 - 450° F (157 - 232° C)	kerosene
450 - 800° F (232 - 427° C)	gas oil
800° F (427° C) and above	residue

Crude oil compositions may vary widely. *Light crude oil* tends to have more gasoline, naphtha and kerosene; *heavy crude oil* tends to have more gas oil and residue. Generally, the heavier the compound, the higher the boiling temperature.

Introduction to Distillation

Distillation is the process of using heat to separate light and heavy crude oil. To begin the distillation process, the crude oil is heated to about 800° F (426° C) and flows to the bottom of the main crude column (Figure 4).

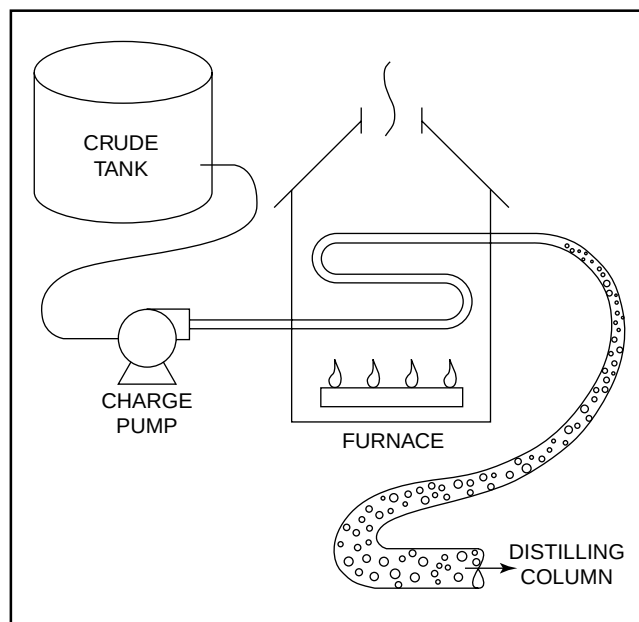


Figure 4: Crude Oil Feed to Distilling

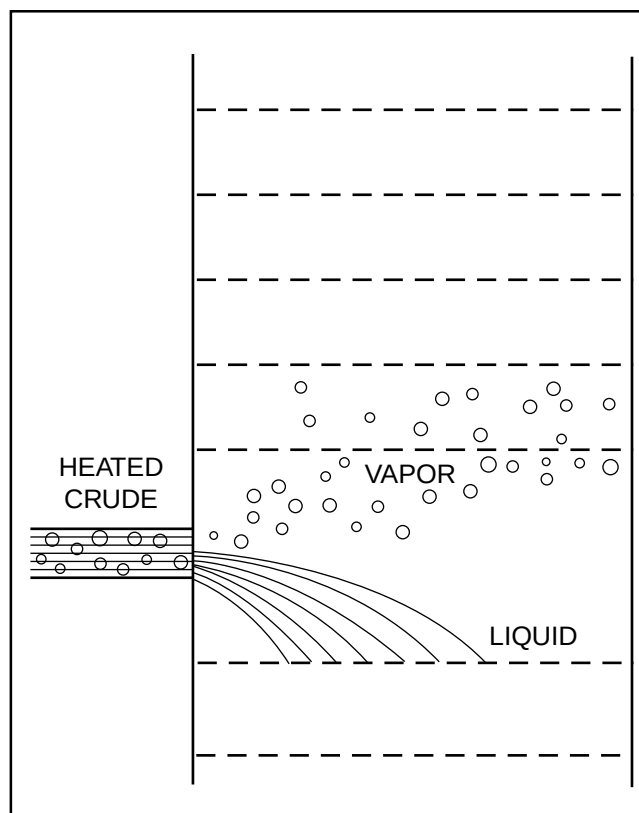


Figure 5: Crude Entering the Distilling Column

Liquid boiling above 800° F (427° C) does not vaporize and exits from the bottom of the column (Figure 5). Inside the distilling column are trays with perforations in them. The perforations permit the vapors to rise through the column. When the crude liquid/vapor charge reaches the inside of the distilling column, gravity causes the denser (heavier) liquid to drop toward the column bottom, but the less dense (lighter) vapors start moving through the trays toward the top.

The perforations in the trays are fitted with a device called *bubble caps* (Figure 6). The bubble caps force the vapor coming up through the trays to bubble through the liquid standing several inches deep on that tray. This bubbling is essential for the distilling operation. The hot vapor bubbles through the liquid and transfers heat to the liquid during the bubbling. As the vapor bubbles cool, some of the hydrocarbons in the bubbles will change from vapor to a liquid state. As heat transfers from vapor to a liquid, the temperature of the vapor drops. The lower temperature of the liquid causes some of the compounds in the vapor to condense and liquefy.

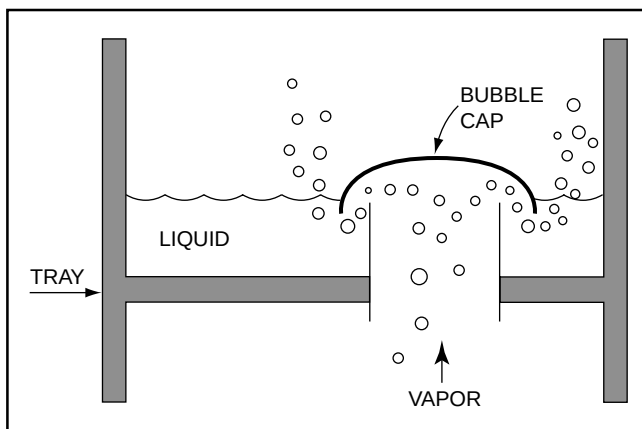


Figure 6: Bubble Cap on a Distilling Column Tray

After the gas has passed through the liquid and sheds some of the heavier hydrocarbons, the vapor then moves up to the next tray where the same process takes place. The amount of liquid on each tray grows as some of the hydrocarbons from the vapor are stripped out. A *downcomer* is installed to permit excess liquid to overflow to the next lower tray. This cycle is continuous and repetitive. Some of the molecules in the compounds make several round trips: up a couple of trays as vapor, finally condensing, then down a few trays via the downcomer as a liquid (Figure 7). This mixing of liquid/vapor creates the separation.

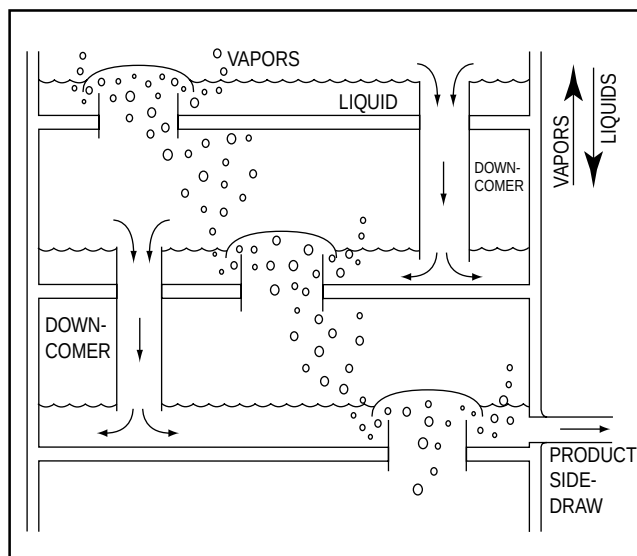


Figure 7: Downcomers and Sidedraws

At several levels on the column, *sidedraws* take the liquid-distilled product off the lighter products (lower boiling points) from the top of the column, and the heavier liquids (higher boiling points) toward the bottom (see Fig. 8).

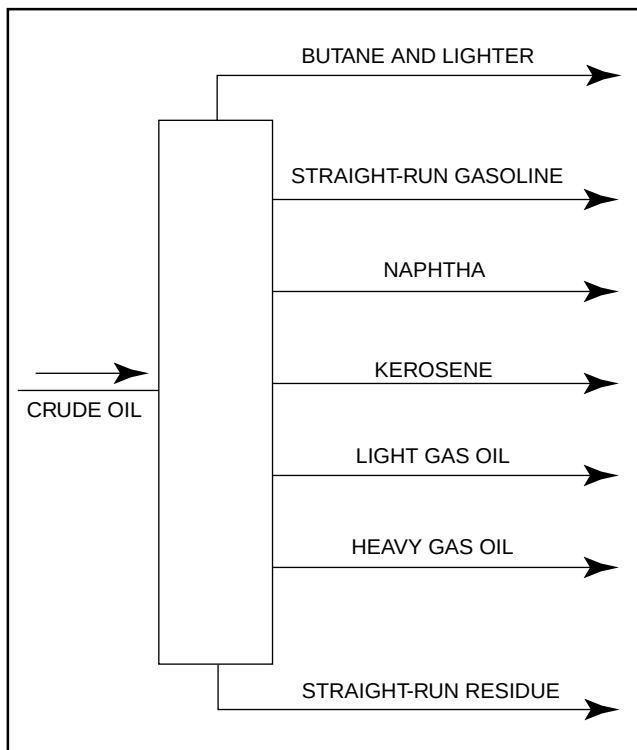


Figure 8: Distilling Sidedraws

Several processes are designed outside the distilling column to facilitate the operation. To assure purity and to eliminate carry-over, a portion of the vapor will be run through a cooler. Condensed liquid is reintroduced to a lower tray, while remaining vapor is sent off as product to the distillation column. This process is called reflux (Figure 9).

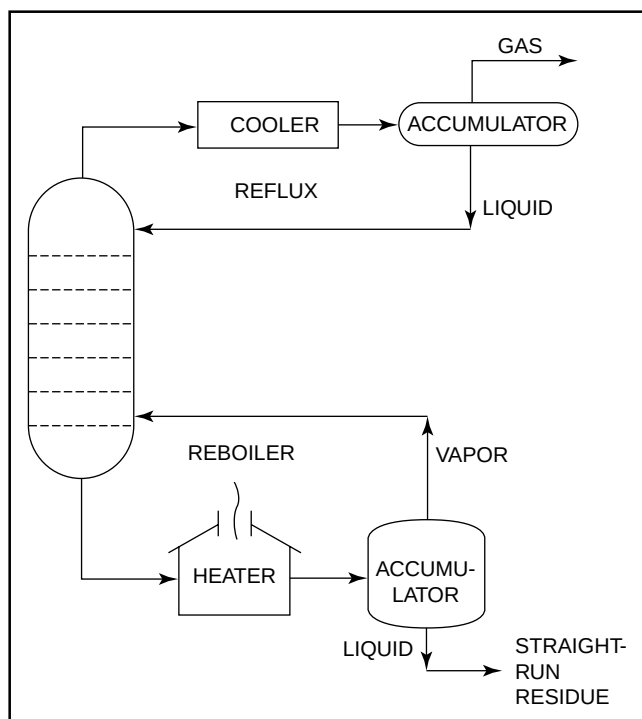


Figure 9: Reboil and Reflux

At the bottom of the column, some of the light hydrocarbons could be entrained with the heavy hydrocarbons. A portion of the bottoms is normally recirculated through a heater to vaporize any light hydrocarbons, which are then reintroduced into the distilling column as a vapor. This process is called reboiling (Figure 9).

The distillation column is the primary separation portion of a refinery. From the distillation column, the initial product cuts are made, and the products flow to other plants within the refinery for further refining (Figure 10).

Control Valve Guidelines

Within a crude unit, the valve body material is normally carbon steel (WCB). The trim material is generally 316 stainless steel. The material selection is based on process temperature and pressure considerations. Corrosion is generally not a problem. Globe-style valves

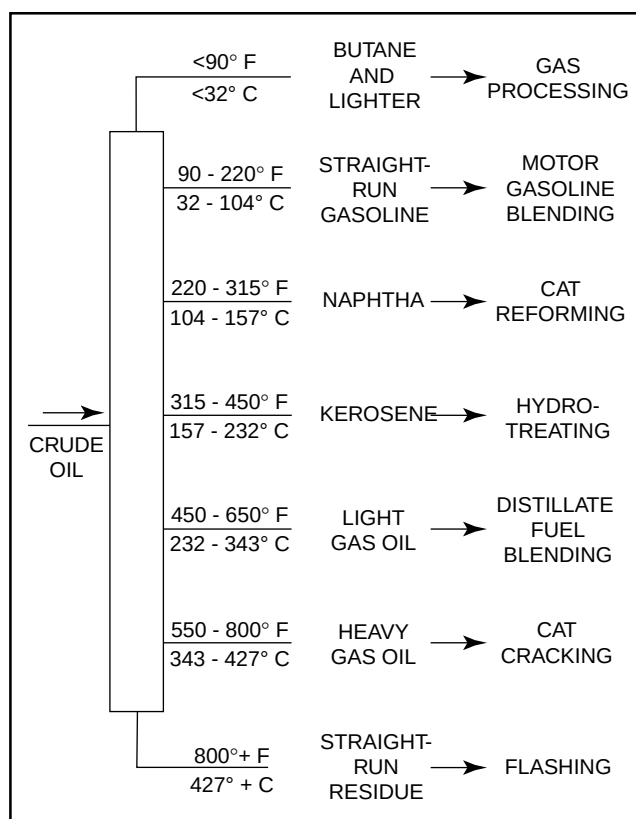


Figure 10: Distilling Crude and Product Disposition

with positioners (such as Valtek Mark One globe valves) are generally used in applications requiring 4-inch (DN 100) and smaller valves. When 6-inch (DN 150) and larger valves are required, rotary valves (such as the Valtek MaxFlo eccentric plug valve) are commonly used, because they are inherently less expensive. Rotary valves are also less susceptible to packing leaks and should be considered when strict environmental regulations are in force.

Control Valve Applications

- VAC/ATM Residue
- VGO/AGO/LDO/HDO/AR/VR Pumparounds
- Bottoms Pump Recirculation
- Fuel Gas Block and Bleed
- Furnace Fuel Gas
- Furnace Pass Flow Control
- Exchanger Bypass
- Product and Unit Tower Cuts
- Stripping Steam Flow Control
- Crude Tower Pumparounds
- Mixing Systems

Recommended Control Valves

Valtek MaxFlo Eccentric Plug Valve

The MaxFlo control valve provides a cost-effective solution to a number of crude distillation operations. The valve is designed with a 200:1 turndown and can be equipped with reduced trim options (which are accomplished by simply changing the seat ring). With various configurations of body and trim materials, the MaxFlo control valve can handle temperatures from cryogenic up to 800° F (427° C). Trim options include NACE, soft seat, hard seat, and solid Alloy 6 configurations. Low fugitive emission packing options are also available. The Valtek rotary-motion spring cylinder actuator provides high torque, and is compact and lightweight for easy maintenance.



Valtek Mark One Globe-style Valve - The Mark One control valve is available in a wide range of sizes (0.5 - 42-inch/DN 15 - 1000) and pressure classes (ANSI Class 150 - 2500/PN16 - 400). It can be constructed from carbon or 316 stainless steels, Hastelloy C, Alloy 20, or other alloys as required. To meet the demands of refining applications, the standard Mark One configuration (carbon steel body/316 stainless steel trim) is built with NACE-compatible materials. The Mark One design is highly versatile, allowing for interchangeable trim installations (including anti-noise, anti-cavitation, high C_v , or low C_v trims). Double-top stem guiding is used to keep the guiding surfaces out of the flow, avoiding the use of cage-guided trim that stick or gall in particulate-laden services. The Mark One design includes large plug stem diameters, which ensures packing and guiding integrity. The high-thrust spring cylinder actuator is compact and lightweight for easy maintenance, field-reversible, and easily disassembled.



Alkylation

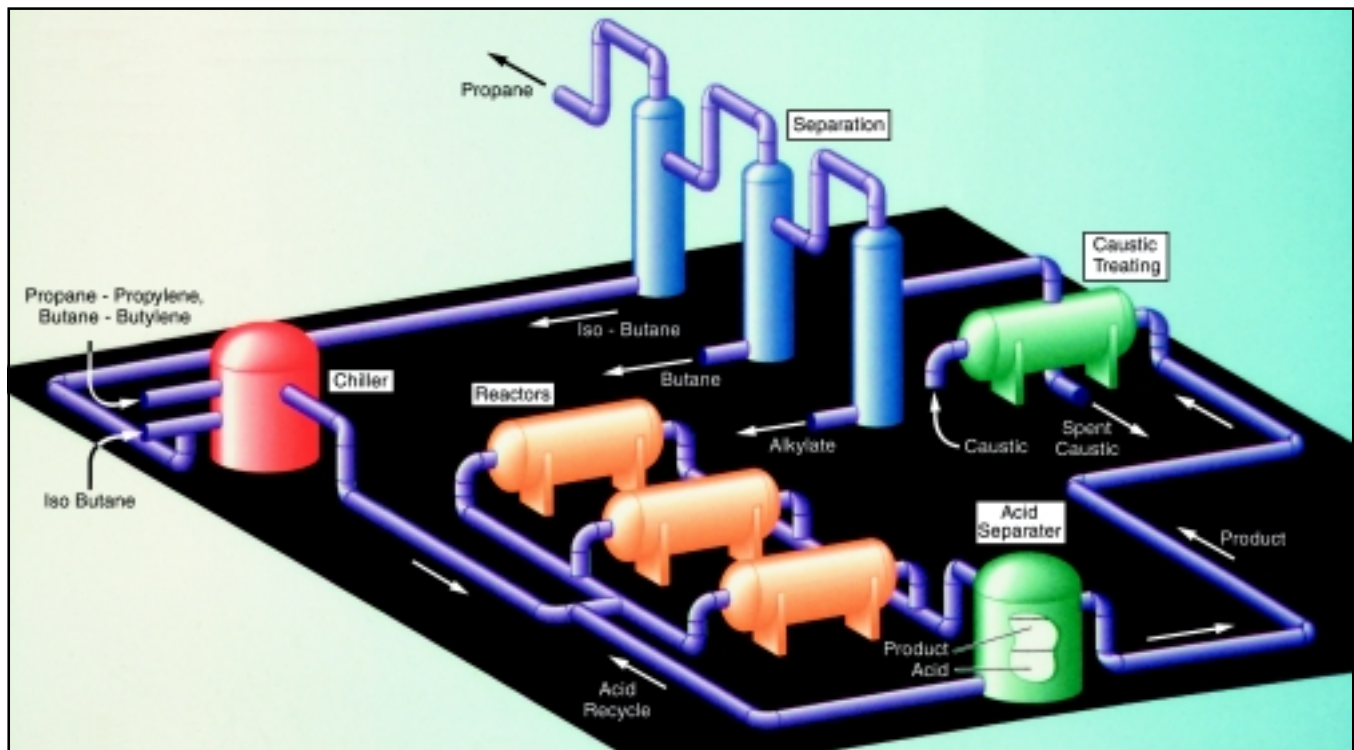


Figure 11: Alkylations Plant

Introduction to Alkylation

Alkylation is an important refining process that converts light olefins (such as propylene and butylene, which are produced in catalytic crackers and cokers) into a more highly valued gasoline component. Alkylate is one of the best gasoline blending components produced in the refinery because of its high octane and low vapor pressure.

Chemistry Overview

The alkylation process converts propylene (C_3H_6), butylene (C_4H_8), pentene (C_5H_{10}) and isobutane (C_4H_{10}) to alkane liquids such as isoheptane (C_7H_{16}) and isoocotane (C_8H_{18}) (Figure 12).

Alkylation Process

The chemical reaction of alkylation is achieved by subjecting the isobutane and olefins to very high pressures. However, the necessary equipment for this procedure is expensive. Therefore, catalysts in the form of hydrofluoric acid or sulfuric acid are used. *Catalysts* allow the reaction to take place at much lower temperatures and pressures, and decrease costs by eliminating the need for expensive equipment. The processes using either chemical are essentially the same: both are done in a large excess of isobutane, because an

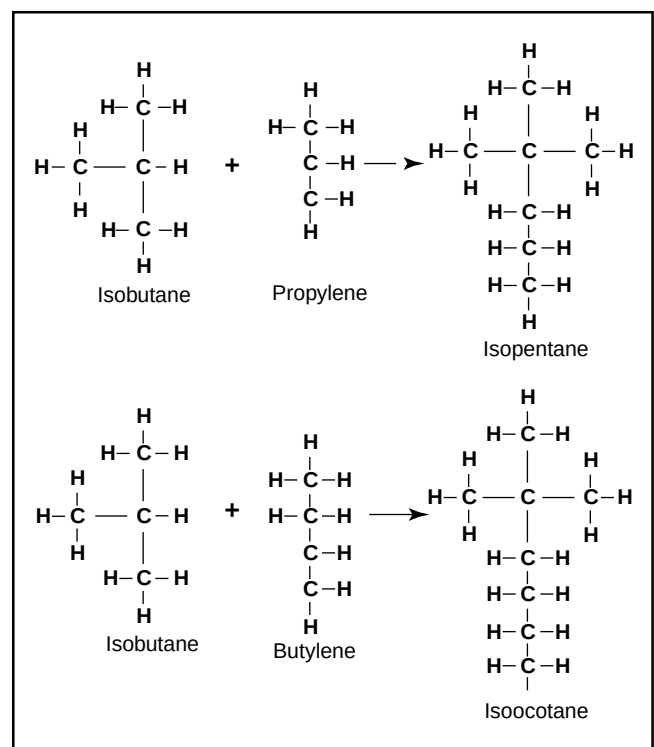


Figure 12: Alkylation Process

olefin molecule will react with the first molecule it interacts with. Thus, maximizing excess isobutane minimizes unwanted secondary reactions, such as polymer formation. If sulfuric acid is used, however, the process must be refrigerated to about 40-50° F (10° C). With hydrofluoric acid, the process is performed at ambient temperature. Octane rating is better with the sulfuric acid process, and acid consumption is also lower. In addition, the safety considerations of using hydrofluoric acid result in sulfuric acid being the preferred catalyst in most refineries today. This is the case even though extra costs exist that are associated with refrigeration required by the sulfuric acid process.

Hydrofluoric Acid Alkylation Process

The alkylation process converts propylene (C_3H_6), butylene (C_4H_8), pentene (C_5H_{10}) and isobutane (C_4H_{10}) to alkane liquids, such as Isoheptane (C_7H_{16}) and iso-octane (C_8H_{18}). Anhydrous hydrofluoric acid is the name for this process (Figure 12).

The feed containing the *olefins* (butylene, propylene and pentene) and isobutane are charged into a combined reactor settler of Phillips design. The hydrogenated phase that is produced in the Phillips combined reactor settler is fed to the main fractionator, which separates the reactants to the *alkylate products* (isoheptane and iso-octane), propane and recycle isobutane. Small amounts of dissolved hydrofluoric are removed from the propane by the hydrofluoric stripper and recycled (Figure 13).

Removal of n-butane from the alkylate product is accomplished by a main fractionator vapor side stream. Alternately, a debutanizer may be added to the system for complete removal of n-butane from the alkylate product (Figure 13).

Control Valve Guidelines (Hydrofluoric Acid Applications)

Generally HF Alkylation requires the use of a globe-style control valves with carbon steel or monel bodies and monel or k-monel trim. Gaskets and packing must be virgin PTFE (no glass binder). Rotary valves are also ideal for this service.

Sulfuric Acid Alkylation Process

A simplified flow diagram for the Exxon Research and Engineering stirred auto refrigerated alkylation process is shown in Figure 14. Olefin feed is first mixed with recycled isobutane from the deisobutanizer overhead, then cooled before entering the reactor. Insoluble water, which is condensed at a lower temperature, is removed in the coalescer. The isobutane-olefin mixture, along with recycle acid and refrigerant, is introduced to the reactor. The reactants and the acid catalyst are then mixed. In the presence of sulfuric acid, the olefin and isobutane react very quickly to form alkylate and release reaction heat. In the autorefrigeration system, the reaction heat is removed by vaporizing some isobutane from the reaction mixture. The vapors leave-

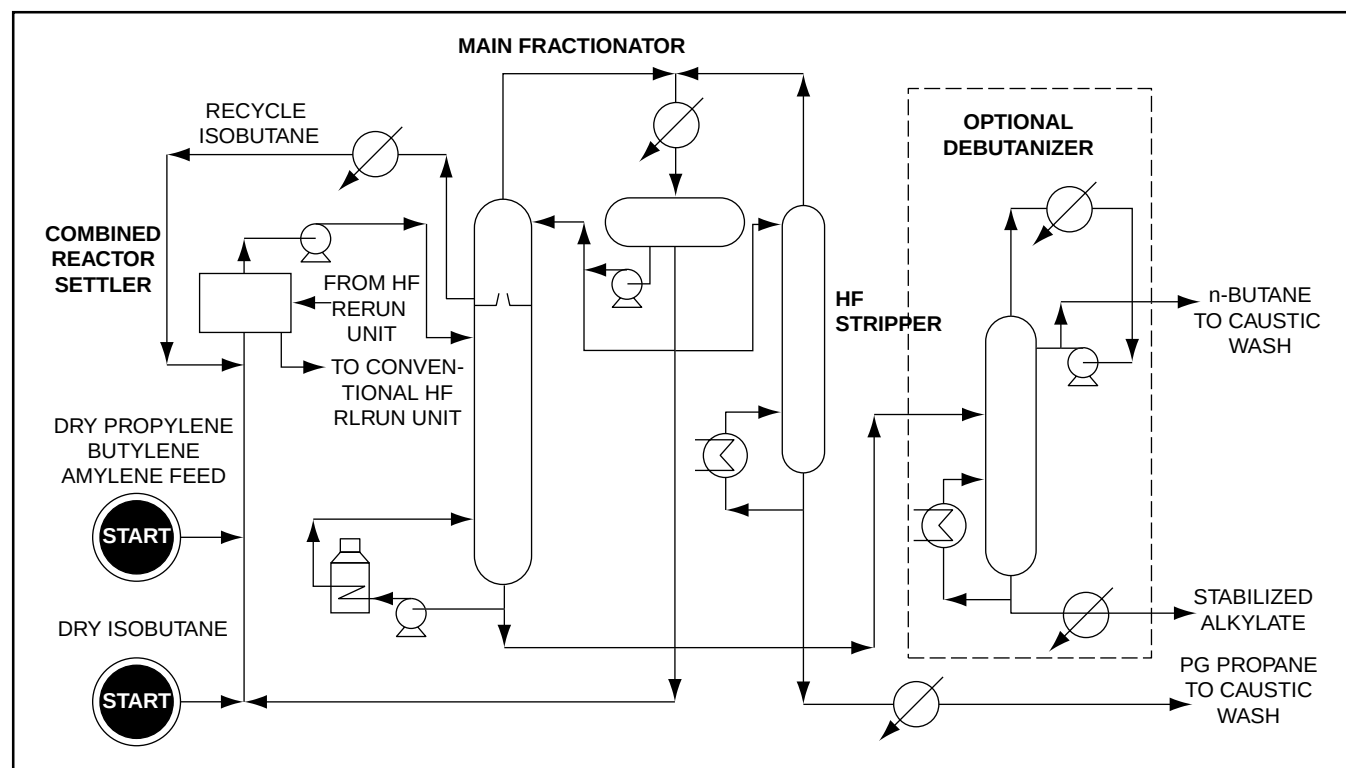


Figure 13: Hydrofluoric Alkylation Process

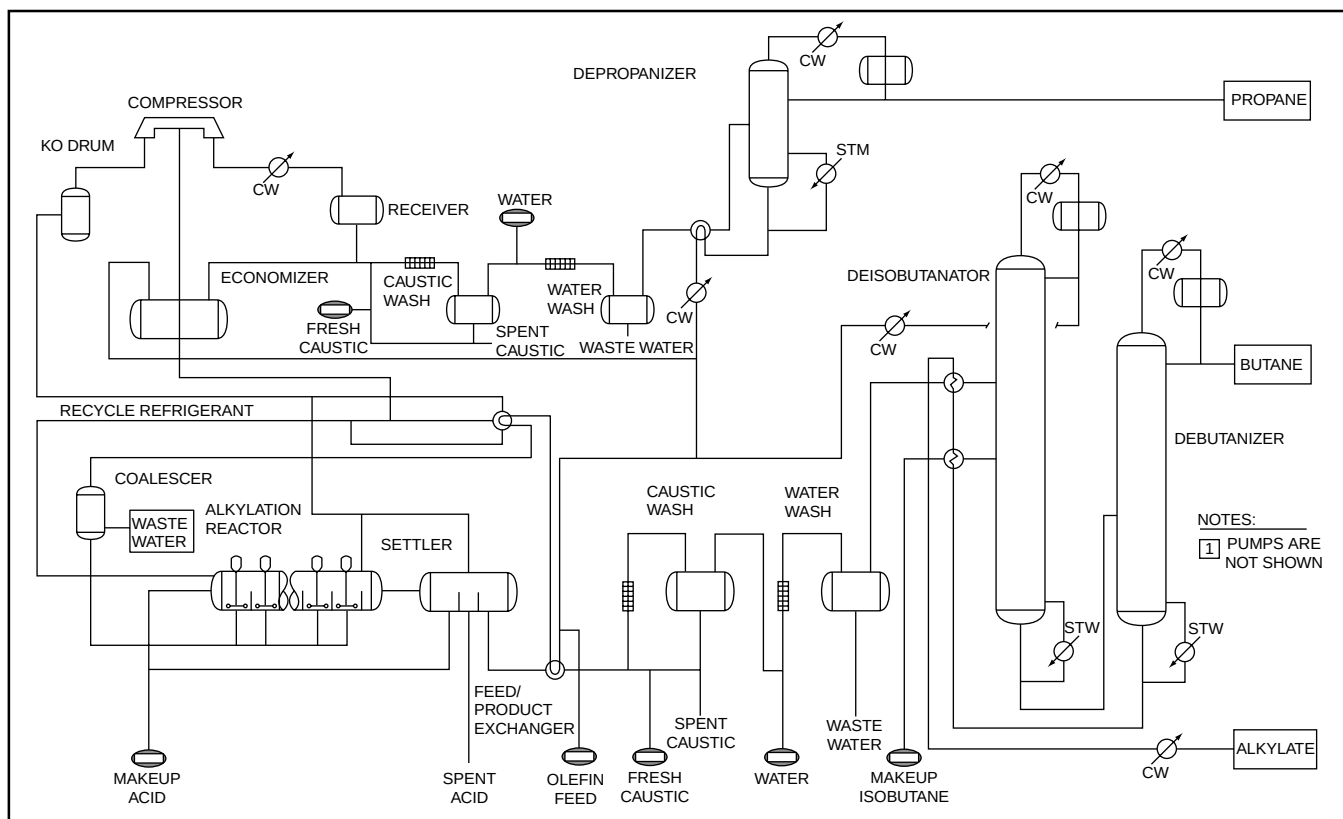


Figure 14: Simplified Flow Diagram of ER&E Stirred, Auto-refrigerated Alkylation Process

ing the reactor are routed to the refrigeration section where they are compressed, condensed and sent to the economizer before being returned back to the reactor. Thus, the reactor is held at an optimal temperature of about 40° F (4° C). Any propane introduced with the feed concentrates in the refrigeration section and must be removed from the alkylation plant. Therefore, a small slipstream of refrigerant is depropanized after being caustic and water-washed to remove any SO₂. The propane overhead is sent to storage, while the isobutane-rich bottoms are returned to the process. Thus, the depropanizer operation avoids building up propane in the alkylation plant.

Returning to the reactor, the reactor product is routed to the settler, where the acid is settled from the hydrocarbon and is recycled back to the reactor. The hydrocarbon portion of the reactor product (which contains alkylate, excess isobutane and normal butane) is then caustic- and water-washed to remove any acidic components before being fed to the deisobutanizer. Makeup isobutane, which is consumed by the alkylation reaction, is also typically added to the deisobutanizer. The overhead from the tower is an isobutane-rich stream that is recycled back to the reactor, while the bottoms from the tower (which contain normal butane and alkylate) are routed to the debutanizer tower. In the debutanizer, butane is removed overhead, while the alkylate bottoms – which meet vapor pressure speci-

cations – are cooled and routed to alkylate storage. These towers can be designed to operate at a low enough pressure to allow the use of low-pressure steam.

Control Valve Guidelines (Sulfuric Acid Applications)

The sulfuric acid alkylation process involves concentrated H₂SO₄ which requires the use of carbon steel and 316 stainless steel due to their resistance to corrosion. Generally, these alloys are specified. By design, the temperature of the process stays relatively low, which aids in the prevention of corrosion damage. The other process fluid constituents are petroleum-based and are not corrosive. The valve bodies are generally carbon steel or 316 stainless steel and the valve trim is 316 stainless steel. Occasionally, Alloy 20 or Hastelloy C may be specified when dilute acid is encountered in the process. In the reforming process, light petroleum distillate (naphtha) is contacted with a platinum-containing catalyst at elevated temperatures and hydrogen pressures ranging from 50 to 500 psig (3.5 to 34.5 barg). Reforming produces a high-octane liquid product that is rich in aromatic compounds. Hydrogen, light gas and liquefied petroleum gas (LPG) are also produced as reaction by-products. Do not use graphite packing or gaskets in an acid-based application. Rotary valves are well-suited for this application also.

Control Valve Applications

- Control Valve Applications
- HF Alkylation
- Sulfuric Alkylation

Recommended Control Valve

Valtek Mark One Globe-style Valve - The Mark One control valve is highly recommended for both HF and sulfuric alkylation services. With HF alkylation service, the Mark One valve is generally configured with a carbon steel or Monel 500 body, K-Monel plug and seat ring,



and Monel 500 seat retainer. With sulfuric alkylation service, the valve bodies are constructed from carbon steel, Hastelloy B or Alloy 20 with corresponding trim materials depending on service conditions and specifications. The Mark One design uses double-top stem guiding to keep the guiding surfaces out of the flow stream, and to avoid the galling and sticking associated with caged-guiding.

The standard trim is interchangeable with special trim designs for high C_v or low C_v applications. The Mark One actuator is a spring cylinder design that offers high thrust, features high performance and is easy to handle or maintain.



Catalytic Reformer

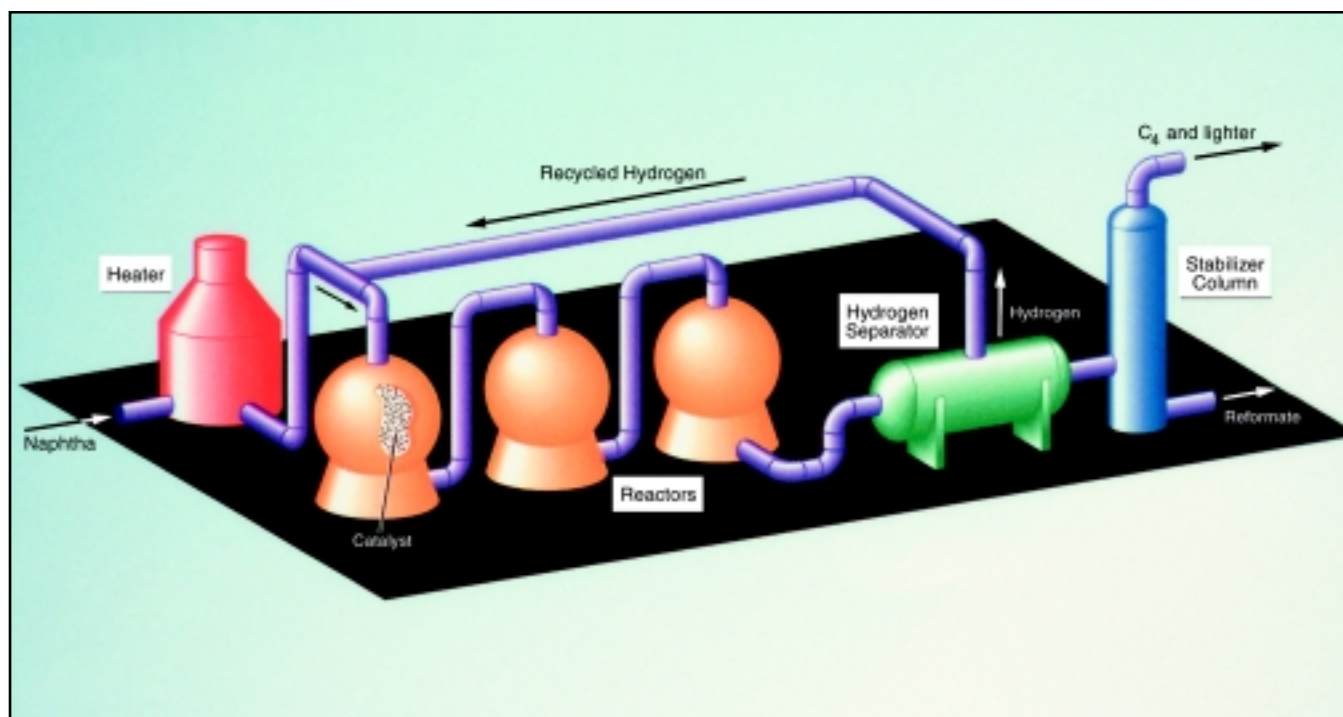


Figure 15: Catalytic Reformer

Introduction to Catalytic Reforming

Catalytic reforming upgrades low octane naphthas to a high octane-blending component reformat. It was originally developed to upgrade low-octane-number straight-run naphtha to high-octane motor fuels; the process has been applied to the production of LPG and high purity aromatics. A wide range of platinum-based catalysts permit tailored processing schemes for optimum operation. Innovation has led to increased yields and octane, while still controlling coke deposition on the catalyst. The path to higher yields and octane lay in operating at low pressure, high temperature. However, high temperature and low pressure lead to coke production and subsequent coke laydown and deactivation of the catalyst. Catalytic reforming typically results in the following changes in the naphtha:

Table II: Catalytic Reforming Changes to Naphtha

	% Volume Feed	Product
Paraffins	50%	35%
Olefins	0%	0%
Naphthenes	40%	10%
Aromatics	10%	55%

The desirable reactions that take place in the cat reforming process are:

1. Paraffins are converted to isoparaffins.
2. Paraffins are converted to naphthenes.
3. Naphthenes are converted to aromatics.

The undesirable competing reactions that take place are:

1. Some of the paraffins and naphthenes crack, forming butanes and lighter gases.
2. Some of the side chains break away from the naphthenes and aromatics, forming butanes and lighter gases.

The main purpose of the cat reformer is to convert paraffins and naphthenes to aromatic compounds and some isomers (Figure 16).

Reformer Equipment

Hydrogen is an important by-product of catalytic reforming. Most of these reactions result in the production of extra hydrogen. This is because aromatics don't have as many hydrogens as the naphthenes that are introduced as feed. Giving up the extra hydrogen is an *endothermic process* and thus the need for various stages as shown, with reactors and furnaces in series. The *reforming process* is also a user of hydrogen in the

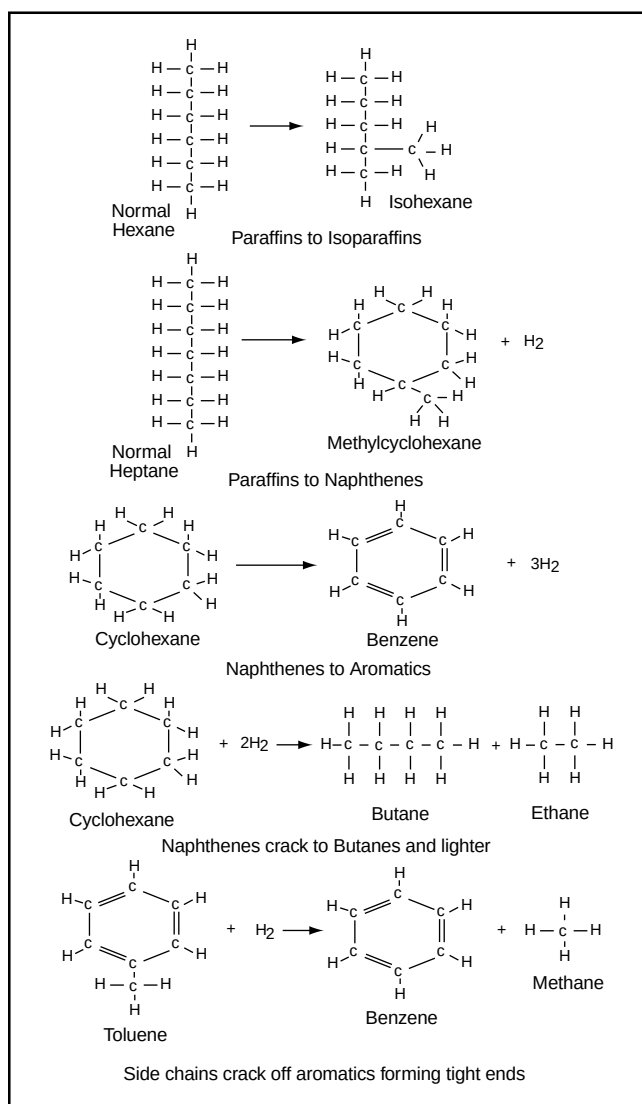


Figure 16: Reformer Reactions

reactors. Hydrogen must be mixed with the feed to keep a high concentration of hydrogen vapors in the reactors. This prevents carbon atoms from depositing on the catalyst, as in cat cracking. Instead, the carbon reacts with the hydrogen and forms a hydrocarbon gas. As shown in Figure 17, part of the hydrogen stream is recycled to the feed while the other part is sent to the gas plant. The liquid product from the bottom of the separator is sent to a fractionator (called a *stabilizer*), which is similar to a debutanizer. The *fractionator* makes a bottom product called reformat, while butanes and lighter product are sent to the sats gas plant.

Regeneration

The three classes of reformers are: 1) semi-regenerative, 2) full regenerative (Figure 17), and 3) continuous regeneration (Figure 18). The *semi-regenerative reformers* were the original units from the early 1950s. When the catalyst became deactivated due to coke for-

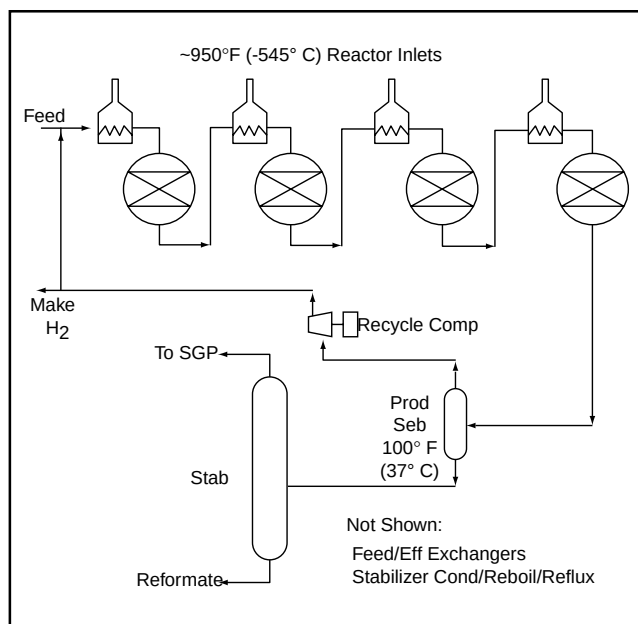


Figure 17: Typical Reformer-Reaction Section

mation, the plant was shut down for regeneration. Thus the catalyst life was required to be at least six months. High pressure (up to 500 psig/34.5 barg) and lower temperatures were required to keep coke formation; thereby, catalyst deactivation was minimized. This produced octanes in the low 90s. *Full regeneration reformers* have five reactors. At any given time, four are in the process loop and one is being regenerated - with a fresh reactor coming on line every 20 to 30 hours. In the full regeneration scheme, pressures around 100 psig (6.9 barg) are possible and octane numbers of the product were about 100. *Continuous regeneration reformers* are similar to full regeneration reformers in that about 20 to 30 percent of the catalyst is regenerated each day (Figure 18). However, in a continuous regeneration unit, this is accomplished by a system of stacked reactors and catalyst lock-hoppers to physically move the catalyst around the system.

The regeneration process is a real key in the cat reforming process. The regeneration section of a full regeneration unit is shown in Figure 19. Of the steps shown, the most crucial step is the chlorination. Platinum is the active dehydrogenation agent on the catalyst, and it tends to agglomerate over the length of a run. The chlorine causes the platinum to re-disperse over the surface of the catalyst. In addition, a small amount of chloride must be placed on the catalyst to give an acidic function for isomerization activity. To summarize, catalytic reforming is an important process for upgrading low octane naphthas to a high octane-blending component reformat. Unfortunately, the higher the octane number of the reformat, the lower the yield and the more light ends produced.

Control Valve Guidelines

The process fluid hydrocarbons within a catalytic reformer plant are generally noncorrosive. Carbon steel bodies with 316 stainless trim can normally be used up to temperatures of 450° F (232° C). Above 450° F (232° C), 316 stainless steel bodies with 316 stainless steel trim with an Alloy 6 overlay should be considered. Globe-style valves with positioners (such as Valtek Mark One

globe valves) are generally specified in valve sizes through 4-inch (DN 100). In valve sizes 6-inch (DN 150) and larger, rotary valves with hardened trim (such as the Valtek MaxFlo eccentric plug valve) are specified. Rotary valves are usually less costly than larger globe-style valves. Because rotary valves have less shaft/packing leakage, they are more attractive to the user when strict environmental standards are in place.

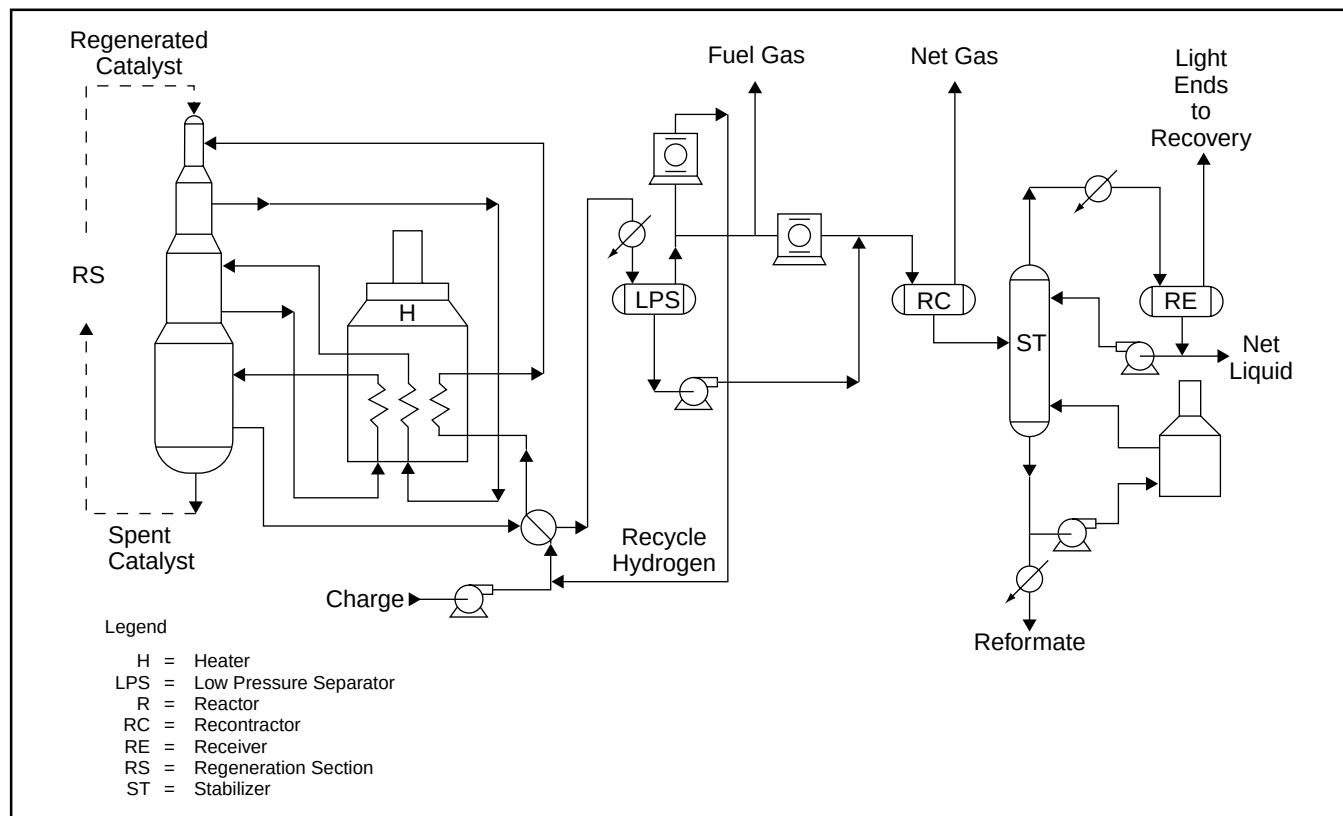


Figure 18: Continuous Regeneration

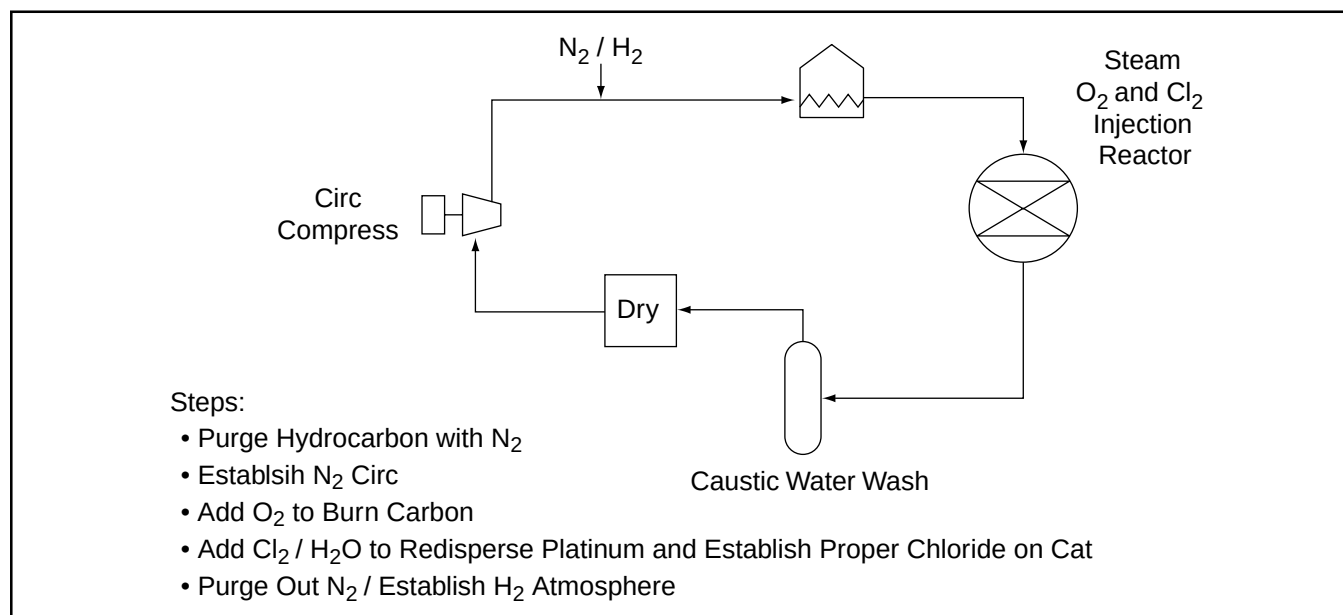


Figure 19: Reformer Regeneration

Control Valve Applications:

- Control Valve Applications
- Recycle Gas
- Vent Gas
- Vent Gas to Vent Drums
- Nitrogen Purge
- Flare Vent
- Recycle Gas
- Nitrogen to Regeneration Tower
- Air to Regeneration Tower

Recommended Control Valves

Valtek MaxFlo Eccentric Plug Valve - The MaxFlo control valve is used in a number of catalytic reformer operations. The valve has a 200:1 turndown and has reduced trim options that are accomplished by simply changing the seat ring. The MaxFlo is offered in various configurations of body and trim materials, which can handle temperatures from cryogenic up to 800° F (427° C). Trim options include NACE, soft seat, hard seat, and solid Alloy 6 configurations. Anti-fugitive emission packing is also available. The Valtek rotary-motion spring cylinder actuator is designed for high performance operation and high torque, and is compact and lightweight.



Valtek Mark One Globe-style Valve - The Mark One control valve (Figure XX) is offered in sizes 0.5 - 42-inch/DN 15 - 1000 and in pressures ANSI Class 150 - 2500/PN16 - 400. It is constructed from carbon or 316 stainless steels, Hastelloy C, Alloy 20, or other alloys as required. To meet the requirements of refining industry, the standard Mark One configuration (carbon steel body/ 316 stainless steel trim) is built with NACE-compatible materials. The Mark One allows for interchangeable trim installations, including anti-noise, anti-cavitation, high C_v , or low C_v trims. Double-top stem guiding is used to keep the guiding surfaces out of the flow stream - this effectively avoids the use of cage-guided trim that stick or gall in dirty services. To ensure a tight packing seal and accurate guiding, the Mark One design includes large plug stem diameters. The Mark One high-performance spring cylinder actuator is field reversible, compact, lightweight, and easy to maintain.



Hydrotreating

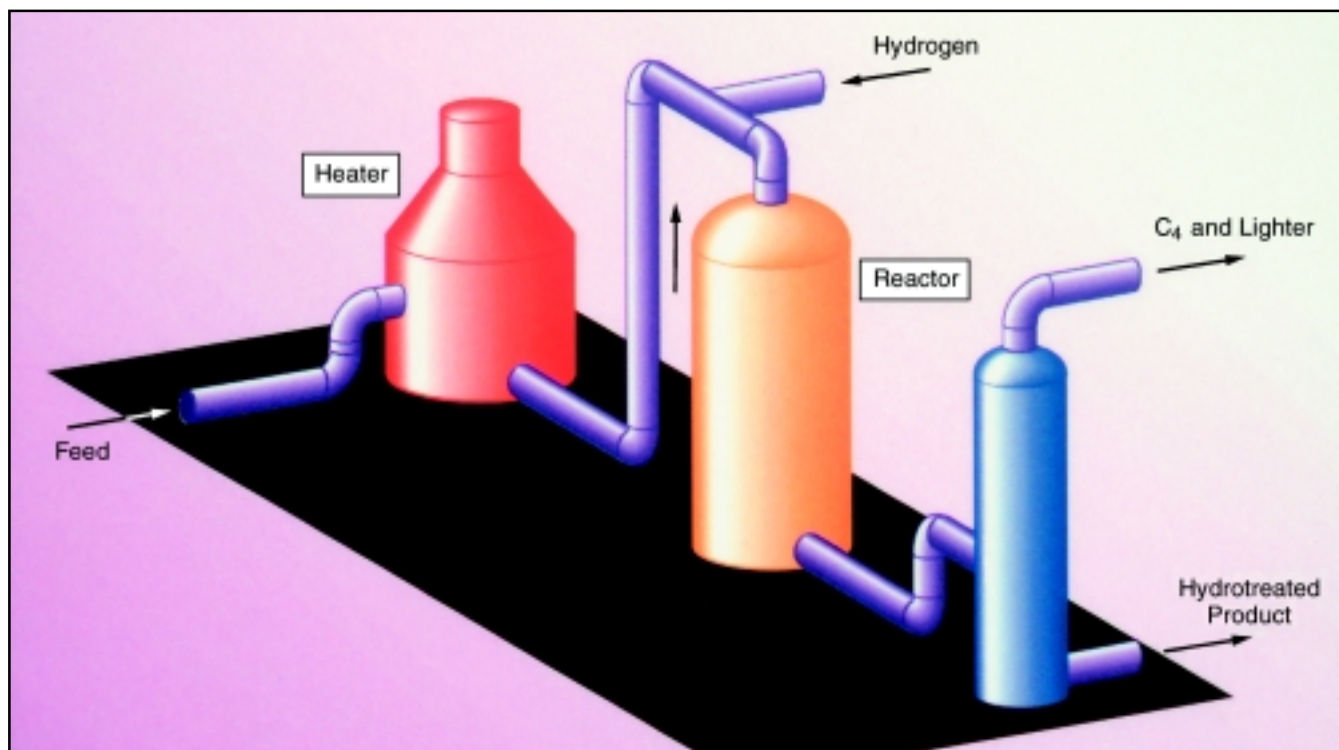


Figure 20: Hydrotreating Process Plant

Introduction to Hydrotreating

Hydrotreating removes many contaminants from the streams. Hydrogen is a vital input to the hydrotreating process. Refinery streams that have C₆ and heavier hydrocarbons are likely to have some sulfur compounds as well. The sulfur can be attached or imbedded anywhere in the molecule and therefore is chemically a part of the stream. Hydrotreating can be used to successfully break the sulfur away.

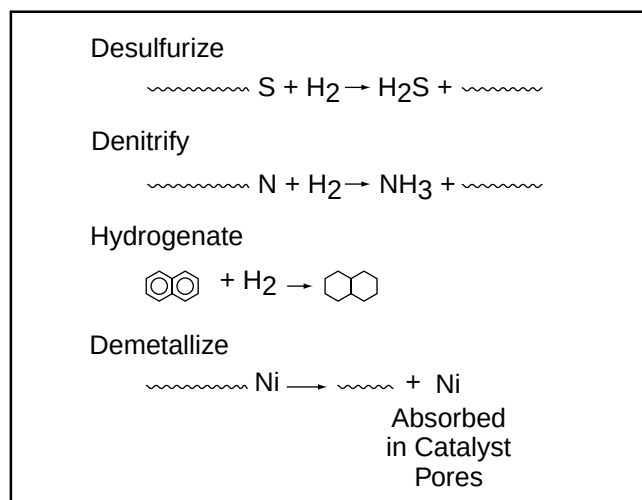


Figure 21: Hydrotreating Reactions

In the hydrotreating process (Figure 20), the stream is mixed with hydrogen and heated from 500° to 800° F (260° to 427° C). The oil combined with the hydrogen is then charged to a vessel filled with a catalyst, which is in pellet form. In the presence of the catalyst, several reactions take place:

- The hydrogen combines with the sulfur atoms to form hydrogen sulfide (H₂S).
- Some nitrogen compounds are converted to ammonia.
- Any metals entrained in the oil are deposited on the catalyst.
- Some of the olefins, aromatics or naphthenes become hydrogen-saturated and some cracking takes place, causing the creation of some methane, ethane, propane, and butane gases (Figure 21).

The stream coming from the reactor is sent to a product separator where most of the propane and lighter (including the H₂S and trace amounts of ammonia) go overhead. To completely strip out these light ends, a small fractionator called a stabilizer is generally added onto the tail end of the process (Figure 22).

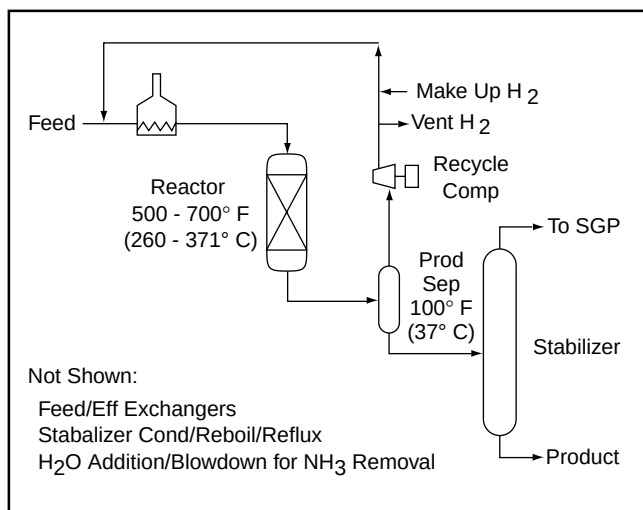


Figure 22: Typical Hydrotreater

The importance of hydrotreating has been gradually increasing for many years for two reasons:

- Removal of sulfur and metals is important protection for the catalysts in reformers, cat crackers and hydrocrackers.
- Air quality regulations are continually lowering the allowable sulfur content in fuel, calling for desulfurization of distillates and jet fuels.

Sulfur Facilities

Hydrotreating creates hydrogen sulfide (H_2S) streams, a deadly, toxic gas that requires disposal. The usual process involves two steps: first, the removal of the H_2S stream from the hydrocarbon streams; second, the conversion of the lethal H_2S to elemental sulfur (a useable innocuous chemical).

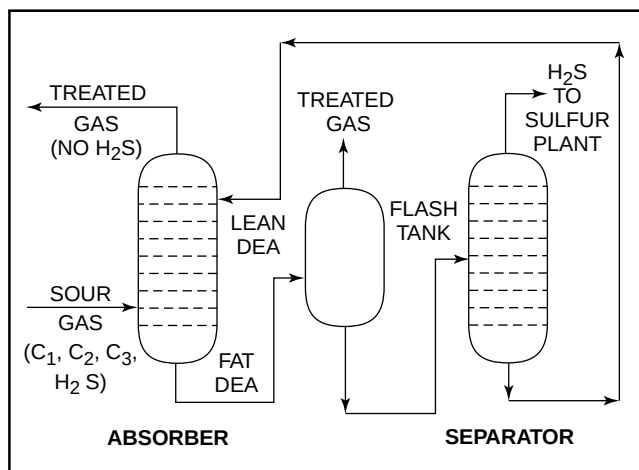


Figure 23: Diethanolamine Treater

Until about 1970, most of the H_2S produced by refineries was used, along with the other light ends, as refinery fuel. When H_2S burned in the furnaces, sulfur dioxide (SO_2) was formed. Air quality regulations now limit SO_2 emissions to the extent that most of the H_2S must be kept out of the fuel systems.

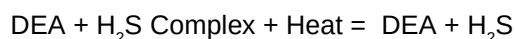
Recovery of the H_2S can be done by a number of different chemical processes. The most widely used is solvent extraction using diethanolamine (DEA). A mixture of DEA and water is pumped down through a vessel with trays or packing in it. The gas stream containing the H_2S is injected from the bottom. As the streams circulate, the DEA will selectively absorb the H_2S gas. The rich DEA is fractionated to separate the H_2S , which is then sent to a sulfur recovery plant. The stripped DEA is recycled (Figures 23 and 24)

Table III: Sulfur Reactions

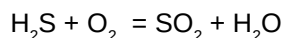
- Absorption**



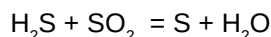
- Stripping**



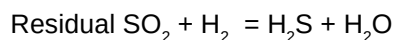
- Partial Combustion**



- Claus Reaction**



- SCOT Reaction**

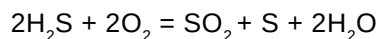


Sulfur Recovery

The conversion of H_2S to plain sulfur is accomplished in a *Claus unit* (the process was first developed in 1885 by a German scientist named Claus). Variations of the process exist today that are suited to various H_2S /hydrocarbon ratios, but they mainly use a basic two-step, split-stream process (Figure 24).

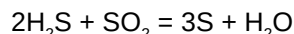
Combustion

Part of the H_2S stream is burned in a furnace, producing SO_2 , water and sulfur. The sulfur is formed because the air (oxygen) admitted to the furnace is limited to one-third the amount needed to make all SO_2 (Table III).



Reaction

The remainder of the H_2S is mixed with the combustion products and passed over a catalyst. The H_2S reacts with the SO_2 to form sulfur (see Table III).



The sulfur drops out of the reaction vessel in the molten (melted) form. Most refineries store and ship sulfur in the molten state, although some companies store sulfur by pouring it on the ground (in forms), letting it solidify. Sulfur can be stored indefinitely in this dry state, called a *pile*.

Claus units convert about 90 to 93 percent of the H_2S to sulfur. Depending on local environmental conditions the balance may be burned in the refinery fuel system. Or, alternatively, the tail gas could be processed for high percentage H_2S removal as in the SCOT (Shell Claus Off-gas Treating) process (Figure 24) where residual SO_2 is converted back to H_2S across a catalyst bed. The H_2S is then scrubbed out using a DEA absorber/stripper unit, with H_2S being recycled back to the Claus unit. The tail gas incinerator ensures that the small amount of sulfur which escapes to the atmosphere is in the form of SO_2 (and not the highly poisonous H_2S).

Control Valve Guidelines

The control valves in a hydrotreater are subjected to a fluid comprised of hydrocarbon + hydrogen gas + H_2S (hydrogen sulfide). Under 450°F (232°C) the valves are generally constructed of carbon steel with 316 stainless steel trim. Above 450°F (232°C), valves constructed of 316, 347 or 321 stainless steels should use 316 stainless steel trim with Alloy 6 overlay. In the sulfur plant, the fluid the valves are subjected to is acid gas ($\text{H}_2\text{S} + \text{CO}_2 + \text{SO}_2$). If the gas can be kept above the dew point of approximately 225°F (107°C) carbon steel valves with 316 stainless steel trim will suffice. Below the dew point, 316 stainless steel valves with 316 stainless steel trim should be used. For molten sulfur, jacketed carbon steel valves with 316 stainless steel trim should be considered. Applications requiring valve sizes 4-inch (DN 100) and smaller usually use globe-style valves with positioners (such as the Valtek Mark One globe valve). In applications where valve sizes 6-inch (DN 150) and larger are needed, rotary valves (such as the Valtek MaxFlo eccentric plug valve) are specified. These rotary valves are usually specified with hardened trim and corrosion-resistant materials. Rotary valves are usually less costly than larger globe-style valves and, because rotary valves have less shaft/packing leakage, they are more attractive to the user when strict environmental standards exist.

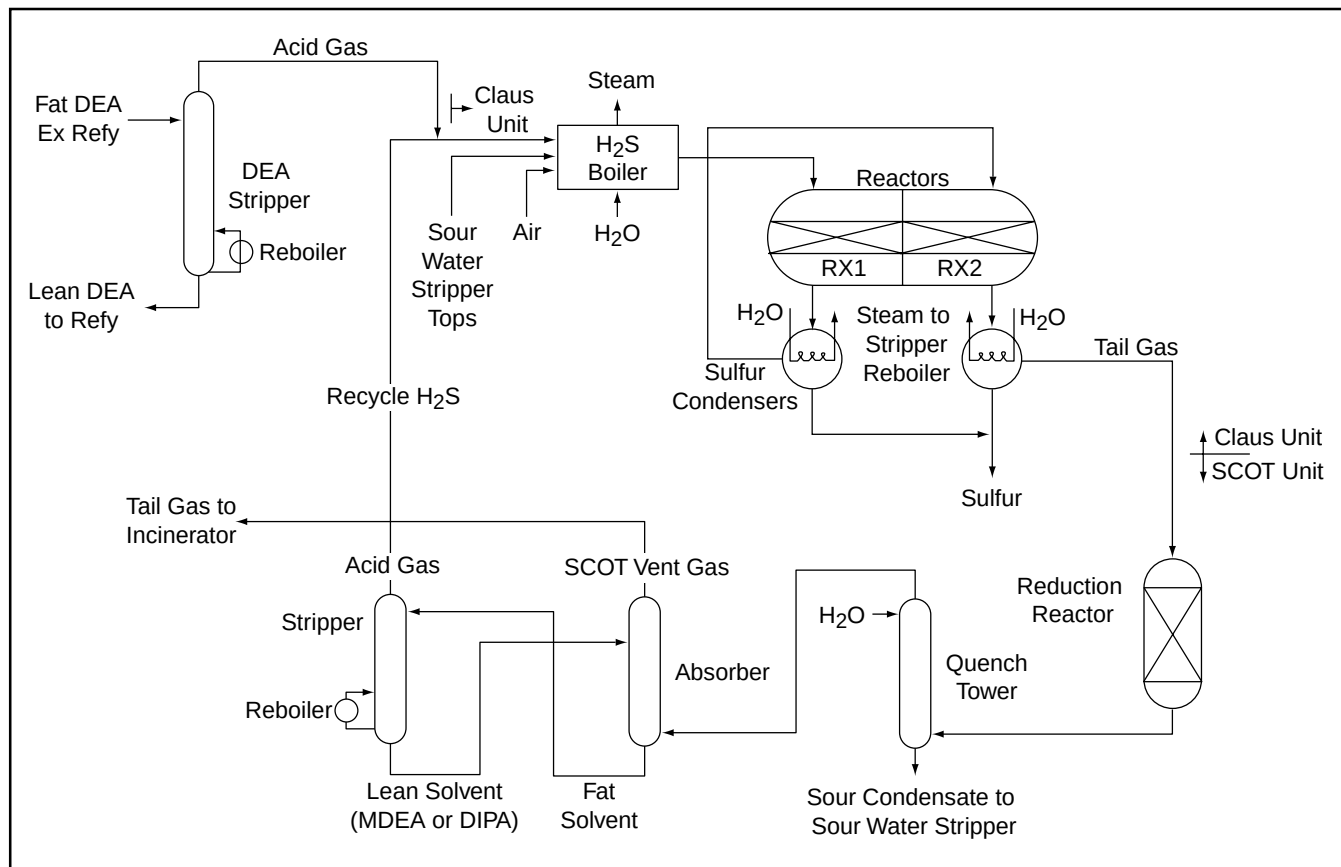


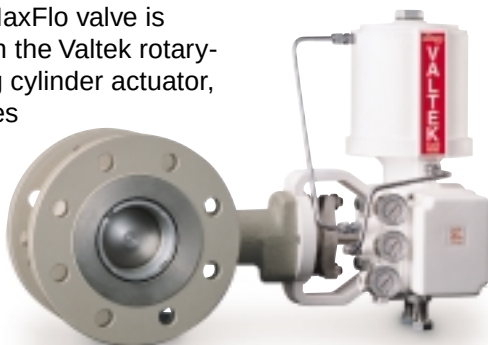
Figure 24: Typical Sulfur Plant

Control Valve Applications:

- Control Valve Applications
- Steam Utilities
- Amine Booster Pump Recirculation
- Sour Water Letdown
- Washwater Injection Pump Spillback
- Cold Separator Letdown
- Charge Pump Recirculation

Recommended Control Valves

Valtek MaxFlo Eccentric Plug Valve - The MaxFlo control valve is recommended as a cost-effective valve for most hydrotreating applications. The valve design features a 200:1 turndown and is equipped with a reduced trim option that is accomplished by simply changing the seat ring. The MaxFlo control valve is available with a variety of body and trim materials, allowing it to handle temperatures from cryogenic up to 800° F (427° C). Trim options include NACE, soft seat, hard seat, and solid Alloy 6 configurations. The MaxFlo packing box also allows for a low fugitive emission packing option. The MaxFlo valve is equipped with the Valtek rotary-motion spring cylinder actuator, which provides high torque and is compact and lightweight for easy maintenance.



Valtek Mark One Globe-style Valve - The Mark One control valve is highly versatile. It is available in a wide range of sizes (0.5 - 42-inch/DN 15 - 1000) and pressure classes (ANSI Class 150 - 2500/PN16 - 400). It is available in carbon or 316 stainless steels, Hastelloy C, Alloy 20, or other alloys as required. To meet the demands of hydrotreating applications, the standard Mark One material configuration (carbon steel body and 316 stainless steel trim) is NACE-compatible. The Mark One design allows for a number of trim options, including anti-noise, anti-cavitation, high C_v , or low C_v trims. Double-top stem guiding is standard; this guiding design effectively keeps the guiding surfaces out of the flow and avoids the use of cage-guided trim that have a tendency to stick or gall. The Mark One design includes large plug stem diameters, which ensures proper packing and guiding performance. The Mark One linear-motion spring cylinder actuator is compact and lightweight for easy maintenance, high thrust, field-reversible, and easily disassembled.



Vacuum Flashing

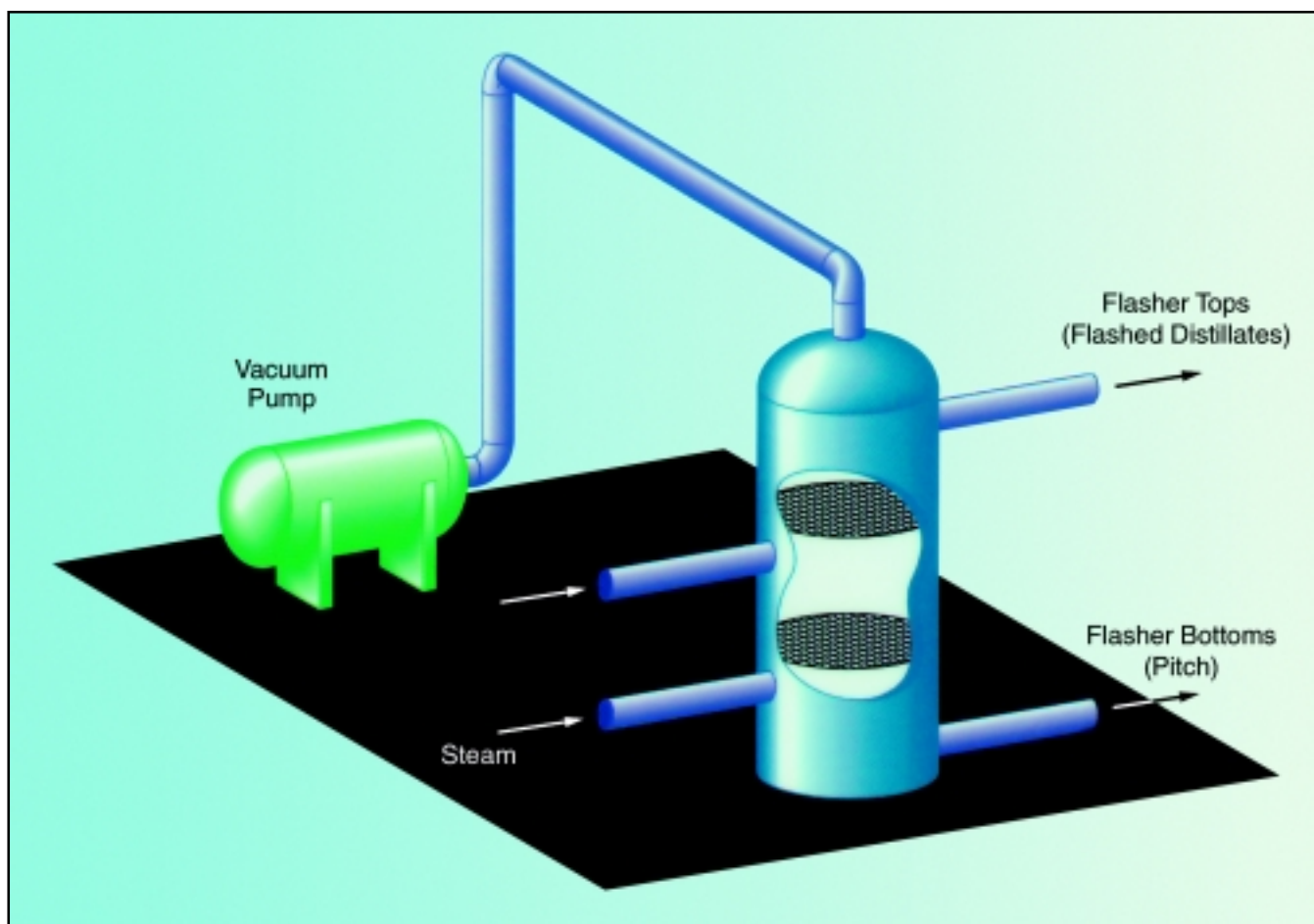


Figure 25: Vacuum Flasher

The Cracking Phenomenon

When distillation curves and distillation columns were discussed in the *Crude Distilling Unit* section, the operating temperature of the process fluids was purposely kept below 900° F (482° C). With temperatures above 900° F (482° C), a phenomenon known as cracking begins. As the large and complicated hydrocarbon molecules that have not yet vaporized at 900° F (482° C) are heated to higher temperatures, the energy transfer from the heat is enough to crack the molecules into two or more smaller molecules. For example, a molecule of $C_{16}H_{34}$ may crack into three pieces: C_8H_{18} , C_6H_{12} , and C_2H_4 (Figure 26). This process must be controlled. A further discussion will take place on cracking in the *Catalytic Cracking* section.

Smaller molecules boil at much lower temperatures than the larger ones. As they are created by cracking, they readily boil out of the high temperature crude. More volume is also created because the smaller molecules cumulatively take up more volume than the tightly packed larger molecule. The smaller molecules

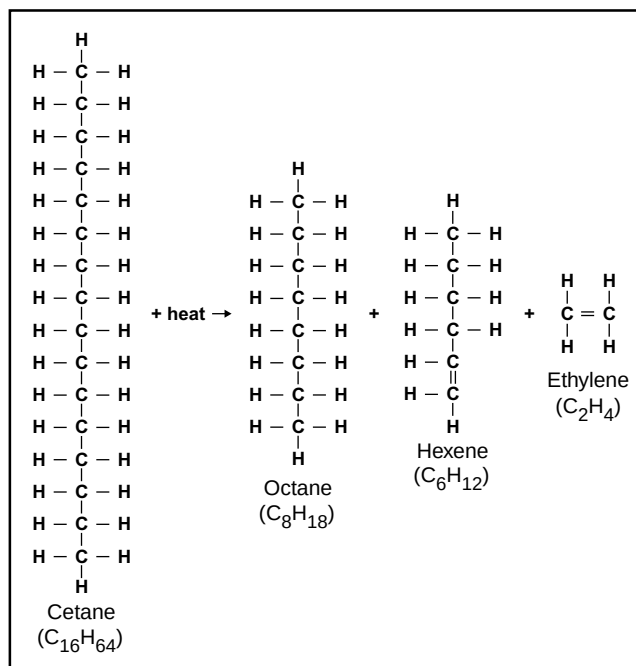


Figure 26: Molecule Cracking

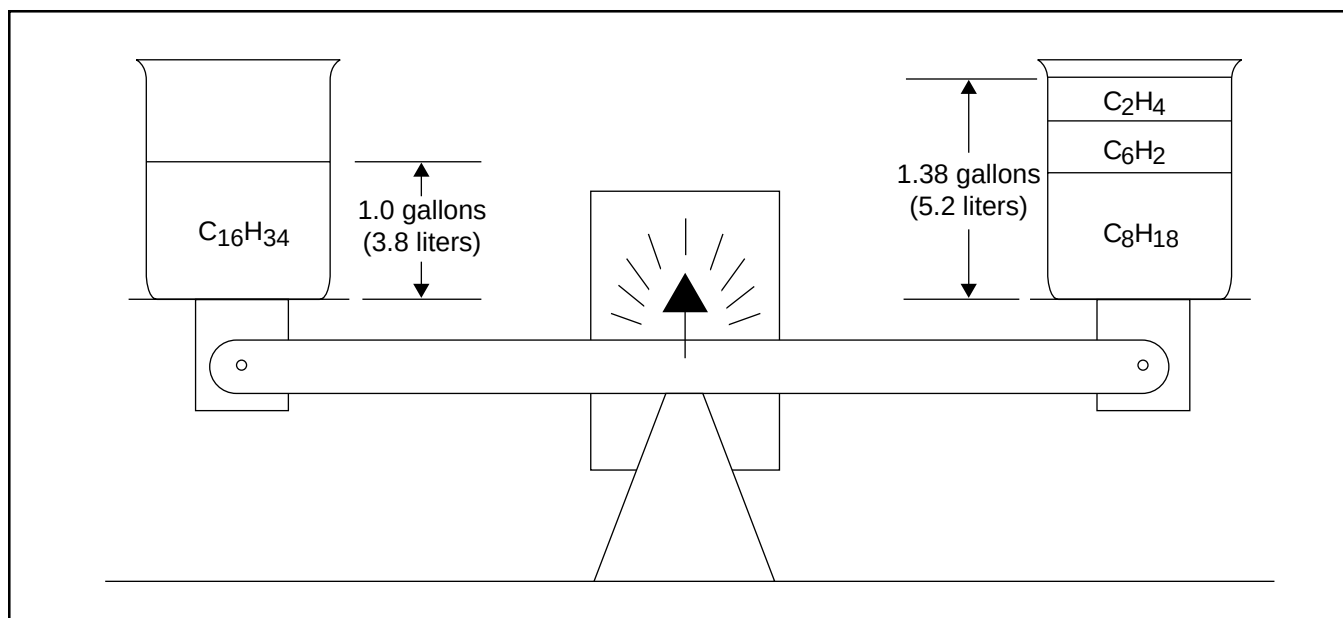


Figure 27: Cracked Components Weight

cumulatively take up more volume than the tightly packed larger molecule. The smaller molecules take up more volume per pound than the large ones. The compound $C_{16}H_{34}$ weighs 7.2 lbs./gallon (12.4 kg/liter), but C_8H_{18} , C_6H_{12} , and C_2H_4 weigh 5.9, 5.6 and 3.1 lbs/gallon (10.1, 9.6 and 5.3 kg/liter) respectively. Therefore, 7.2 lbs. (3.3 kg) of $C_{16}H_{34}$ is a gallon (3.8 liters) of volume, but 7.2 lbs. (3.3 kg) of the three components represents 1.38 gallons (5.2 liters) or 38 percent more space (Figure 27).

Cracking is a lucrative process, but only when it is controlled. The distilling unit is not designed to control it, so temperatures that cause it are avoided in the standard distillation process. The heaviest cut points on the distilling column is around 750° F (399° C). Nevertheless, plenty of hydrocarbons exist that need to be separated in the straight-run residue cut. To do this, a technique called *vacuum flashing* is used.

Low Pressure

Water boils at 212° F (100° C) at sea level, but at the significantly lower temperature of about 202° F (94° C) at a mile-high elevation (1609 meters). This temperature gradient represents the effect of different atmospheric pressure caused by change in altitude. (When higher elevation atmosphere is described as 'thinner' what is understood is that the atmosphere is less dense.)

The relationship between pressure and boiling temperature is simple. The process of heating only assists the molecules to absorb enough energy to escape from the liquid form. The rate at which they escape depends on the rate at which heat is delivered to them and the

pressure of the air above them. The lower the pressure, the less energy is transmitted, and the lower the temperature at which vapor will start forming in the liquid (i.e. boiling). In other words, the lower the pressure, the lower the boiling temperature.

Vacuum Flashing

If the pressure-boiling temperature relationship is applied to the crude oil cracking phenomenon, the straight-run residue will crack if the temperature is too high. The straight-run residue will need to be separated into more cuts. The solution is to do the fractionation at reduced pressure. Straight-run residue is pumped directly from the distilling column to the flasher. The residue is heated to the *initial boiling point* (plus a few degrees) to allow for cooling. The residue is taken into a squat, large diameter column where the pressure has been lowered. Atmospheric pressure is 14.7 psia (1 bar) at sea level. This is approximately the pressure inside a standard distillation column. The pressure in a vacuum flasher is about 4.5 to 5.5 psia (0.3 to 0.4 bar). At that reduced pressure the lighter fraction of the residue will begin to boil or flash (Figure 28).

Flashing is a cooling process. In order to counteract the cooling process, superheated steam is introduced into the vessel. Heat is transferred from the steam to the residue, maintaining the temperature and the flashing. The other function of the steam is vacuum control. Pressure in the vessel is kept very low by a vacuum pump at the top of the vessel.

Several streams can be drawn off the flasher (Figure 28). Light flashed distillate and heavy flashed distillate are sometimes kept segregated. Either one can some-

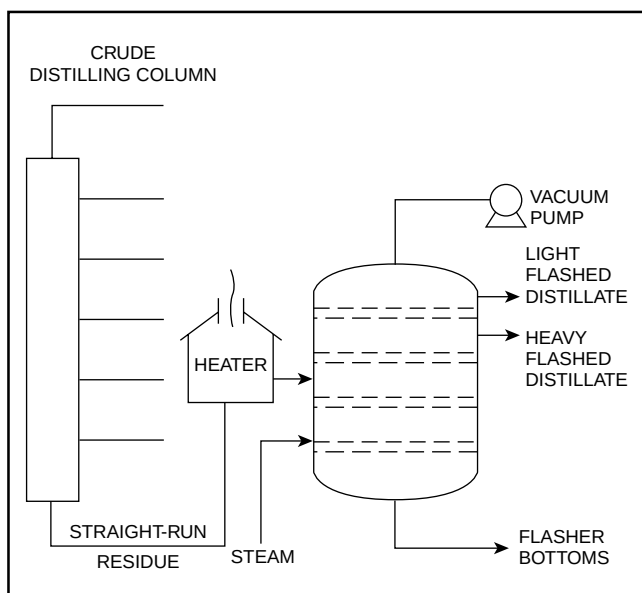


Figure 28: Vacuum Flashing

times be used as lubricating oil feedstocks. Often they are not segregated but drawn off together and called *flasher tops*. The heavy material from the bottom of the flasher is called *flasher bottoms* and is used as the feed to an asphalt plant, a thermal cracker or as a blending component for residual fuel.

Flashing is the equivalent of distilling the straight-run residue at a cut point at approximately between 1000° and 1100° F (539° and 593° C). Most distillation curves are depicted as if the theoretical distillation took place. Because even vacuum flashing has its practical limitations, the end point of the straight-run residue (or in other words, the end point of the crude oil) is never achieved. Other measures, such as gravity and viscosity, are the properties used to control the quality of the flasher bottoms.

Control Valve Guidelines

The valve body material within a vacuum flasher unit is normally carbon steel (WCB). The trim material is generally 316 stainless steel. The material selection is based on process temperature and pressure considerations. Corrosion is generally not a problem. Smaller valves (4-inch/DN100 and smaller) are generally specified with a globe-style body design (such as a Mark One globe valve). For valve sizes 6-inch (DN150) and larger, rotary valves are used (such as the MaxFlo eccentric plug valve.)

Control Valve Applications

- Flashing Tops
- Flasher Bottoms
- Steam

Recommended Control Valves

Valtek MaxFlo Eccentric Plug Valve - The MaxFlo control valve is often selected as a cost-effective valve for vacuum flashing applications. The MaxFlo valve features a better turndown ratio (200:1) than other valve types. It is equipped with a reduced trim option, which is performed by replacing the seat ring. The standard MaxFlo configuration is available with a wide range of body and trim materials, which allows the valve to handle temperatures from cryogenic up to 800° F (427° C). MaxFlo trim options include NACE, soft seat, hard seat, and solid Alloy 6 configurations. The versatile packing box allows for optional low fugitive emission packing. The MaxFlo valve is equipped with a rugged rotary-motion spring cylinder actuator, which provides exceptional performance, high torque and is compact and lightweight for easy maintenance.



Valtek Mark One Globe-style Valve - The Mark One control valve is often specified for vacuum flashing services because of its versatile design. It is available in a wide range of sizes (0.5 - 42-inch/DN 15 - 1000) and pressure classes (ANSI Class 150 - 2500/PN16 - 400). The Mark One material selection consists of carbon or 316 stainless steels, Hastelloy C, Alloy 20, or other alloys as required. To meet the demands of vacuum clashing applications, the standard Mark One configuration (carbon steel body and 316 stainless steel trim) uses NACE-compatible materials. The Mark One design provides for a number of trim options, including anti-noise, anti-cavitation, high C_v , or low C_v trims. Double-top stem guiding is standard, which effectively keeps the guiding surfaces out of the flow. The Mark One design avoids the use of cage-guided trim, which has a tendency to stick or gall, and includes large plug stem diameters for proper packing and guiding performance. The Mark One valve is equipped with the Valtek linear-motion spring cylinder actuator, which is compact and lightweight for easy maintenance, high thrust, field-reversible, and easily disassembled.



Isomerization Plant

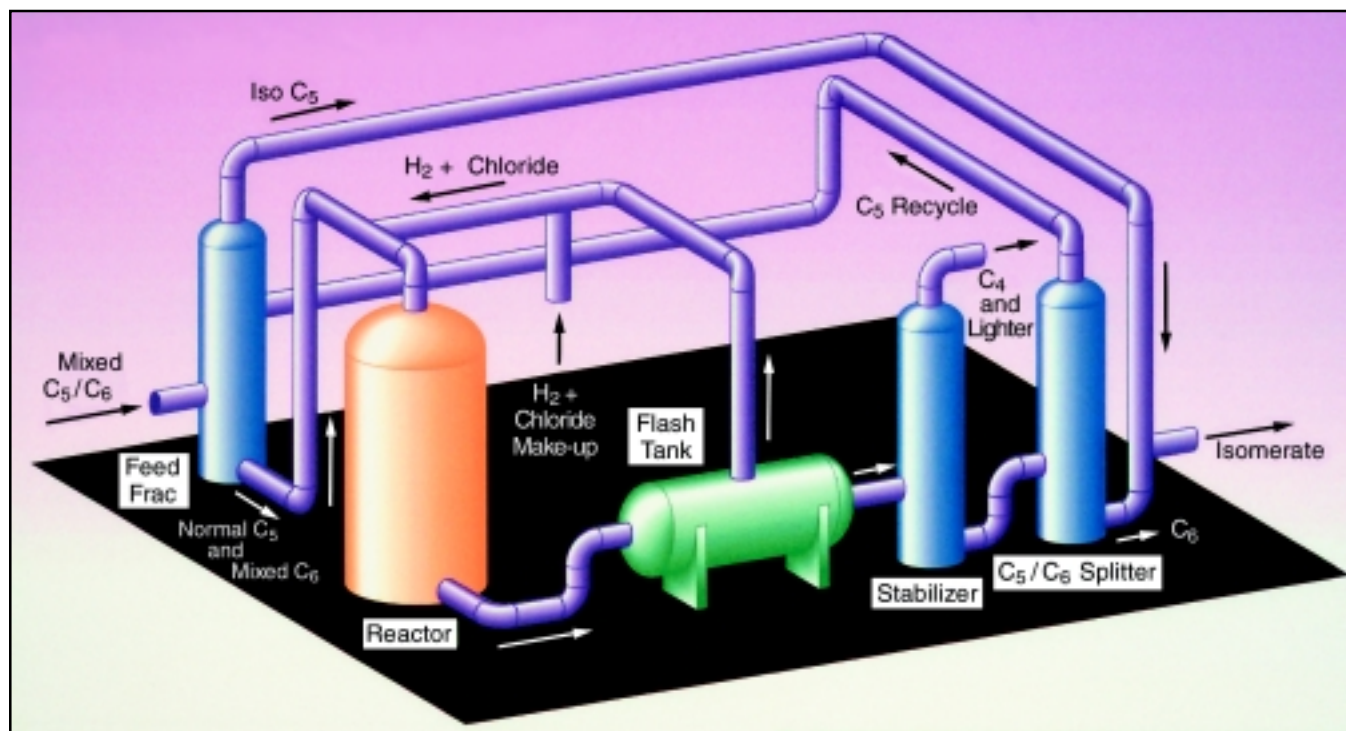


Figure 29: Isomerization Plant

Introduction to Isomerization

The Isomerization plant (Figure 29) is a molecule rearranger, similar to the catalytic reformer (see *Catalytic Cracker* section) except that it converts only normal saturated hydrocarbons (paraffins) to branched saturated hydrocarbons (isoparaffins) (Figures 30 and 31).

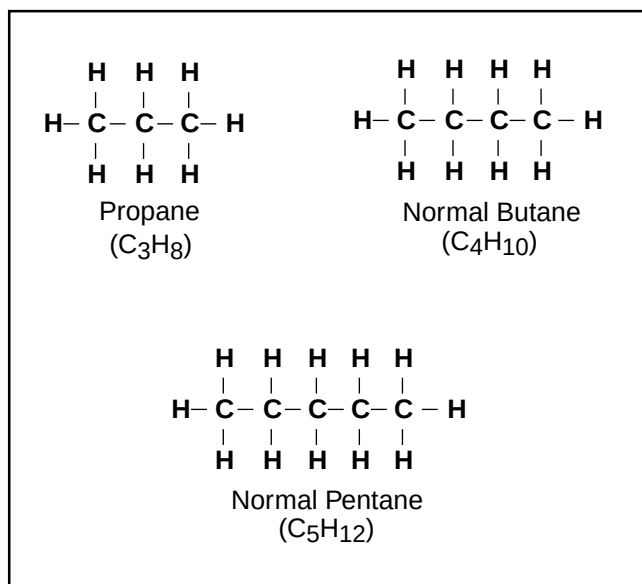


Figure 30: Normal Saturated Hydrocarbons

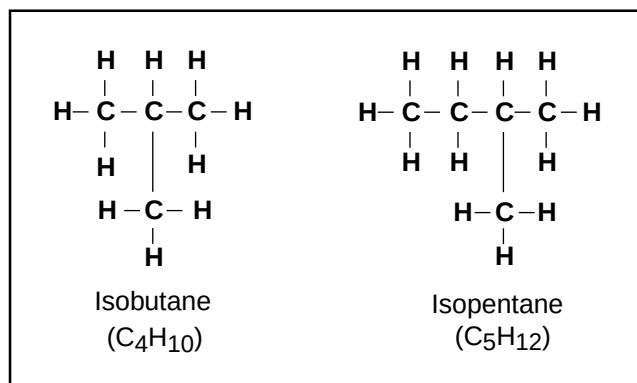


Figure 31: Branched Saturated Hydrocarbons

Butane Isomerization

A refinery with an alkylation plant is not likely to have exactly enough isobutane to match the propylene and butylene requirements. If a hydrocracker exists in the refinery, a surplus of isobutane will result, which is most likely blended off to gasoline. If a hydrocracker does not exist, the supply must be supplemented. This usually requires one of two choices: purchase a supply of isobutane or produce it with a butane isomerization (BI) plant (see Figure 32).

To make isobutane, the feed to the BI plant is normal butane or mixed butanes (ISO and normal), which are

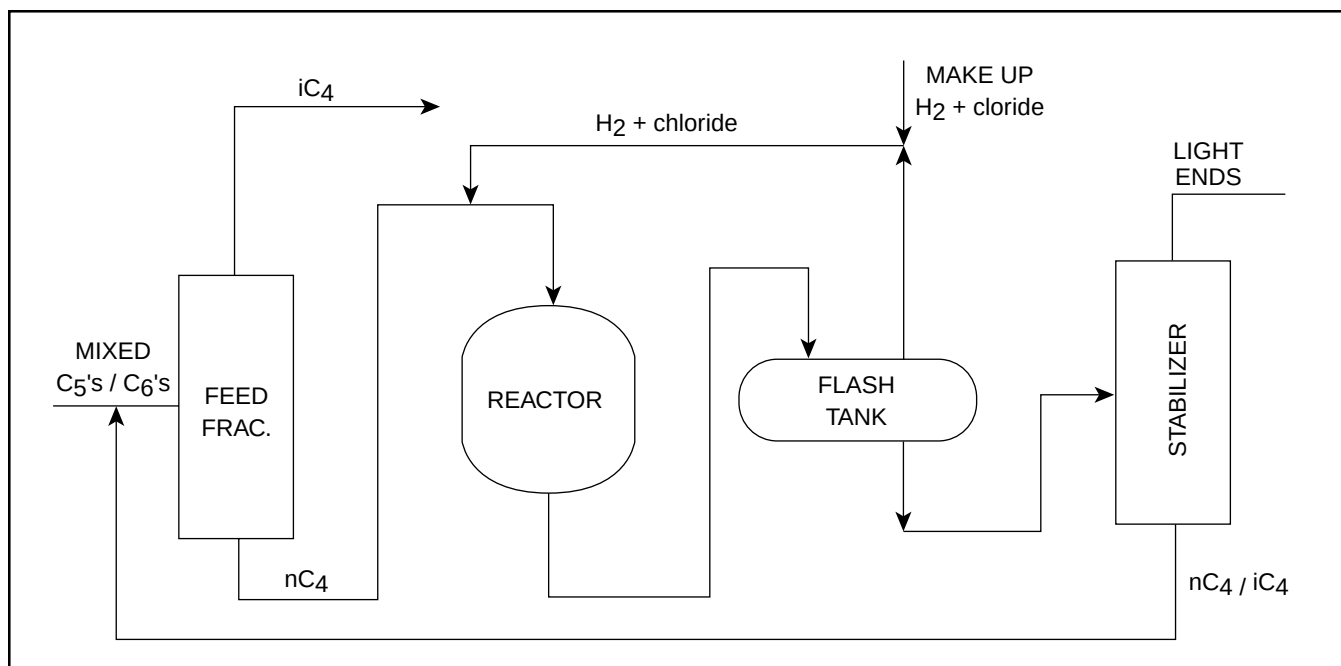


Figure 32: Butane Isomerization Plant

sometimes called *field grade butanes* if they come from a gas processing plant. The butanes should not have any trace of olefins, which would deactivate the catalyst.

The butanes are fed to a feed preparation column, where isobutane is removed. The high purity, normal butane is then mixed with a small amount of hydrogen and chloride, and charged to a reactor containing a platinum catalyst. The catalyst causes the normal butane to reform itself into its isomer (isobutane).

The stream coming from the reactor contains about 60 percent isobutane, 40 percent normal butane, and a minor amount of propane and lighter. In a fractionator, propane and lighter are removed overhead and are sent to the fuel system. The butanes are recycled to the feed fractionator so that the normal butane can be rerun. In other words, the incoming fluid is normal butane and the outgoing fluid is isobutane (Figure 32).

C₅/C₆ Isomerization

For a refinery that cannot meet the octane number of gasoline and has straight-run gasoline available, C₅/C₆ isomerization has economic advantages. Normal pentane, which has a RON (research octane number) of 62, can be converted to isopentane with a RON of 92. Hexanes go from a low 25 RON to about 75; a typical mixture of ISO and normal pentanes and hexanes can be upgraded from 73 to 91 RON.

The C₅/C₆ isomerization plant may have a feed fractionator that concentrates the normal pentanes and hexanes, rejecting the isomers (similar to the BI plant). The

normal paraffins are mixed with a small amount of hydrogen and organic chlorides, and charged to a reactor. The catalyst will cause conversion of about half the feed to isomers (isomerate), allowing the reactor product to be fractionated to recycle the normal pentanes to extinction. Since the hexanes boil at a higher temperature than the normal pentane, and the isopentane boils at a lower temperature, the cost of the additional hexane splitter sometimes precludes recycling the normal hexane (Figure 33).

The C₅/C₆ isomerization is more complex than butane (C₄) isomerization; therefore, about 2 to 3 percent light ends, butane and lighter are created in the process. Depending on the amount of recycle, the octane number of the isomerate can vary from 80 to 91 RON. With the energy cost associated with the process (fractionation and pumping) increasing with the octane number, butane isomerization is used to satisfy the feed needs of alkylation by converting normal butane to isobutane. C₅/C₆ isomerization is a method of increasing the octane number of the light gasoline components (normal pentane and normal hexane) that are found in abundance in light straight-run gasoline.

Control Valve Guidelines

The fluid (hydrocarbon plus small amounts of H₂ + Cl) through an isomerization plant is generally noncorrosive. Carbon steel body valves with 316 stainless steel trim are generally used at temperatures below 450° F (232° C). Above this temperature, valves with chromoly bodies or 316 stainless steel bodies with 316 stainless steel trim are frequently used. Globe-style valves

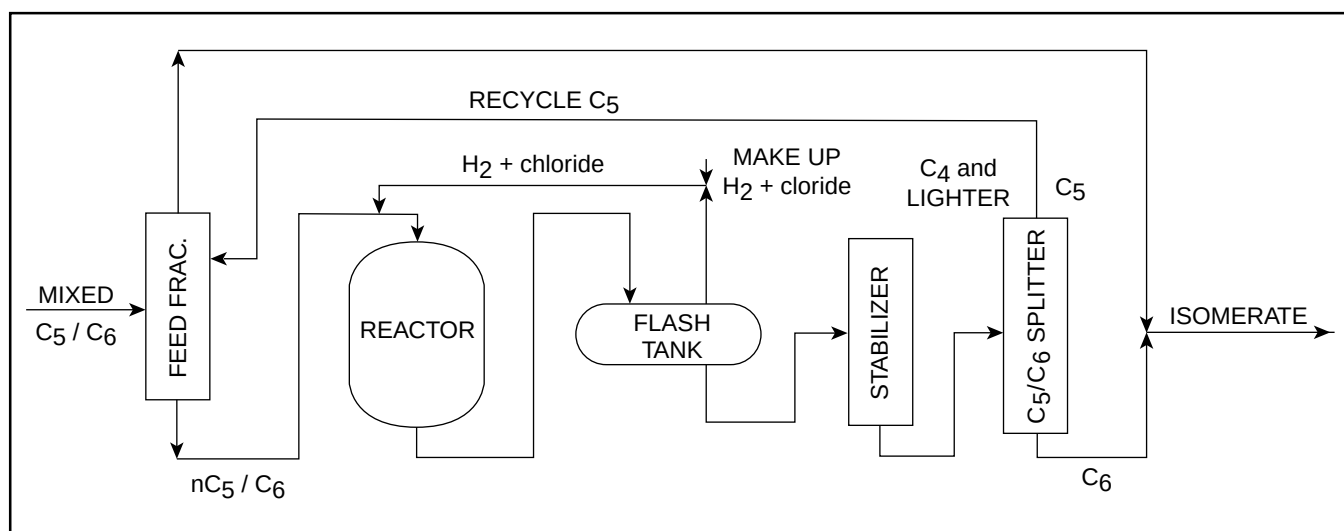


Figure 33: C₅/C₆ Isomerization Plant

with positioners, such as Mark One control valves, are typically specified for size 4-inch (DN 100) and smaller applications. Rotary valves, such as the MaxFlo eccentric plug valve, are generally used in valve sizes 6-inch (DN 150) and larger. Rotary valves have the added benefits of being less costly than comparable globe-style valves and have less shaft/packing leakage (which is beneficial when strict environmental regulations are a concern).

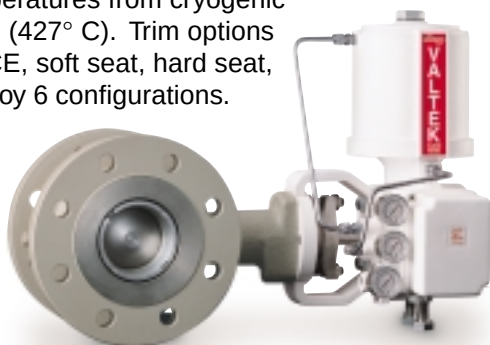
Control Valve Applications

- Reactor Switching
- Recycle Gas
- Reflux Return
- Fractionator Bottoms
- Bottom Pump Recirculation

Recommended Control Valves

Valtek MaxFlo Eccentric Plug Valve - The MaxFlo control valve combines high performance with cost-effectiveness. As an eccentric plug valve, it has exceptional turndown (200:1). Reduced trim is easily accomplished by simply changing the seat ring. With a wide range of body and trim materials, the MaxFlo control valve can handle temperatures from cryogenic up to 800° F (427° C). Trim options include NACE, soft seat, hard seat, and solid Alloy 6 configurations.

Fugitive emission control is accomplished using special anti-



fugitive emission packing. The Valtek rotary-motion spring cylinder actuator provides high torque, and is compact and lightweight for easy maintenance.

Valtek Mark One Globe-style Valve

The Mark One control valve is available in sizes 0.5 - 42-inch/ DN 15 - 1000 and in pressures ANSI Class 150 - 2500/PN16 - 400. Material options include carbon or 316 stainless steels, Hastelloy C, Alloy 20, or other specified alloys. To meet the requirements of refining applications in general, the standard Mark One configuration (carbon steel body/316 stainless steel trim) is built with NACE-compatible materials. The Mark One design allows for interchangeable trim installations - including anti-noise, anti-cavitation, high C_v, or low C_v trims. Double-top stem guiding is standard, keeping the guiding surfaces out of the flow and avoiding the use of cage-guided trim that stick or gall. The Mark One design includes large plug stem diameters, which ensures packing and guiding integrity. The high-thrust Valtek spring cylinder actuator is compact and lightweight for easy maintenance, field-reversible, and easily disassembled.



Gas Plants

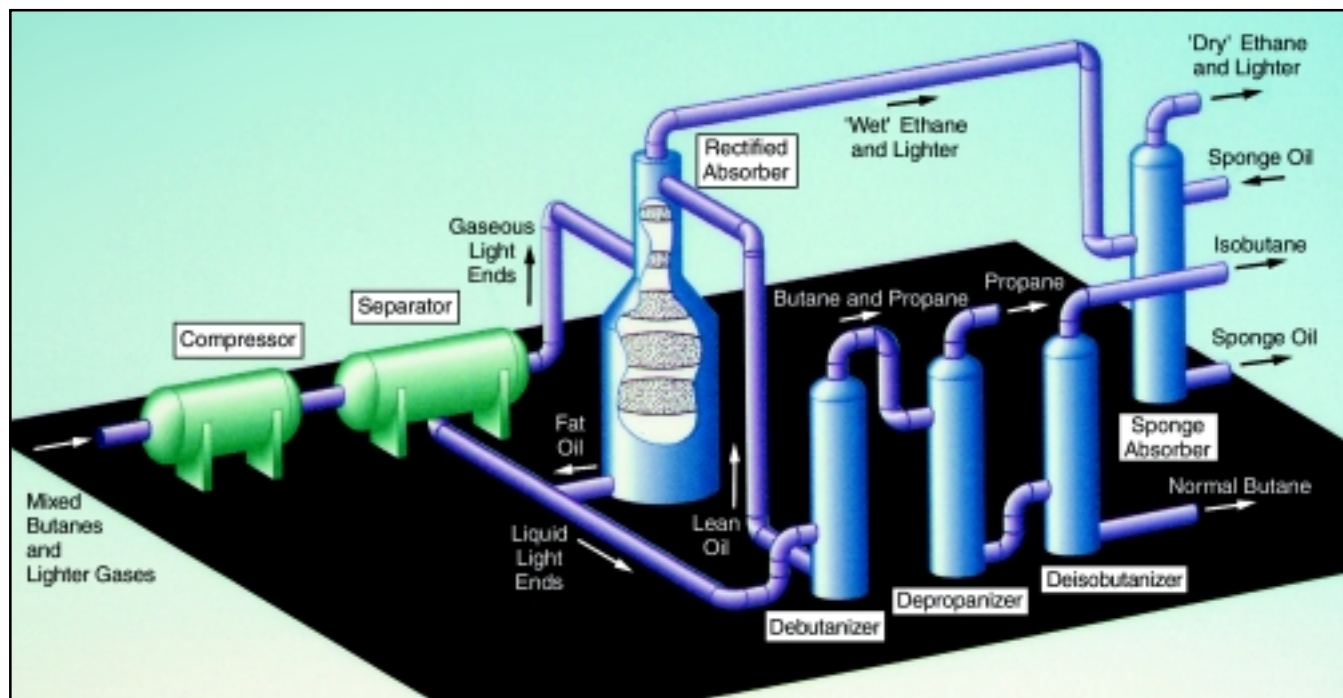


Figure 34: Typical Gas Plant

Introduction to Gas Plants

Normally two gas plants can be found in a refinery: the saturates (sats) gas plant and the cracked gas plant. They both function to separate volatiles into appropriate product streams. A *saturate gas plant* collects gases from hydroprocessing units (hydrocrackers, hydrotreaters and reformers) where the excess of hydrogen causes the gases to become saturated (paraffins). In contrast, the *cracked gas plant* processes hydrocarbons from carbon concentrating conversion units (cat crackers and cokers), which contain substantial quantities of olefins as a result of hydrogen deficiency.

Saturates (Sats) Gas Plant

A central piece of process equipment of the sats gas plant is the rectifier-absorber (RA) column. Its function is to de-ethanize, routing C_2 and lighter hydrocarbons to fuel and recovering C_3 and higher for product needs. C_2 products readily separate in the RA column and move to the top. The difficulty is keeping the C_3 out of the top. Keeping the heavy product out of the top is the function of the rectification. The absorption takes place by using a heavier liquid (in this case debutanizer bottoms) as the absorption medium. Figure 35 shows a description of the separations normally made in a saturates gas plant. A schematic flow diagram of the process is shown in Figure 37.

Incoming Feeds Contain $C_1 - C_7$

Finished Products:

H_1 } Fuel Gas for Refinery Fuel System
 C_1 } or Feed Gas for SMR
 C_2 }

C_3 Propane for Sale as LPG

C_4 Butane for Alky and Mogas

C_5 } Light Gasoline for OP Feed or Isom Feed
 C_6 }

Cyclo- C_6 } Light Naphtha for Reformer Feed
 C_7 }

Figure 35: Sats Gas Separations

- Fuel Gas - H_2 , C_1 , C_2
- Propylene/Propane to Alky, or Dimersol, or Chemical Feedstock
- Butylene/Butane to Alky
- Cracked Gasoline to Products

Treating Requirements

- Fuel Gas - H_2S Removal via DEA
- C_3 - H_2S and Mercaptan Removal via DEA/Caustic
- C_4 - Mercaptan Removal Via Caustic
- Gasoline
 - Mercaptan Removal via Caustic
 - Final Mercaptan - Disulfide Sweetening by Air or Merox
 - Also Treats SR Gasoline via Solutizer

Figure 36: Cracked Gas Plant Separation

Cracked Gas Plant

Cracked gas separations are shown in Figure 36 and a schematic flow diagram is shown in Figure 38. The primary difference between a sats gas plant and a cracked gas plant is that the cracked gas plant does not have a deisohexanizer. Cracked gas plants process material from carbon concentrating conversion units. Generally, their products are already aromatic (unsaturated ringed products, such as benzene) and don't need to be reformed. Since no reforming is required, no need exists for a deisohexanizer (DIH).

Control Valve Guidelines

The valves in a gas plant are generally constructed with carbon steel bodies and 316 stainless steel trim. In general, corrosion is not a problem as long as the temperature is maintained below 350° F (177° C). If the temperature is above 350° F (177° C), stainless steel bodies and 316 stainless steel trim should be considered. For applications requiring 4-inch (DN100) or smaller valves, globe-style valves with positioners (such as Mark One control valves) are usually used. In larger sizes, rotary valves are used (such as the MaxFlo eccentric plug valve).

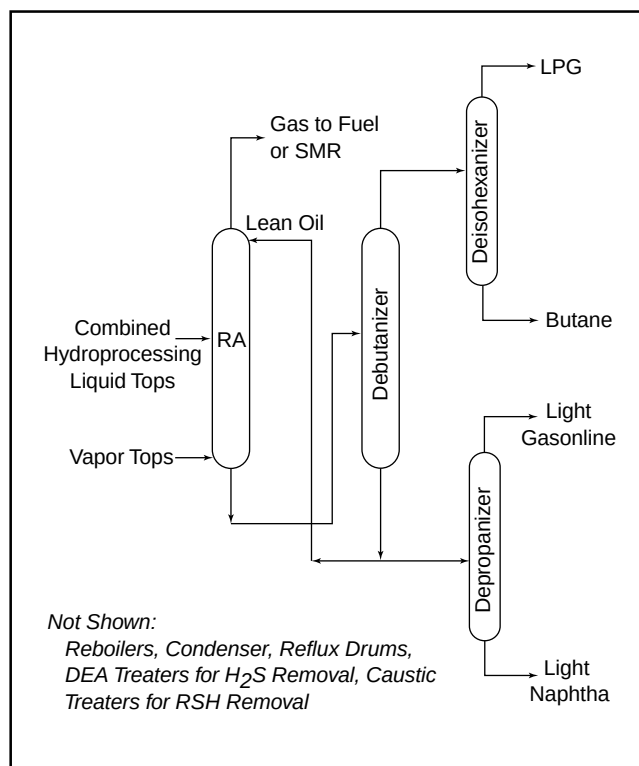


Figure 37: Sats Gas Plant

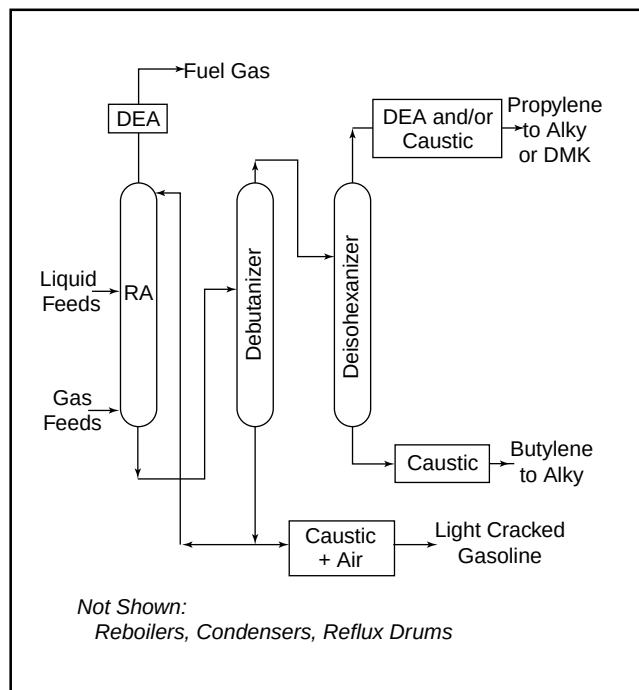


Figure 38: Typical Cracked Gas Plant

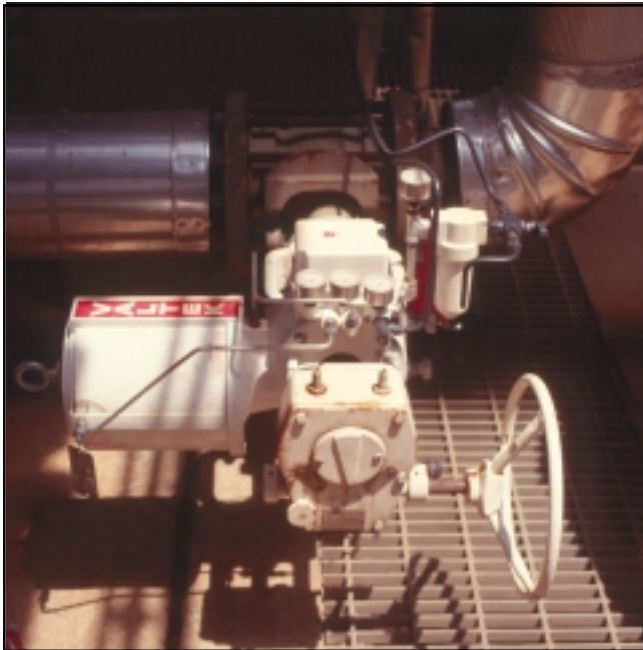
Control Valve Applications

- Control Valve Applications
- Steam Process
- Compressor Surge Control
- DEA and Caustic Service
- Interstage Reflux
- Stabilizer Pressure Control
- Splitter Pressure Control

Recommended Control Valves

Valtek MaxFlo Eccentric Plug Valve

Valve - The MaxFlo control valve is recommended as a cost-effective valve for gas plant applications. The valve design features a 200:1 turn-down and is equipped with a reduced trim option that is accomplished by simply changing the seat ring. The MaxFlo control valve is available with a variety of body and trim materials, allowing it to handle temperatures from cryogenic up to 800° F (427° C). Trim options include NACE, soft seat, hard seat, and solid Alloy 6 configurations. The MaxFlo packing box also allows for a low fugitive emission packing option. The valve is equipped with the Valtek rotary-motion spring cylinder actuator, which provides high torque and is compact and lightweight for easy maintenance.



Valtek Mark One Globe-style Valve - The Mark One control valve is highly versatile - available in a wide range of sizes (0.5 - 42-inch/DN 15 - 1000) and pressure classes (ANSI Class 150 - 2500/PN16 - 400). It is available in carbon or 316 stainless steels, Hastelloy C, Alloy 20, or other alloys as required. The standard Mark One material configuration (carbon steel body and 316 stainless steel trim) uses NACE-compatible materials. The Mark One design allows for a number of trim options, including anti-noise, anti-cavitation, high C_v , or low C_v trims. Double-top stem guiding is standard. This guiding design effectively keeps the guiding surfaces out of the flow and avoids the use of cage-guided trim that have a tendency to stick or gall. The Mark One design includes large plug stem diameters, which ensures proper packing and guiding performance. The Mark One linear-motion spring cylinder actuator is compact and lightweight for easy maintenance, high thrust, field-reversible, and easily disassembled.



Olefins Plant

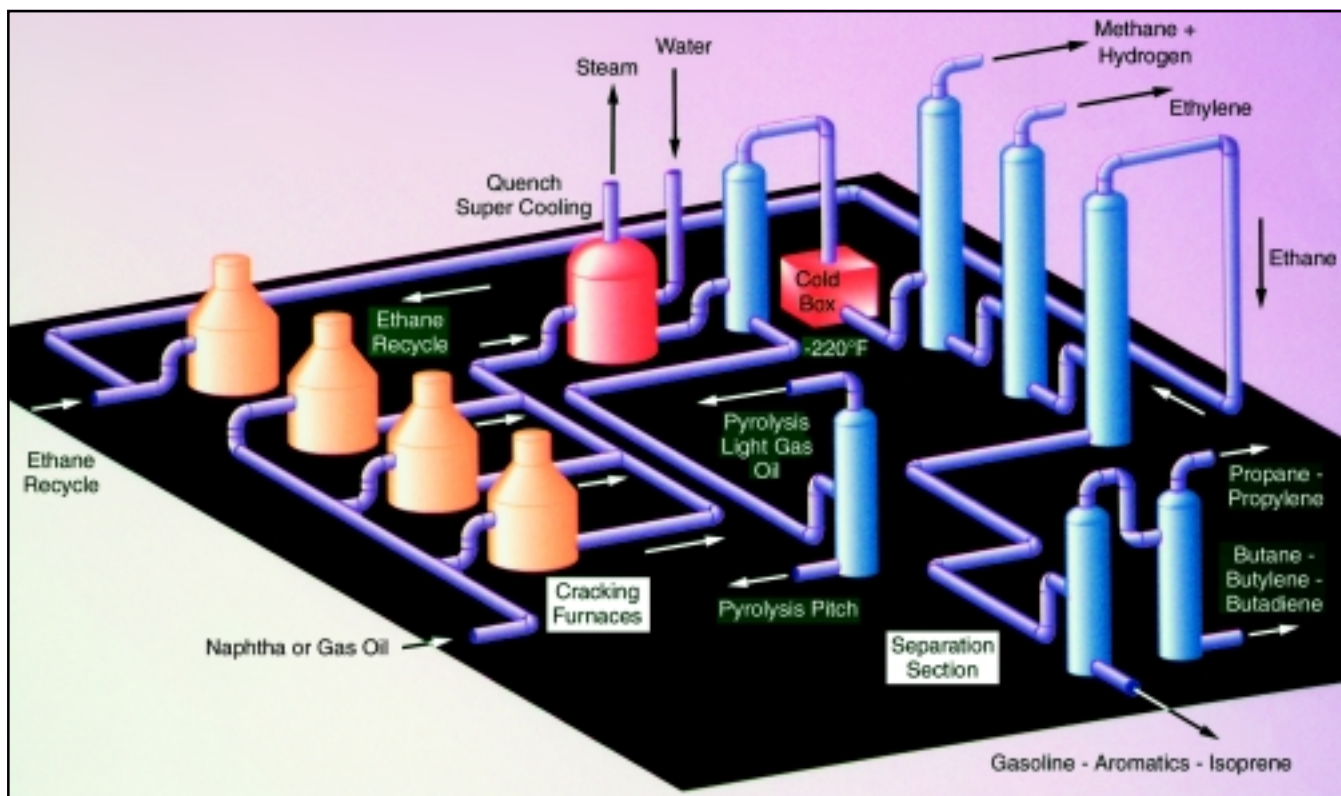


Figure 39: Typical Olefins Plant

Ethylene Plants

Chemical producers are often involved in petroleum refining through their ethylene plants. That is the reason why so many large ethylene plants are built by integrated oil/chemical companies. Ethylene plants are called *olefins plants* (OP), but are sometimes referred to as *ethylene crackers* (which is incorrect terminology), *steam crackers* (because steam is mixed with the feed) or *crackers* (with a suffix denoting the feed, such as ethane cracker.)

Olefins plants are designed to crack a number of feed stocks. They usually fall into the following categories: ethane, ethane/propane mix, propane butane naphtha, and gas oil.

The original olefins plants were built to produce ethylene to feed the growing needs of the chemical industry. Propylene was of less interest because a large pool of the hydrocarbon could be requisitioned from the refinery alkylation plant. Therefore, many of the early olefins plants were designed to reform ethane or ethane and propane (because the yield of ethylene from ethane is very high).

Later development of technology led to the use of the heavier feed stocks because of the larger availability

of the feeds and because olefins plants cracking naphtha and gas oils produce a high octane gasoline blending component. A number of huge olefins plants have grown in size equivalent to medium-sized refineries. Many have been integrated into refineries and produce a significant amount of the gasoline.

Refinery Interaction

Olefins plants provide a home for a number of junk streams in a refinery. For example, the dry gas stream from a cat cracker is usually sent to the fuel system, even though it contains ethane, ethylene, some propane, and propylene. However, at the olefins plant, these components can be separated and put to higher value use.

Some of the naphthas, such as benzene raffinate, are low octane and of little value as a blending component. These streams make an attractive feedstock for olefins plants, not only because of their low alternate value, but because they yield a higher octane component as a by-product of ethylene manufacture. On the other side of the ethylene plant, the butylenes and heavier feed can generally find a use in the refinery processes.

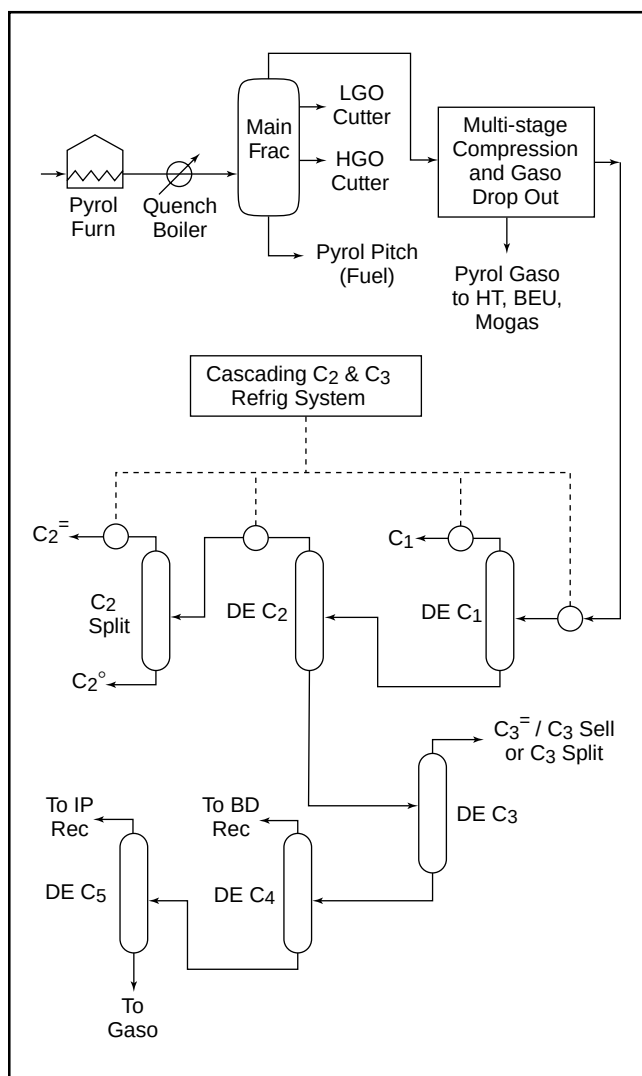


Figure 40: Overview of Olefins Plant

Olefins Process

The olefins reaction is thermal pyrolysis. Temperature is 1400° to 1650° F (760° to 899° C) with contact time of 0.3 to 0.8 seconds. Feed is preheated to around 900° F (482° C) and enters a radiant section of the pyrolysis furnace. The actual reaction takes place in the furnace tube, and the furnace effluent is quickly quenched below reaction temperature. Since this is a carbon concentrating process, products are either *olefinic* (light fragments) or *aromatic* (heavy fragments). Feeds can be anything from ethane to gas oils with end points up to about 750° F (399° C). The lighter the feed, the more severe the pyrolysis conditions, with each different feed requiring different pyrolysis conditions. Flexibility of feed material does exist to a limited extent. For example, during the summer months when gasoline is in great demand and furnace oil is of lower value, the olefins plant feed is shifted to heavier liquids - sometimes even using furnace oil for olefins plant feed. In winter, however, with furnace oil in demand,

the olefins plant feed is shifted to the lighter end with feeds such as condensate and sometimes naphtha. Figure 40 shows an overview of an olefins plant, which is really three plants in one: the pyrolysis section, the process gas compression/gasoline recovery train, and the fractionation/refrigeration train.

Figure 41 shows a diagram of the pyrolysis section of the olefins plant. The pyrolysis fractionator is a variant of the multicomponent distillation process. Two ways of quenching are shown: direct quench by generating steam in a quench boiler, and indirect quench by injection of a relatively cool oil stream.

The direct quench boiler operates at a temperature where ultra-high pressure steam (1200 psig/82.8 barg) can be generated. In the oil injection system, the heat is recovered in a circulating reflux loop on the fractionator. The operating temperature of the fractionator is high enough only to generate 200 psig (13.8 barg) steam. An advantage of generating the steam in the direct, quench boiler at 1200 psig (82.8 barg), is that this steam can be used to run a turbine and generate a big block of horsepower. The 200 psig (13.8 barg) steam is still available as exhaust from the turbine. The direct quench boiler is much more energy efficient; however, it tends to foul regularly on heavier feeds (Figure 41). Using modern quench boilers feeds as heavy as kerosene may be used in the process.

Downstream of the quench is the main fractionator column, where the overheads go to the compression train (Figure 42). The bottoms of the column is pyrolysis pitch and some gas oils are removed from the center of the column.

Olefins Plant Compression Train

In the olefins plant compression train, the overheads from the main fractionating column are compressed, usually in a number of stages. The gases are compressed, which usually raises the temperature about 120° F (49° C) per stage. The compressors have interstage coolers for two reasons: First, so the gas temperature does not get too high and reach a fouling and cracking temperature. Second, at the higher pressures and cooled temperature, the gases condense and product drops out. Any product that condenses out does not have to be compressed in the next stage; this is an energy savings.

At the end of the compression train the gases remaining at about 500 psig (34.5 barg) and ambient temperature must be refrigerated for further separation into products. This takes place in the olefins plant refrigeration section (Figure 43). In this section of the plant, the gases remaining are cooled through what is known as *Joule-Thompson expansion*. This is the same phenomenon that takes place in an automobile refrigeration

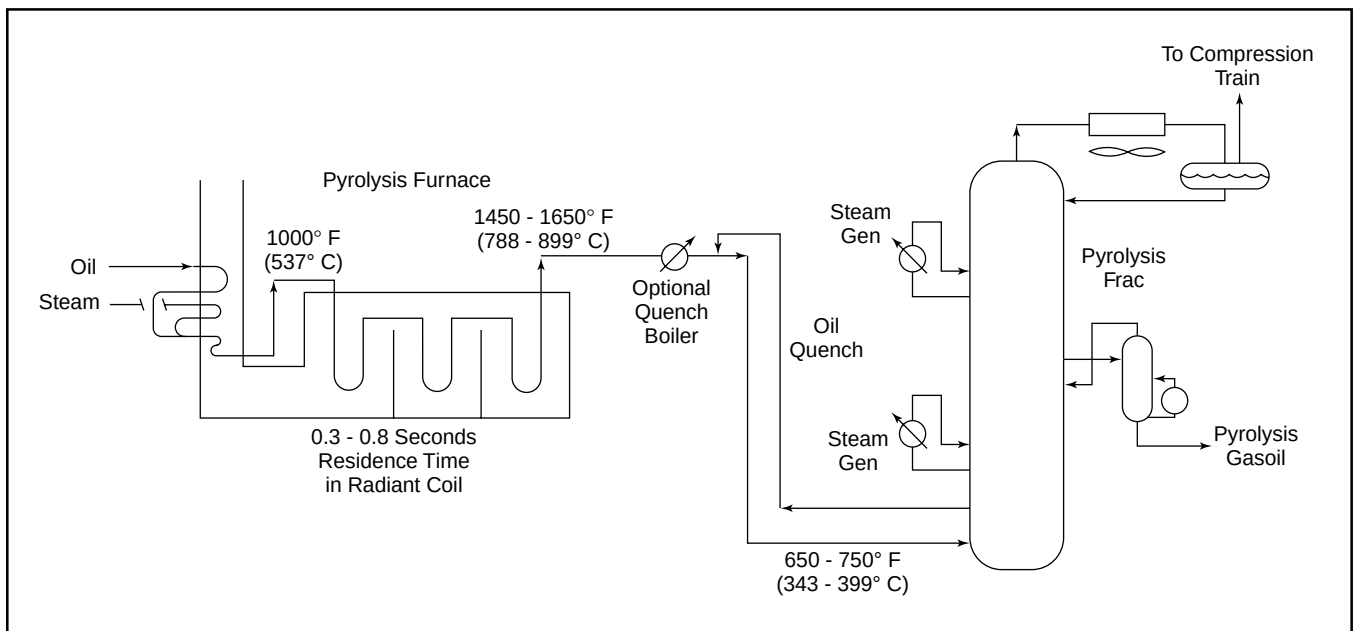


Figure 41: OP 'Hot' End

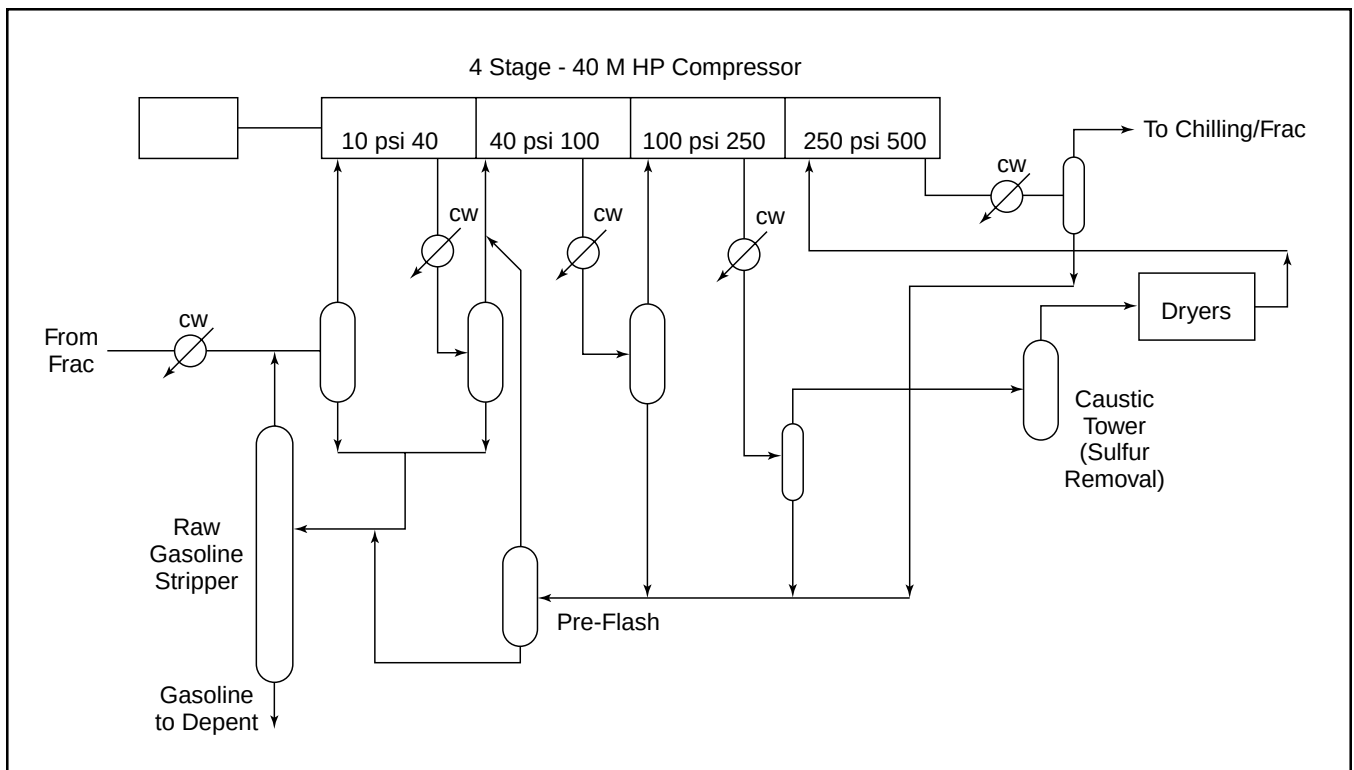


Figure 42: OP Compression Train

system in which freon is the working fluid. In the OP refrigeration plant, C_2 and C_3 gases are used as the refrigerant. By the end of the process, the methane, ethane, ethylene, propane, propylene, butane, butylene, and other products have been separated out. The propane and ethane are recycled, and converted to ethylene and propylene in the system.

Control Valve Guidelines

The olefins plant has a variety of fluid flow conditions that affect valve design and configuration. The control valves installed before the pyrolysis furnace operate at temperatures of 900° F (482° C) and higher. This requires the use of valves with stainless steel bodies (316 or 347 stainless steel), as well as stainless steel

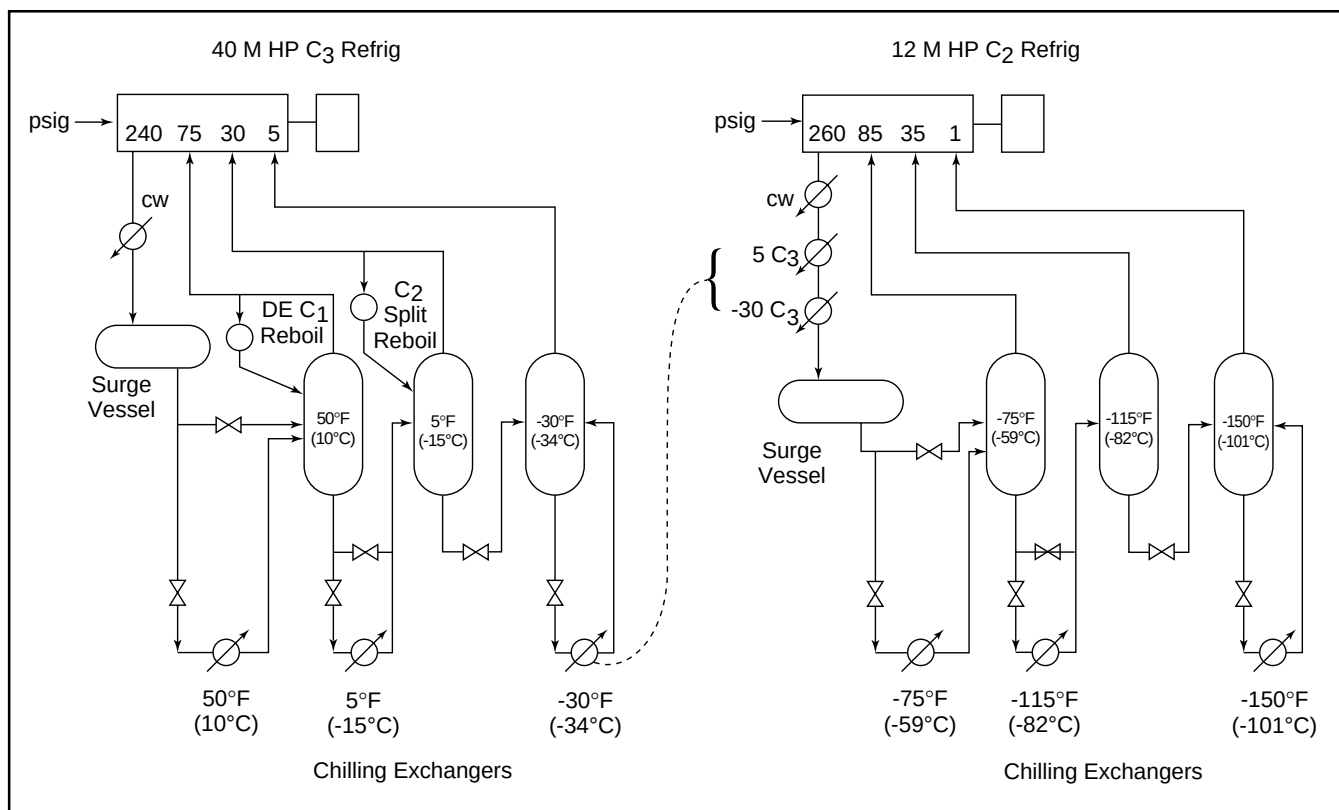


Figure 43: OP Refrigeration System

trim that has been hard-faced with Alloy 6 or colmonoy. Guides or bearings should also be of Alloy 6 or colmonoy. Extended bonnets to protect the packing from the heat are required and a graphite-based packing is generally used. Chemical-based corrosion is not generally a problem; therefore, when the temperature is below 500° F (260° C) and above -20° F (-29° C), carbon steel valves with 316 stainless steel trim is sufficient. In the refrigeration section of the olefins plant with temperatures lower than -20° F (-29° C) 316 stainless steel valves with cryogenic extended bonnets are required. Globe-style valves, such as Mark One control valves, are generally specified for high temperatures (above 800° F/427° C) and for valve sizes 4-inch (DN100) and smaller. In larger sizes (6-inch/DN 150 and larger), rotary valves are often specified (such as MaxFlo eccentric plug valves) because they are less costly. Rotary valves also provide less packing/shaft leakage and are well-suited for applications where environmental regulations are in effect.

Control Valve Applications:

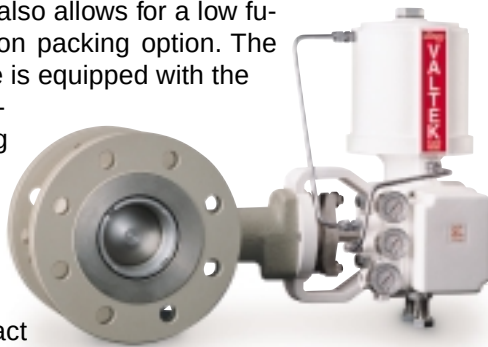
- Control Valve Applications
- Pyrolysis Furnace Service
- High Pressure Steam
- Chilling / Fractionator Service
- Compression Train Flow Control

Recommended Control Valves

Valtek ShearStream Ball Valve - The ShearStream control valve has been specially modified for service for olefins furnace applications. This modified ShearStream valve is a segmented ball valve with trim constructed from 316 stainless steel or 316 stainless steel with overlaid Alloy 6. It also features an extended body and an Inconel shaft. This valve is designed to operate reliably and efficiently with ethylene feedstock at high temperatures up to 900° F (482° C). The ShearStream has a high turndown (300:1), high C_v s, and the ability to resist coking. The valve is equipped with the Valtek rotary-motion spring cylinder actuator, which provides high torque and is compact and lightweight for easy maintenance.



Valtek MaxFlo Eccentric Plug Valve - The MaxFlo valve design features a 200:1 turndown and is equipped with a reduced trim option that is accomplished by simply changing the seat ring. The MaxFlo control valve is available with a variety of body and trim materials, allowing it to handle temperatures from cryogenic up to 800° F (427° C). Trim options include NACE, soft seat, hard seat, and solid Alloy 6 configurations. The MaxFlo packing box also allows for a low fugitive emission packing option. The MaxFlo valve is equipped with the Valtek rotary-motion spring cylinder actuator, which provides high torque and is compact and lightweight.



Valtek Mark One Globe-style Valve

Valve - The Mark One control valve is available in a wide range of sizes (0.5 - 42-inch/DN 15 - 1000) and pressure classes (ANSI Class 150 - 2500/PN16 - 400). It is available in carbon or 316 stainless steels, Hastelloy C, Alloy 20, or other alloys as required. To meet the demands of refining applications, the standard Mark One features a carbon steel body and 316 stainless steel trim (which are built with NACE-compatible materials). The Mark One design allows for a number of trim options, including anti-noise, anti-cavitation, high C_v , or low C_v trims. Double-top stem guiding is standard. This guiding design effectively keeps the guiding surfaces out of the flow and avoids the use of cage-guided trim that have a tendency to stick or gall. The Mark One design includes large plug stem diameters, which ensures proper packing and guiding performance. The Mark One linear-motion spring cylinder actuator is compact and lightweight for easy maintenance, high thrust, field-reversible, and easily disassembled.



Catalytic Cracking Plant

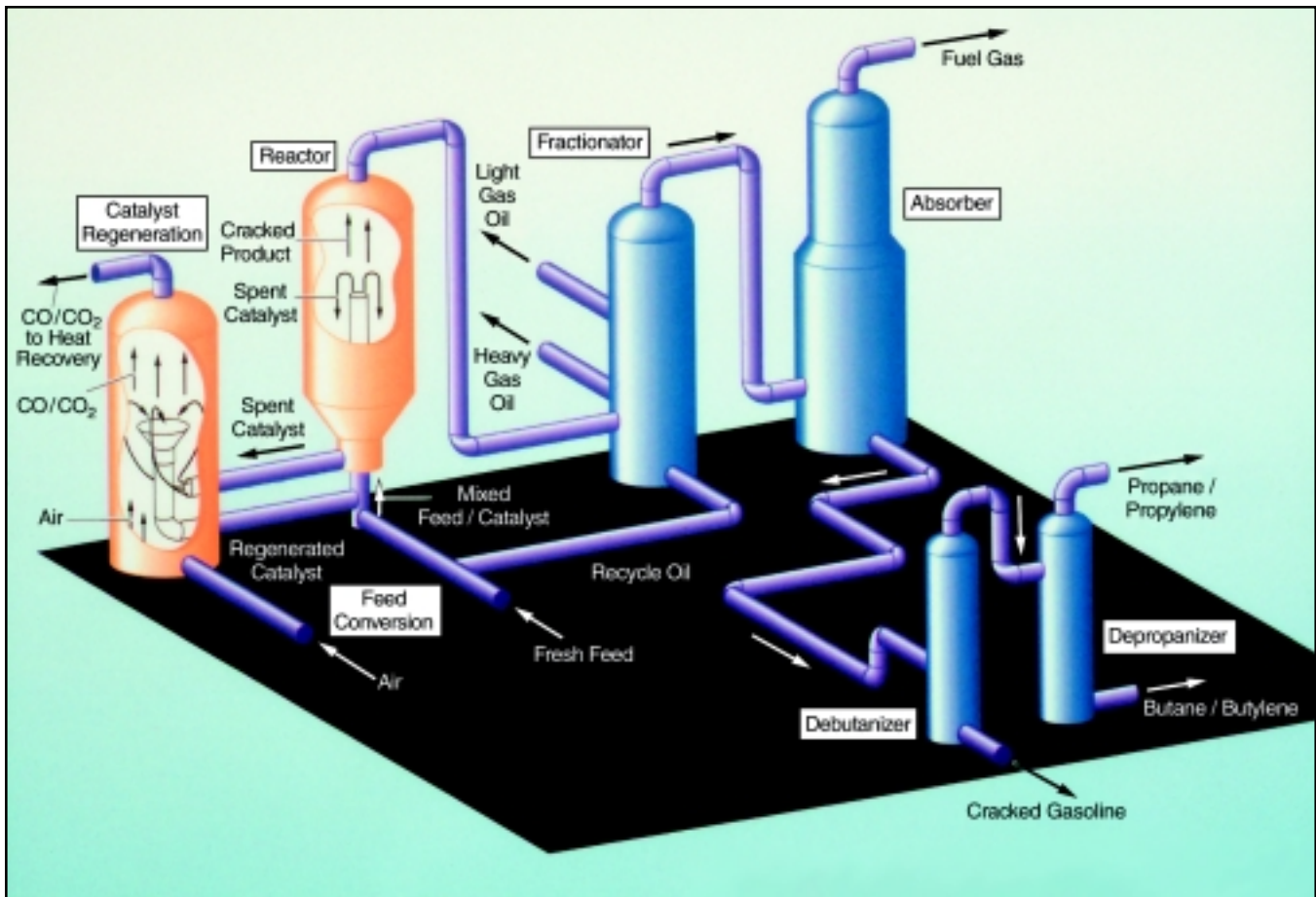


Figure 44: Catalytic Cracker

Introduction to Catalytic (Cat) Cracking

In the early years of the petroleum industry, the proportion of the crude oil barrel that consumers wanted in the form of gasoline increased faster than fuel oil. It became readily apparent that the production of enough straight chain gasoline to satisfy the market would result in a glut of heavy fuel oils. The economic symptoms of this problem were the increasing price of gasoline and the declining price of the heavier cuts. To cope with this physical and economic problem, the process engineers developed a number of cracking techniques, the most popular of which is *cat cracking*.

Cat Cracker Process

In a cat cracker, straight-run heavy gas oils are subjected to heat and pressure and come into contact with a catalyst to promote cracking.

A catalyst is a substance added to a chemical and facilitating a chemical reaction, but when the reaction is complete the catalyst is removed. In other words, the catalyst does not change chemically; it causes reac-

tions between other chemicals. A catalyst lowers the activation energy of the reaction, making the reaction take place more readily.

The feed to the cat cracking process is usually a straight-run heavy gas oil, as well as the top from the vacuum flasher. The boiling point for cat feed can be anywhere in the 650° to 1100° F (343° to 593° C) range. Heat is required for the process. Temperatures in the cat cracker where the cracking takes place are approximately 900° F (482° C).

The process is designed to promote cracking in a specific way. The object is to convert the heavy cuts to gasoline. Ideally, all the product would be in the gasoline range, but the technology is not that perfect. During the cracking process, several phenomena occur: As the large molecules crack, the lack of sufficient hydrogen to saturate all the carbons causes some small amounts of carbons to form coke, which are virtually pure carbon atoms stuck together. As the large molecules break up, a full range of smaller molecules including methane are formed. Due to the deficiency of hydrogen, many of the molecules are olefins. In the

case where the large molecules in the feed are made up of several aromatic or naphthene rings stuck together, smaller aromatic or naphthenic compounds and some olefins result. Finally, large molecules, made up of several aromatic or naphthenic rings plus long side chains, are likely to crack where the side chains are attached. The resulting molecules, though lower in carbon count, are more dense, have a higher specific gravity and a higher boiling temperatures. The irony of this is that these molecules form a product that is heavier than the feed. The products of cat cracking are the full range of hydrocarbons (from methane through the residue range) plus coke.

The three parts to the cat cracking hardware are: the reaction section, the regenerator, and the fractionator.

Reaction Section

The guts of the cat cracker is the reaction section (see Figure 45). The cat feed is pumped through a heater, mixed with catalyst being gravity-fed into a line called a riser, which goes to the bottom of a large vessel called a reaction chamber. By the time the feed reaches the vessel, the cracking process is well underway, so the residence time in the vessel is only seconds. In fact, in the more modern cat crackers, all cracking takes place in the riser. The reactor is used only as a catalyst/hydrocarbon separator, using a cyclone, which is a mechanical device using centrifugal motion.

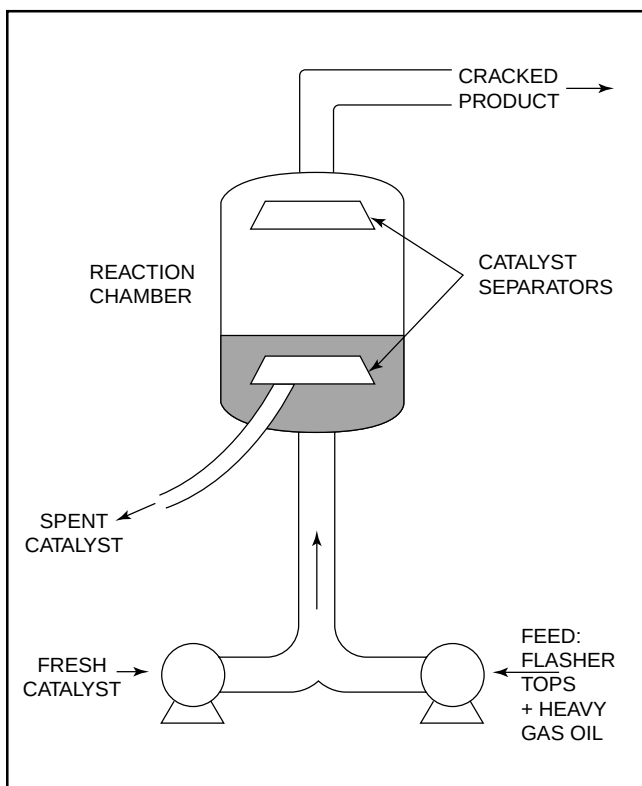


Figure 45: Cat Cracker Reaction Chamber

The *catalyst* is generally one of two types: *beads* or *particles*. The beads are 0.125- to 0.25-inch (3 to 6 mm) in diameter, while the particles are much smaller (with the appearance of talcum powder). Today, beads are not used very often due to the limitations of that medium. On the other hand, particles are more commonly used because of two unusual characteristics: If a container of particles is shaken or tilted, the powder reacts much like a fluid. Hence, the process is sometimes called fluid cat cracking. The second characteristic is common to both the beads and the particles, but is not apparent to the naked eye. Under a microscope, it becomes apparent that each has a large number of pores and, as a consequence, a tremendous surface area. Because the influence of the catalyst depends on contact with the cat feed, the large surface area is important to the process.

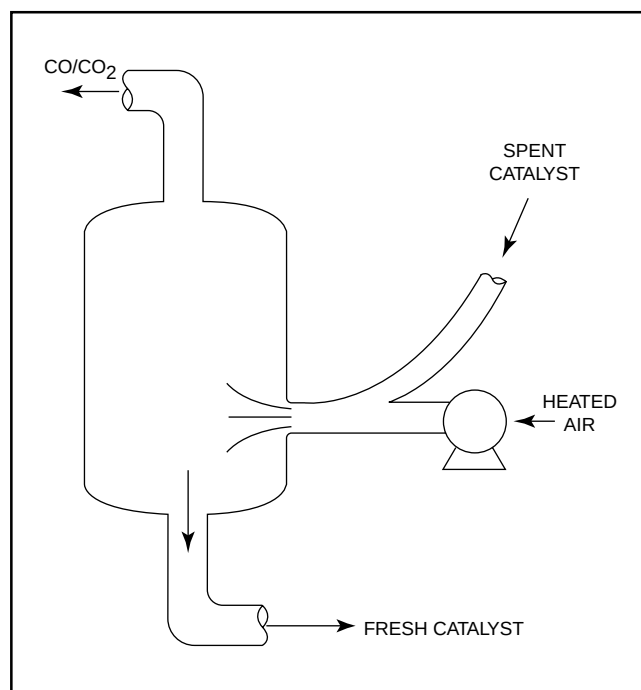
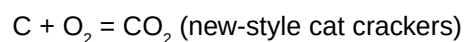
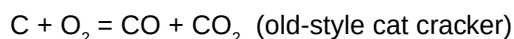


Figure 46: Catalyst Regenerator

The Regenerator

During the cracking process, the cracked hydrocarbon that is formed as coke ends up as a deposit on the catalyst, and as the catalyst surface is covered up, the catalyst becomes inactive (spent). This catalyst is erosive and requires refractory-lined ducts. To remove the carbon, the spent catalyst is circulated with air to a vessel called a regenerator (Figure 46). Heated air (1100° F/593° C), is mixed with the spent catalyst and the following chemical reaction takes place:



This process oxidation of coke is similar to burning coal or briquettes in that carbon unites with oxygen and gives off carbon dioxide (CO_2), sometimes carbon monoxide, (CO), for incomplete combustion and a large amount of heat. The heat, in the form of hot CO/CO_2 , is generally used in some other part of the process, such as raising the cat feed temperature in a heat exchanger. In the older cat crackers, the CO/CO_2 is sent to a CO furnace where oxidation of the rest of the CO to CO_2 is finally blown out to the atmosphere.

From the bottom of the regenerator flows fresh regenerated catalyst, ready to be mixed with cat feed on its way to the reaction chamber. Thus, the catalyst is in continuous motion going through the cracking/regeneration cycle.

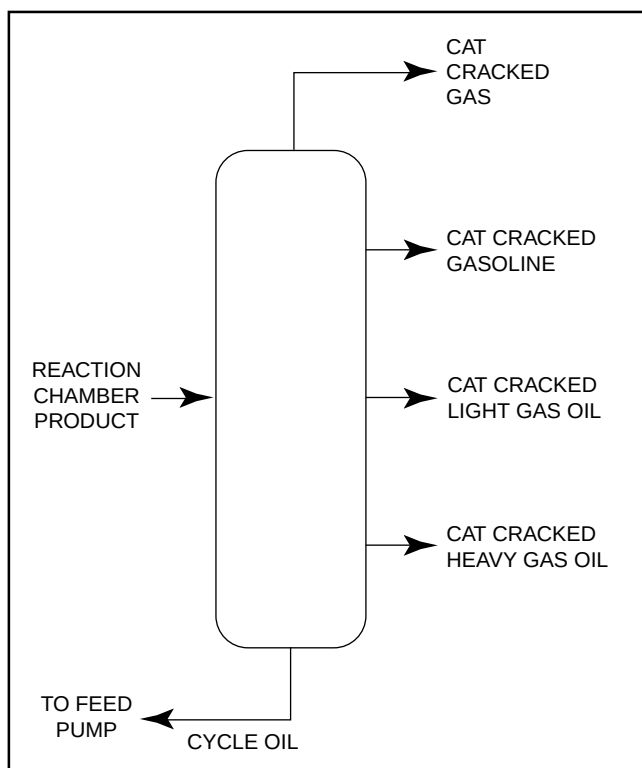


Figure 47: Fractionation

The Fractionator

When the cracked product leaves the reaction chamber, it is charged (pressurized) to a fractionating column dedicated to the cat cracker product. The products separated generally are the gases (C_4 and lighter), cat cracked gasoline, cat cracked light gas oil, cat cracked heavy gas oil, and the fractionator bottoms, called *cycle oil*. Cycle oil can be used in a variety of ways, but the most common use is to mix it with the fresh cat feed and run it through the reaction again. A portion of the cycle oil cracks each time through the reactor. By recycling, eventually all the cycle oil can be made to react. The process is designated as *recycling to extinction* (Figure 47).

The cat cracked heavy gas oil can be used as feed to a thermal cracker or as a residual fuel component. The light gas oil makes a good blending stock for distillate fuel, and the cat cracked gasoline makes a good motor gasoline blending component.

The refinery has some latitude in the cut point between the gasoline and light gas oil stream. This is one way to regulate the balance between gasoline and distillate as the seasons change. As the winter heating oil season begins, many refineries go into a *max distillate* mode. One of the operations that changes is the cat cracked gasoline end point. This is done in order to drop more volume into the cat light gas oil. In the summer, during the max gasoline mode, the shift is in the opposite direction.

The light ends from the fractionator are different in composition than those from the crude distilling column light ends. The cracking process results in the creation of olefins, so the C_4 and lighter stream not only contain methane, ethane, propane, and butanes, but also hydrogen ethylene, propylene and butylenes. Because of these extra components, this stream is separated at the cracked gas plant. This contrasts with the gas from operations like distilling where the gases contain only saturated compounds, and are sent to the saturated gas plant for separation. The isobutane, propylene and butylenes from the cat cracker are sometimes sent to the alkylation plant, which converts these olefins into gasoline blending components.

As shown in Figure 48, two circular flows are found within the cat cracking unit. On the left side the catalyst goes through the reaction, is regenerated and is charged back to the reaction again. On the right side, hydrocarbon flows in and flows out, but the cycle oil causes continuous circulation of some components.

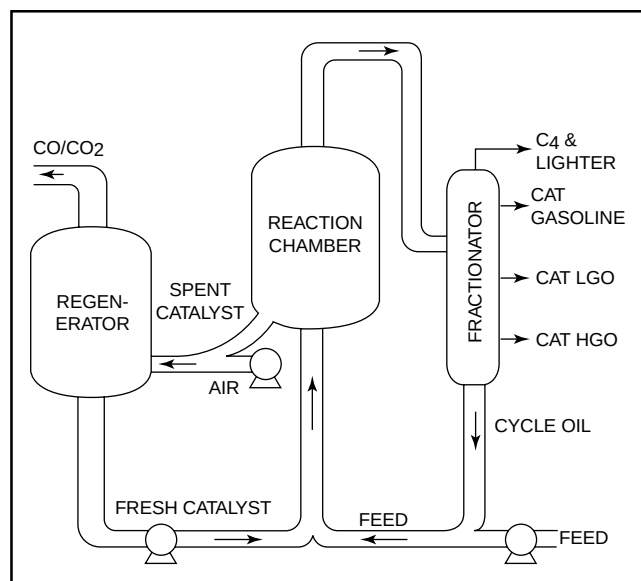


Figure 48: Cat Cracking Unit

Process Variables

Usually a cat cracker is run to the limit of its coke-burning capacity. That can be reached in a number of ways, but it becomes apparent when the yields of gasoline fall off and either heavy gas oil or C_4 and lighter yields start to increase. Some of the things that affect cat cracker yields are the quality of the feed, the reactor temperatures, the feed rate, the recycle rate, and the time of day and temperature of the ambient air.

Feed Quality

The cracking reaction is very complex, and data is available to predict yields from different feed characteristics. The gravity of the feed and its paraffin, naphthene, and aromatic content are all important to the quality of the product.

Reactor Temperature

The higher the temperature, the more cracking occurs; however, at some point the amount of gases created substantially increases at the expense of the cat gasoline or cat light gas oil. The optimum reactor temperature is a function of economic incentive.

Feed Rate and Recycle Rate

The yields will suffer at higher feed rates, so the trade-off with the volume of fractionator bottoms being recycled or left in the cat heavy gas oil is monitored.

Time of Day and Temperature

In order to regenerate the spent catalyst, fresh air is pumped into the regenerator continuously. As the temperature of the air outside goes down, the air becomes more dense. Since the blowers that pump the air operate at a fixed speed, more oxygen is actually pumped into the regenerator when it is cold rather than when it is hot. With more available oxygen, more coke is burned off the catalyst. The fresher the catalyst, the better the reaction proceeds, and the better the reaction, the more gasoline produced. From operator data logs, the swings can actually be plotted, and as night comes and temperature drops, the yield becomes better. With the heat of the afternoon, the yield falls off. Summer and winter have the same effects, with yields up in winter and down in summer.

From a process point of view, using the whole refinery as a basis, the cat cracker unit is shown in Figure 49 in respect to where it relates to other units in the refinery.

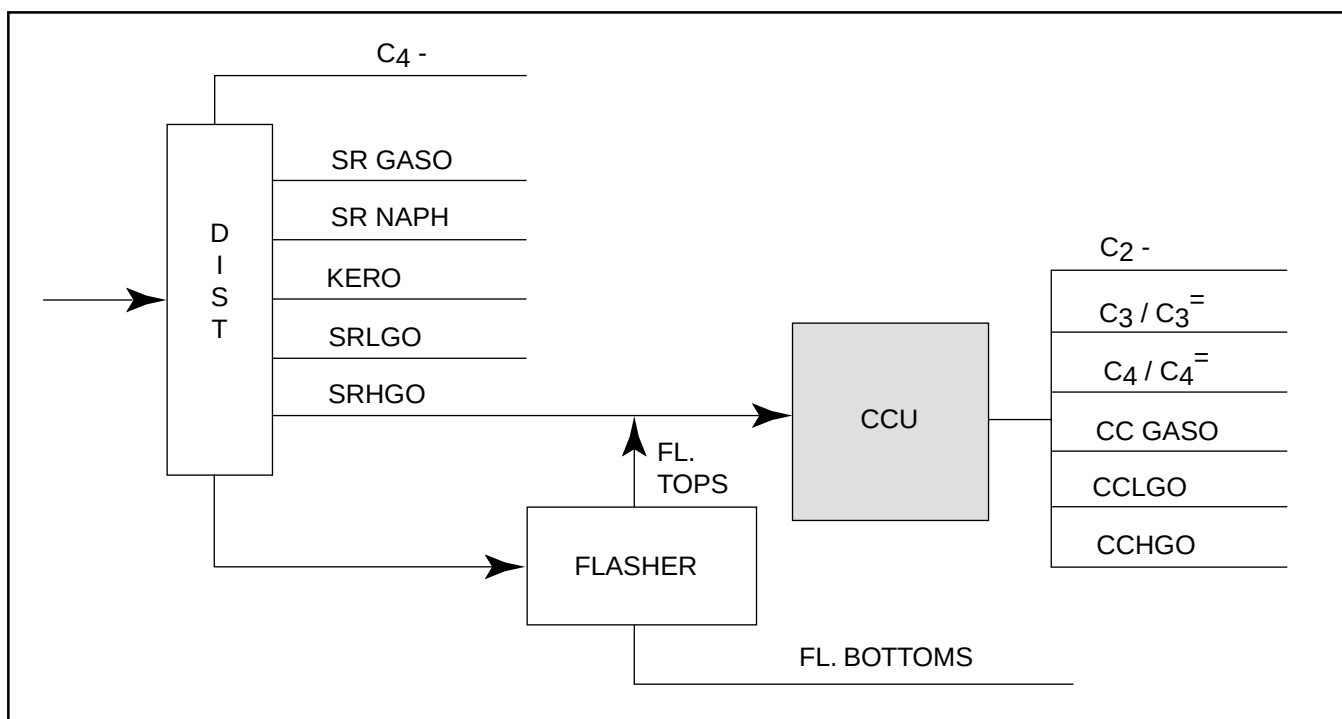


Figure 49: Refinery Flow Diagram

Control Valve Applications

- Feed Drum Flow Control
- Torch Fuel Control
- Reactor Stripping Steam
- Recycle / Surge Control
- Blow Air to Heater
- Mogas to Offsite
- Heavy/Light Cycle Oil Recycle
- Feed Pump Recycle

Recommended Control Valves

Valtek MaxFlo Eccentric Plug Valve - The MaxFlo control valve is often selected as a cost-effective valve for catalytic cracking applications. The MaxFlo valve features a better turndown ratio (200:1) than other valve styles. It is equipped with a reduced trim option, which is performed by replacing the seat ring. The standard MaxFlo configuration is available with a wide range of body and trim materials, which allows the valve to handle temperatures from cryogenic up to 800° F (427° C). MaxFlo trim options include NACE, soft seat, hard seat, and solid Alloy 6 configurations. The versatile packing box allows for optional low fugitive emission packing. The valve is typically equipped with a rugged rotary-motion spring cylinder actuator, which provides exceptional performance, high torque, and is compact and lightweight for easy maintenance.



Valtek Mark One Globe-style Valve - The Mark One control valve is available in a wide range of sizes (0.5 - 42-inch/DN 15 - 1000) and pressure classes (ANSI Class 150 - 2500/PN16 - 400). The Mark One material selection consists of carbon or 316 stainless steels, Hastelloy C, Alloy 20, or other alloys as required. To meet the demands of vacuum clashing applications, the standard Mark One configuration is built with NACE-compatible materials (carbon steel body and 316 stainless steel trim). The Mark One design provides for a number of trim options, including anti-noise, anti-cavitation, high C_v , or low C_v trims. Double-top stem guiding is standard, which effectively keeps the guiding surfaces out of the flow. The Mark One design avoids the use of cage-guided trim, which has a tendency to stick or gall, and includes large plug stem diameters for proper packing and guiding performance. The valve is equipped with the Valtek linear-motion spring cylinder actuator, which is compact and lightweight for easy maintenance, high thrust, field-reversible, and easily disassembled.



Hydrocracking Plant

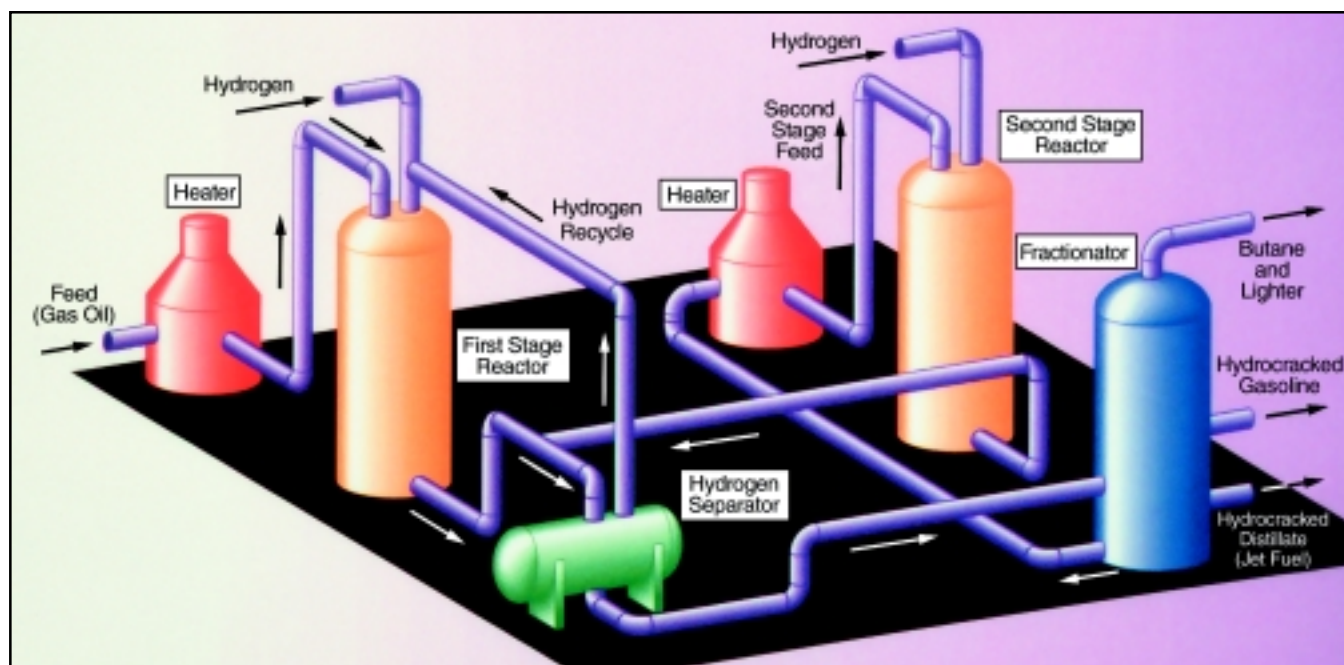


Figure 50: Hydrocracker

Introduction to Hydrocracking

Hydrocracking is a later generation process than cat cracking or cat reforming, but it was designed to accomplish more of what each of those processes start. Hydrocracking can increase the yield of gasoline components, usually at expense of gas oil range process stocks. It produces gasoline blending components of a quality not obtainable by recycling the gas oils through the cracking process that generated them. Hydrocracking can also be used to produce light distillates (jet fuel and diesel fuel) from heavy gas oils. One major advantage is that hydrocracking produces no bottom-of-the-barrel residue (coke, pitch, or resid). The outturn is all light oils.

Hydrocracking Process

Hydrocracking is cat cracking in the presence of hydrogen. The combination of the hydrogen (the catalyst) and the operating conditions permit cracking of low quality light gas oils from the other crackers, which would otherwise become distillate fuel. The process provides a high yield of good quality gasoline.

The most important benefit of a hydrocracker is its ability to swing the refiner outturns from high gasoline yields when the hydrocracker is running to high distillate yields when it is shut down. Hydrocracking improves the quality of both the gasoline blending pool and the distillate pool. It takes in the worst of the distillate stocks and produces a better than average gasoline blending com-

ponent. Hydrocracking produces a relatively large amount of isobutane, which is useful in balancing feed to the alkylation plant.

Hydrocracking catalysts are fortunately less expensive than reforming catalysts. Usually, they consist of sulfur compounds with cobalt, molybdenum or nickel plus alumina. In contrast to cat cracking, but similar to cat reforming, hydrocrackers have catalysts in a fixed bed. Like cat reforming, the process is carried out in more than one reactor (Figure 51).

Feed is pressurized to 1200 to 2000 psig (82.8 to 137.9 bar), mixed with hydrogen vapor, heated to 550° to 750° F (288° to 399° C), and charged to the first stage reactor. As it passes through the catalyst, about 40 to 50 percent of the feed is cracked to gasoline range material.

The hydrogen and the catalyst are complementary in several ways. First, the catalyst causes cracking, but the cracking process is endothermic and requires heat to continue. Fortunately, as the cracking takes place, the hydrogen saturates (fills out) the molecules, producing heat. This process is called hydrogenation and is exothermic. Thus, hydrogenation produces the heat necessary to continue the cracking.

Another way in which the hydrogen and catalyst are complementary is in the formation of isoparaffins. Cracking forms olefins, which could join together to form normal paraffins. Hydrogenation rapidly fills out all the double bonds, often forming isoparaffins and prevent-

ing reversion to less desirable molecules. (Isoparaffins have higher octane numbers than normal paraffins.)

After the hydrocarbon leaves the first stage, the process is cooled and liquefied, and then run through a hydrogen separator. The hydrogen is recycled to the feed, and the liquid is charged to a fractionator. Depending on the products desired (gasoline components, jet fuel or gas oil), the fractionator is run to remove some portion of the first-stage reactor product. Kerosene range material could be taken as a separate side draw product or could be included in the fractionator bottoms with the gas oil.

The fractionator bottoms are again mixed with a hydrogen stream and charged to the second stage. Since this material has already been subjected to some hydrogenation, cracking and reforming in the first stage, the operations of the second stage are of a higher temperature and pressure. Similar to the outturn of the first stage, the second-stage product is separated from the hydrogen and charged to the fractionator.

An extremely expensive and fortified vessel is necessary to handle the extreme operating conditions of 750° F (399° C) and 2000 psig (138 barg). The steel reactor walls are sometimes 6 inches (15 cm) thick. A critical concern of the operating personnel is the possibility of runaway cracking. Since the overall process is exo-

thermic, rapid temperature increases are possible, accelerating the cracking rates dangerously. Elaborate quench systems are built into most hydrocrackers to control runaway.

A few hydrocrackers have been constructed to handle straight-run residue or flasher vacuum flasher bottoms as feed. Most of them are operated as hydrotreaters.

Adding the hydrocracker to the refinery processing scheme, the absolute requirement for integrated operations becomes apparent. In one sense, the hydrocracker is the pivotal unit since it can swing the refinery yields between gasoline, distillate fuel and jet fuel.

Control Valve Guidelines

Hydrocracker control valves are generally constructed from carbon steel with 316 stainless steel trim below 550° F (288° C). Above that temperature, valve bodies are specified with 316 or 347 stainless with 316 stainless steel trim. (With the trim, an Alloy 6 overlay should be considered.) At these elevated temperatures, the addition of H₂ gas into the hydrocarbon fluid can increase the tendency for hydrogen attack and decarburizations which can cause premature failure of the valve body. Globe-style valves with positioners – such as Valtek Mark One valves – are generally specified in valve sizes 4-inch (DN 100) and smaller. In valve sizes

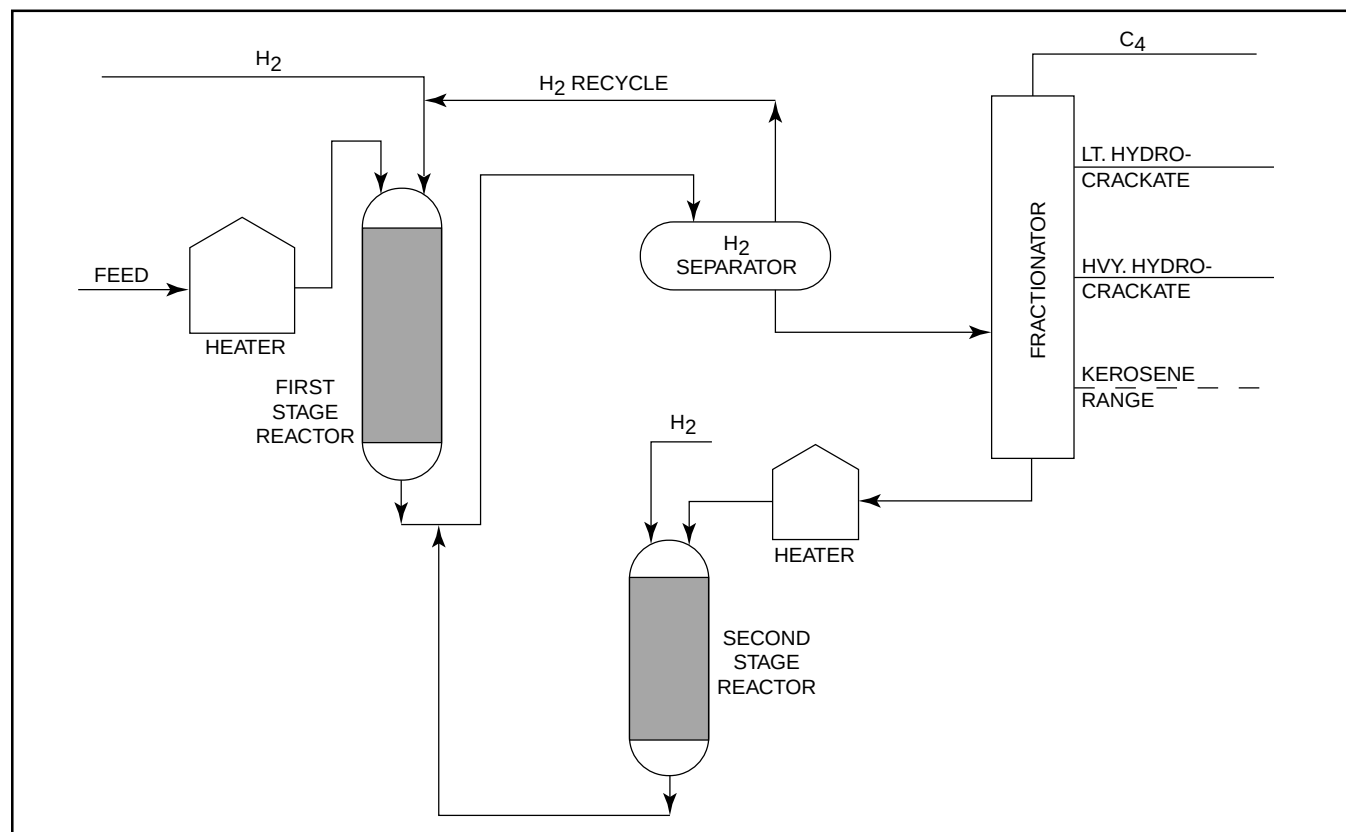


Figure 51: Two-stage Hydrocracker

6-inch (DN 150) and larger, rotary valves (such as the Valtek MaxFlo eccentric plug valve) are specified. Rotary valves have less shaft/packing leakage than comparable linear-motion valves; therefore, they are ideal when strict environmental standards are required.

Control Valve Applications

- Heater Fuel Control
- Reactor Recycle
- Fractionator Recycle
- Heat Exchanger Reboiler Bypass
- Hydrogen Feed Process Control
- Reactor Switching

Recommended Control Valves

Valtek Mark One Globe-style Valve - The Mark One control valve is highly versatile and is available in a wide range of sizes (0.5 - 42-inch/DN 15 - 1000) and pressure classes (ANSI Class 150 - 2500/PN16 - 400). It is constructed from carbon or 316 stainless steels, Hastelloy C, Alloy 20, or other alloys as required. The standard Mark One configuration (carbon steel body and 316 stainless steel trim) is built with NACE-compatible materials. The Mark One design allows for a number of trim options, including anti-noise, anti-cavitation, high C_v , or low C_v trims. Double-top stem guiding is standard. This guiding design effectively keeps the guiding surfaces out of the flow and avoids the use of cage-guided trim that have a tendency to stick or gall. The Mark One design includes large plug stem diameters, which ensures proper packing and guiding performance. The Mark One linear-motion spring cylinder actuator is compact and lightweight for easy maintenance, high thrust, field-reversible, and easily disassembled.



Thermal Cracking Plant

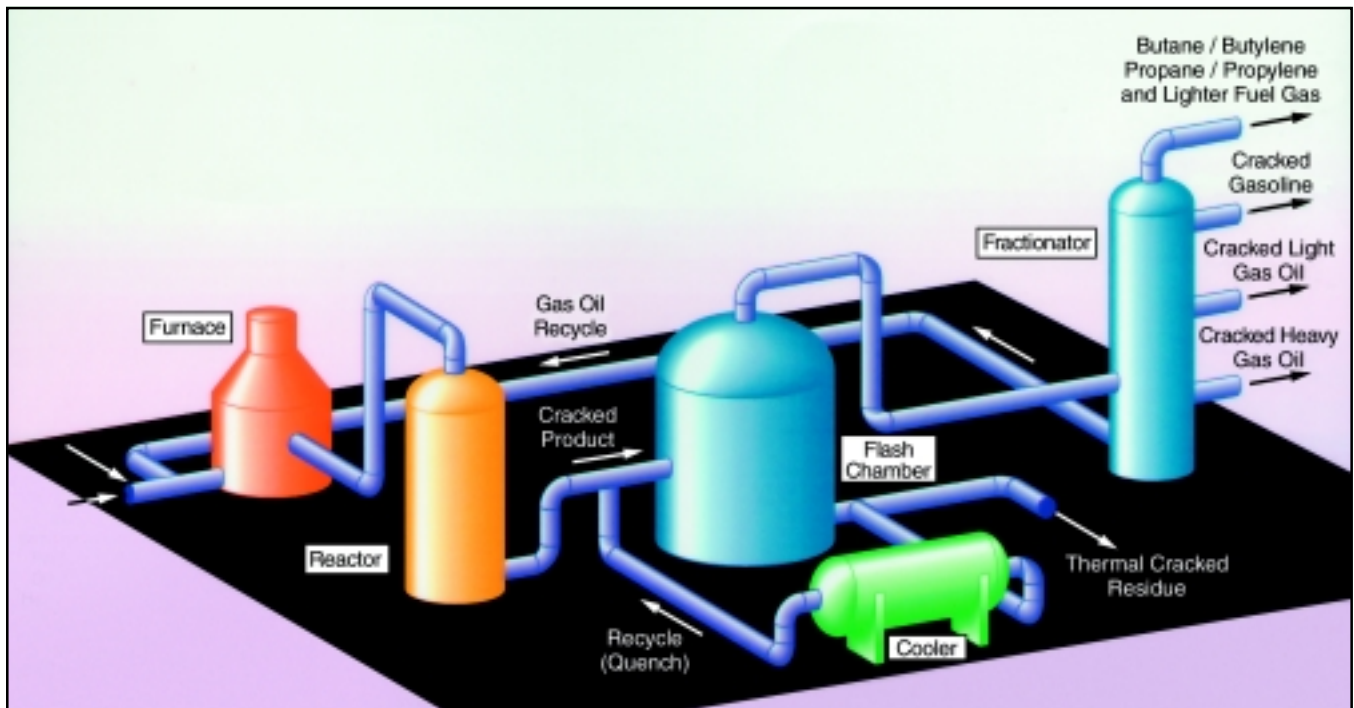


Figure 52: Thermal Cracker

Introduction to Thermal Cracking

Thermal cracking is the process that breaks down hydrocarbon molecules into smaller compounds (usually olefinic due to the absence of extra hydrogen). Long chain paraffins can separate at any point. For the cy-

clic compounds, the break tends to be at the point where a straight chain, if any, is attached. As a consequence, the heavier products of cracking tend to have high olefin, naphthene and aromatic contents.

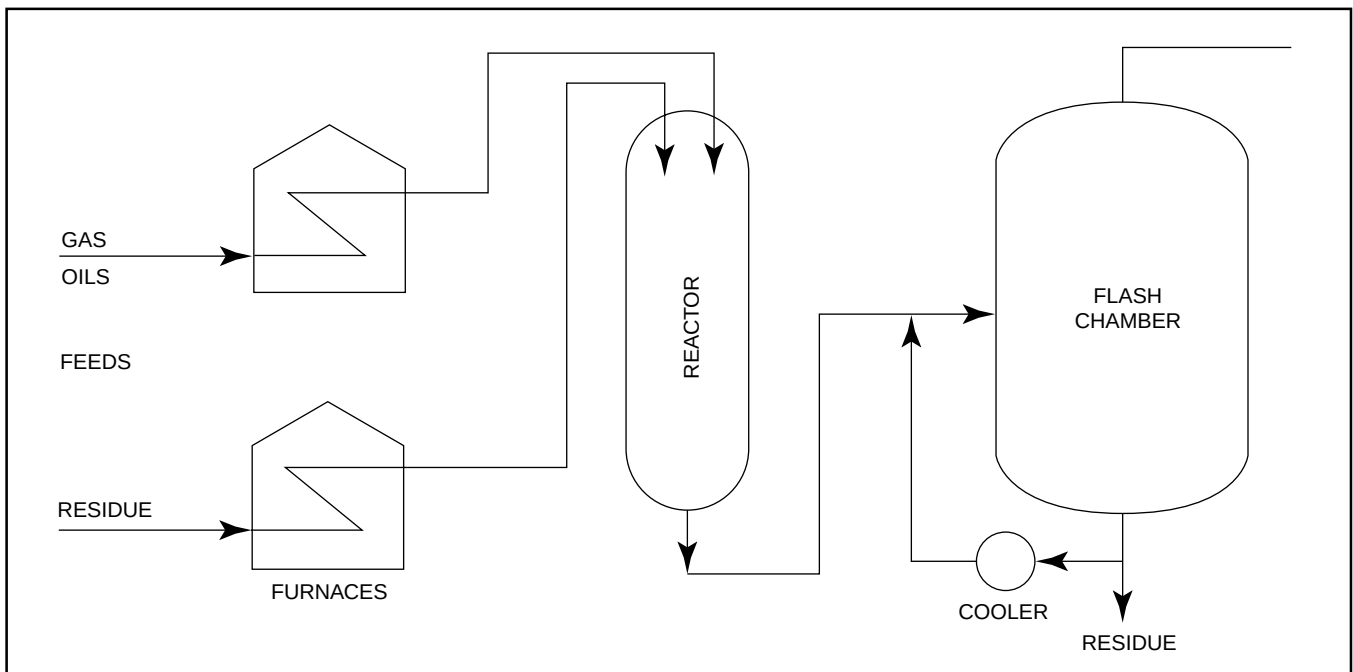


Figure 53: Thermal Cracker Reaction Section

Feed to the thermal cracker is usually vacuum flasher bottoms (pitch), but sometimes cat cracked heavy gas oil and cat cracked cycle oil are used for feed. If the broader range of streams is fed to the thermal cracker, the lighter distillate range hydrocarbons are kept separate from the heavier stocks. Though the streams are shown combined in Figure 53, each is fed to a separate furnace, since the temperature requirements are higher (and more severe) for the lighter products. The furnaces heat the feed to the 950° to 1020° F (510° to 549° C) range. Residence time in the furnaces is kept short to prevent much reaction from taking place in the tubes going through the furnace. Otherwise, the formation of coke can take place, quickly clogging the furnace tubes and shutting the operation down. The heated feed is then charged to a reaction chamber, which is kept at a pressure high enough (about 140 psig / 9.7 barg) to permit cracking but not coking.

From the reaction chamber, the product is mixed with a somewhat cooler recycle stream, which stops the cracking process. Both streams are charged to a flasher chamber where the lighter products go overhead because the pressure is reduced as in a vacuum flasher. The bottoms are a heavy residue, part of which is the recycle stream for the reaction chamber. The balance is usually blended in residual fuel.

The lighter products from the top of the flash chamber are charged to the fractionator (Figure 54). The C₄ and lighter streams are sent to the cracked gas plant. The thermal cracked gasoline and naphtha are used for gasoline blending or can be sent to the reformer. The gas oils can be used as a distillate fuel or, like the fractionator bottoms, can be recycled to extinction.

Control Valve Guidelines

The control valves applied in a thermal cracker are usually constructed with carbon steel bodies and 316 stainless steel trim for applications up to 650° F (343° C). Above this temperature, 316 or 347 stainless steel bodies with 316 stainless steel trim is usually specified. (Alloy 6 overlay is recommended with the trim.) Corrosion is not normally a problem in the thermal cracker. Globe-style valves with positioners (such as Valtek Mark One control valves) are typically used in applications requiring 4-inch (DN 100) and smaller valves. When 6-inch (DN 150) and larger valves are required, rotary valves (such as the Valtek MaxFlo eccentric plug valve) are commonly used because they are inherently less expensive. Rotary valves are also less susceptible to packing leaks and are advantageous where strict environmental regulations are in force.

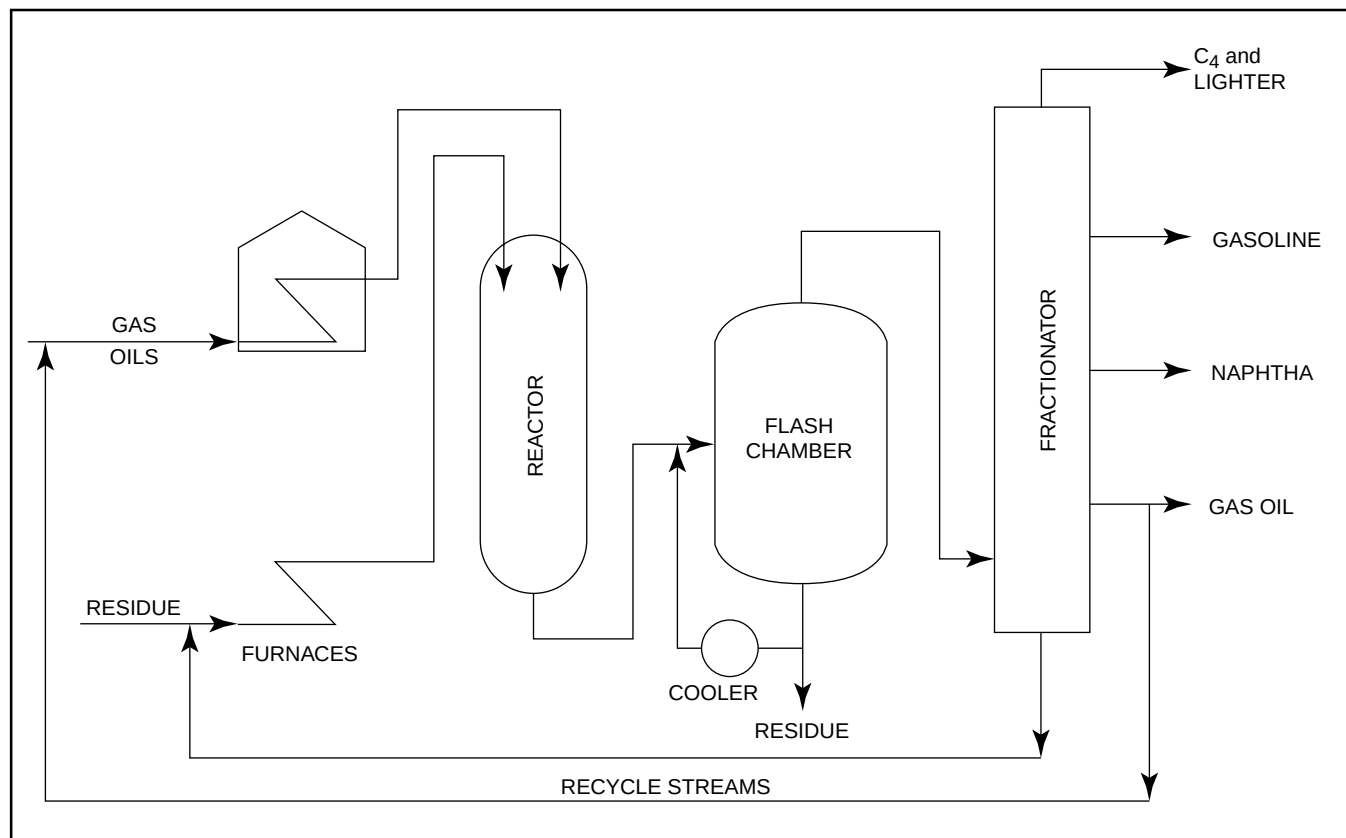


Figure 54: Thermal Cracker

Control Valve Applications

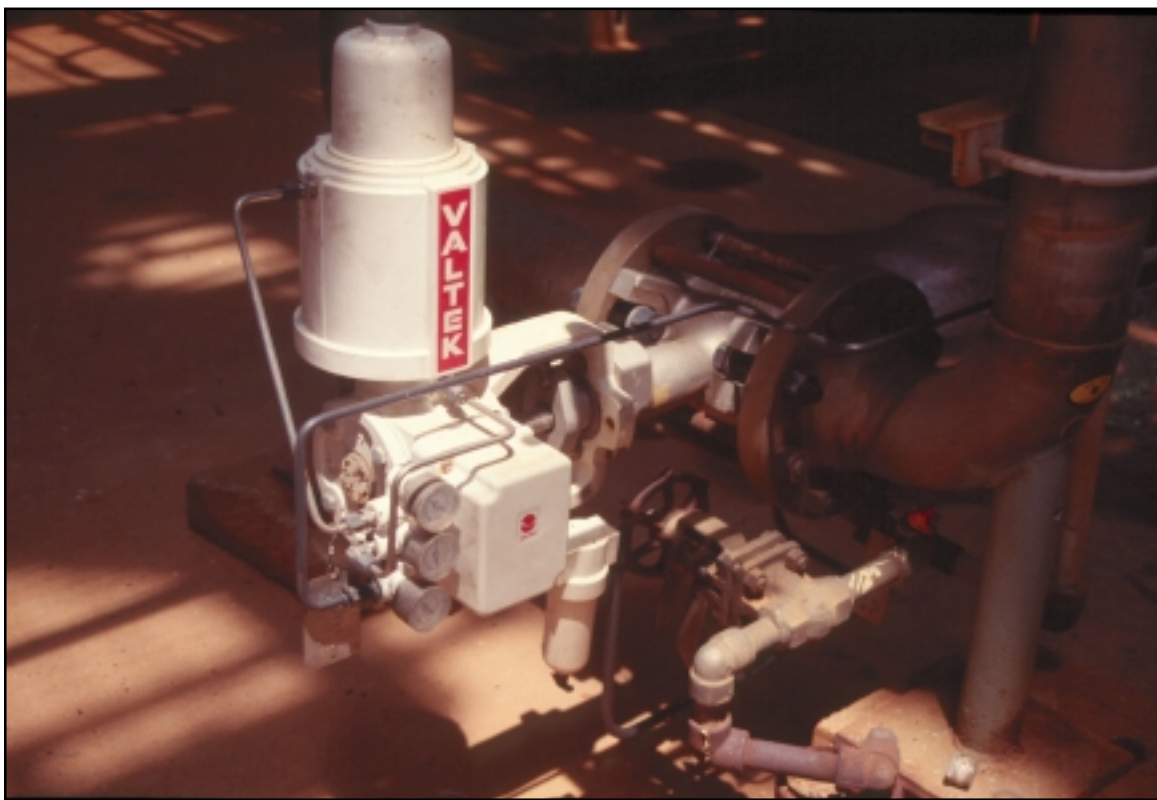
- Reactor to Flash Control
- Gas/Oil Feed
- Residue to Furnace Feed
- Cooler to Flash Control

Control Valve Application

Valtek MaxFlo Eccentric Plug Valve - The MaxFlo control valve provides a cost-effective solution to a number of thermal cracking applications. The valve is designed with a 200:1 turndown and can be equipped with reduced trim options (which are accomplished by simply changing the seat ring). With various configurations of body and trim materials, the MaxFlo control valve can handle temperatures from cryogenic up to 800° F (427° C). Trim options include NACE, soft seat, hard seat, and solid Alloy 6 configurations. Low fugitive emission packing options are also available. The Valtek rotary-motion spring cylinder actuator provides high torque, and is compact and lightweight for easy maintenance.



Valtek Mark One Globe-style Valve - The Mark One control valve is available in a wide range of sizes (0.5 - 42-inch/DN 15 - 1000) and pressure classes (ANSI Class 150 - 2500/PN16 - 400). It can be constructed from carbon or 316 stainless steels, Hastelloy C, Alloy 20, or other alloys as required. To meet the demands of refining applications, the standard Mark One configuration (carbon steel body/316 stainless steel trim) is built with NACE-compatible materials. The Mark One design is highly versatile, allowing for interchangeable trim installations (including anti-noise, anti-cavitation, high C_v , or low C_v trims). Double-top stem guiding is used to keep the guiding surfaces out of the flow, avoiding the use of cage-guided trim that stick or gall in particulate-laden services. The Mark One design includes large plug stem diameters, which ensures packing and guiding integrity. The high-thrust spring cylinder actuator is compact and lightweight for easy maintenance, field-reversible, and easily disassembled.



Coking Plant

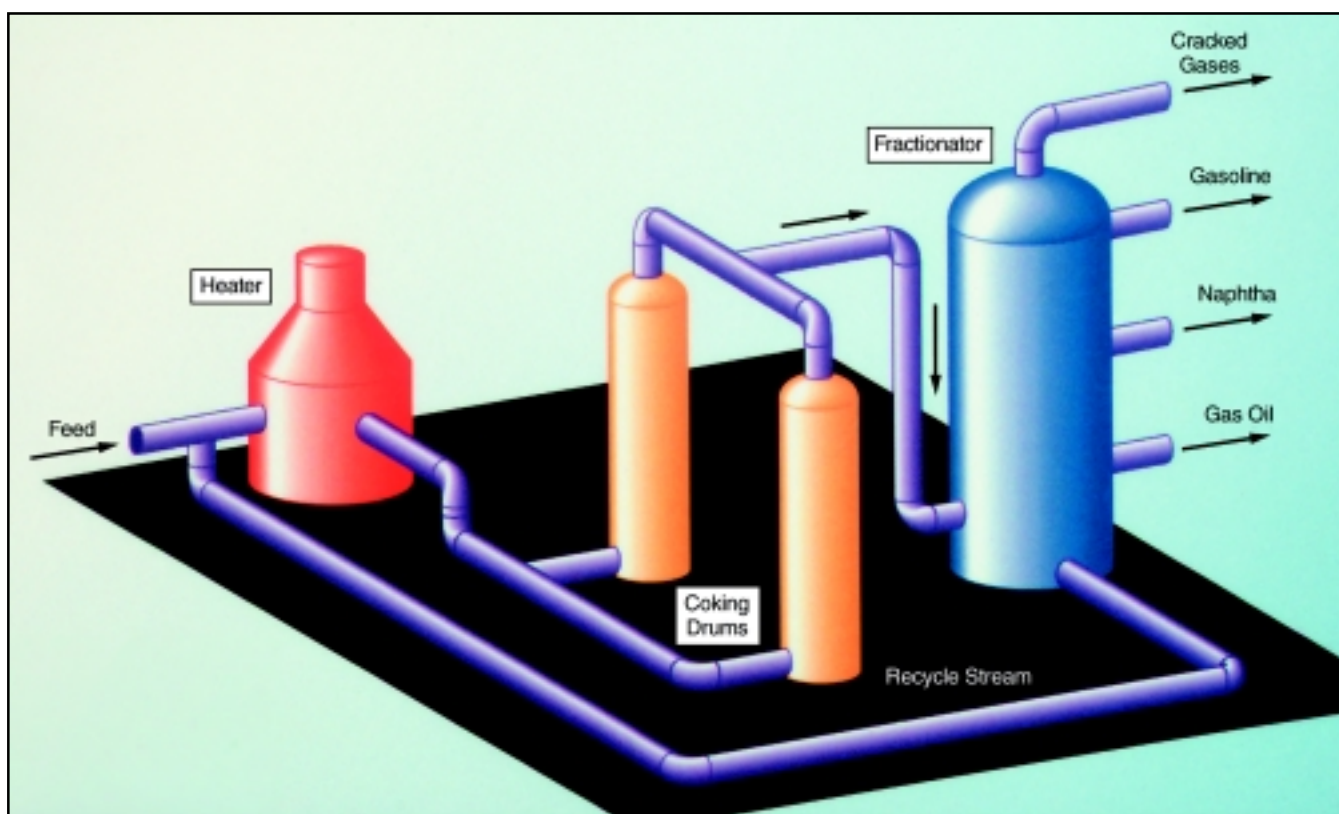


Figure 55: Coker

Introduction to Coking

Coking is severe thermal cracking. As thermal cracking became common, the process was studied extensively. These studies showed that high temperatures and very high velocities postpone the formation of coke until the pitch moves from the furnace tubes to a large surge tank. Retaining the hydrocarbon in this insulated vessel called a coke drum, permits extensive and controlled cracking and coking. Over time, technology was developed to handle this process efficiently on a continuous flow basis. While the concept is simpler than thermal cracking, the hardware is mechanically more complicated because of the coke handling facilities required. Since coke is a solid, it presents a number of problems with removal, transport, storage, etc.

Coking Process

The feed to the coker (same ones as the thermal cracker) is heated to about 1000° F (538° C) and then charged to the bottom of a coke drum (Figure 56). The cracked lighter product rises to the top of the drum and is drawn off. The heavier product remains and, because of the retained heat, cracks to coke (a solid coal-like substance of almost pure carbon). Vapors

from the top of the drum are sent to a fractionator for separation, similar to the thermal cracker process.

Coke removal from the drum is a special problem because it is a solid cake. If an upset occurs in a thermal cracker reaction chamber, and the reaction chamber gets coked up, the only way to get the coke out is to send workers into the vessel with chipping hammers and oxygen masks. In a coker, this occurrence is a daily routine, with the exception that it is planned for and is mechanized. The process is accomplished by using a high pressure water jet (about 2000 psi/138 bar). First a hole is drilled in the coke from the top to the bottom of the drum. Then a rotating stem is lowered through the hole, spraying a jet of water sideways. The high pressure cuts up the coke into lumps, and it drops out of the bottom of the drum into trucks or rail cars for shipment or hauling to the coke barn.

Typically the drums are on about a 48-hour cycle. Filling a drum with coke takes about 24 hours. Switching, cooling, decoking and emptying take about 22 hours, during which time another drum is filling.

While the thermal cracker uses about 80 percent of the residue, the coker uses 100 percent – but it also makes 30 percent coke for which a market must be found. Both

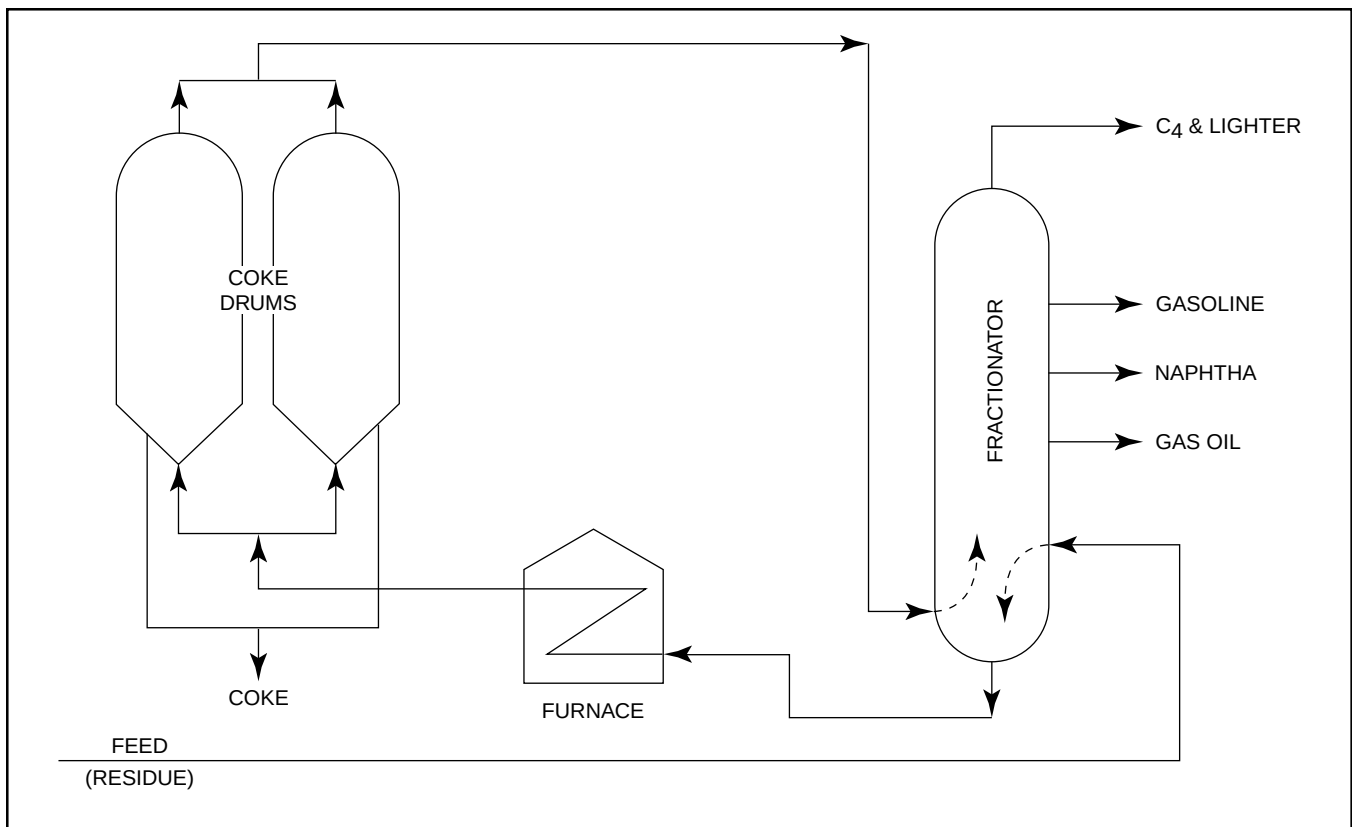


Figure 56: Coker Diagram

the thermal cracker and the coker processes make gasoline, naphthas and gas oils that are low in quality. The naphtha is often processed further in a cat reformer and the gas oil in a hydrocracker. However, the residue is eliminated, which is the primary objective.

Coke

Coke is used as a refinery fuel, much in the same way as coal. Most coke produced in a refinery is sponge-like in appearance. The main use for *sponge coke* is for the manufacture of electrodes and anodes, a carbon source for carbides and the manufacture of graphite. The strength of sponge coke is not sufficient for its use in blast furnaces for pig iron or in foundry work.

A second form, *needle coke*, derives its name from its microscopic elongated crystalline structure. Needle coke requires special coker feeds with sever operating conditions. When compared to the quality of sponge coke, needle coke is preferred in the manufacture of electrodes. These factors combine to increase the value of needle coke over sponge coke.

Coke usually has water and some liquid hydrocarbon mixed in, and before it is used it must be dried. Crushing and heating coke to drive off this material is called *calcining*.

Control Valve Guidelines

The process conditions for the coking process is similar to the thermal cracking conditions. Therefore, the control valves are similar in most respects. Control valves are usually constructed with carbon steel bodies with 316 stainless steel trim up to about 650° F (343° C). Above this temperature, valve bodies are constructed of 316 or 347 stainless steel. 316 stainless steel trim is specified and an Alloy 6 overlay is recommended. For valves handling coke or streams of hydrocarbon with entrained coke, special abrasion resistant valves and trim must be supplied. Valtek Survivor™ valves with ceramic trim are especially suited to the task. V-Port ball valves with ceramic or hardened trim may be used. Eccentric plug valves with hardened trim or ceramic trim can also be successfully applied.

Control Valve Applications

- Solvent Recycle
- Residual Oil Separator Bottoms
- Coking Furnace Pass Flow Control
- Coke Drum Water Quench
- Steam Drum Boiler Feedwater
- Steam Pressure Reducing

Recommended Control Valves

Valtek MaxFlo Eccentric Plug Valve - The MaxFlo control features a 200:1 turndown and is equipped with a reduced trim option that is accomplished by simply changing the seat ring. The MaxFlo control valve is available with a variety of body and trim materials, allowing it to handle temperatures from cryogenic up to 800° F (427° C). Trim options include NACE, soft seat, hard seat, and solid Alloy 6 configurations. The MaxFlo packing box also allows for a low fugitive emission packing option. The MaxFlo valve is equipped with the Valtek rotary-motion spring cylinder actuator, which provides high torque and is compact and lightweight for easy maintenance.



Valtek Mark One Globe-style Valve - The Mark One control valve is highly versatile - it is available in a wide range of sizes (0.5 - 42-inch/DN 15 - 1000) and pressure classes (ANSI Class 150 - 2500/PN16 - 400). The body is available in carbon or 316 stainless steels, Hastelloy C, Alloy 20, or other alloys as required. To meet the demands of hydrotreating applications, the standard Mark One material configuration (carbon steel body and 316 stainless steel trim) is built with NACE-compatible materials). The Mark One design allows for a number of trim options, including anti-noise, anti-cavitation, high C_v , or low C_v trims. Double-top stem guiding is standard. This guiding design effectively keeps the guiding surfaces out of the flow and avoids the use of cage-guided trim that have a tendency to stick or gall. The Mark One design includes large plug stem diameters, which ensures proper packing and guiding performance. The Mark One linear-motion spring cylinder actuator is compact and lightweight for easy maintenance, high thrust, field-reversible, and easily disassembled.



Glossary

Alkylation The process that converts light olefins into gasoline components by using relatively high pressures in the presence of a catalyst.

Aromatics Heavy fragments of a carbon concentrated feed.

Bubble Cap A device used with perforated trays (inside columns) that force vapors from boiling crude oil into a bubbling action, which is essential to distillation.

Calcining The process of crushing and heating coke to remove water and liquid hydrocarbons.

Cat Cracking The process of subjecting heavy gas oils to heat and pressure to promote additional cracking, resulting in the additional production of gasoline products.

Catalyst An inexpensive method that allows a refining reaction to take place at lower temperatures and pressures. Common catalysts include hydrofluoric acid or sulfuric acid. Common forms include beads and particles.

Catalytic Reforming A process that upgrades low octane naphthas to high octane blending component reformate. This process is also applied to the production of LPG and other high purity aromatics.

Claus Reaction A process that uses combustion and catalysts to convert H_2S to sulfur.

Condensate The liquid resulting when a vapor is subjected to cooling and/or pressure reduction.

Coking A severe form of thermal cracking that requires high temperatures and fluid velocities to permit extensive and controlled cracking.

Coke The residue of the coking process which, as a solid, is used as a refinery fuel. It is also used in the manufacture of electrodes and anodes.

Continuous Regenerator Reformer A class of reformer where a portion (usually 30 percent) of the reactor's catalyst is regenerated each day.

Control Valve A throttling valve equipped with an actuator or actuation system to respond to an input signal from a controller. Control valves are used to regulate the flow, temperature or pressure of a process system. Also known as *automatic control valves*.

Cracked Gas Plant A refinery gas plant that processes hydrocarbons from cat crackers and cokers, which contains substantial quantities of olefins as a result of hydrogen deficiencies.

Cracking A process that breaks down a complex hydrocarbon molecule into two or more smaller molecules.

Crude Oil A carbon- and hydrogen-based natural resource used to produce petroleum products.

Cycle Oil A term for the bottom feeds from the fractionator.

Distillation A process of using heat to separate light and heavy crude oil.

Distillation Column The primary separation structure of a refinery from which the initial product cuts are made.

Distillation Curve A plot of temperature and percent evaporated for crude oil.

Downcomer A special piping device inside a column that permits excess hydrocarbons to overflow to the a lower tray.

Endothermic Process The process which causes extra hydrogen to be drawn out, which is mixed with feed to maintain high concentration of hydrogen vapors in the reactors.

Evaporation The change of state from a liquid to a vapor.

Field Grade Butanes Normal or mixed butanes produced by a gas processing plant that is used as feed for a butane isomerization plant.

Flashing A process where the pressure inside the vessel is manipulated to cause varying weights of fluid to boil and separate.

Flasher Bottoms The heavy material from the bottom of the vacuum flasher, which is typically used as feed for asphalt.

Flasher Tops The portion of the flashed distillate taken from the upper portion of the vacuum flasher.

Fractionator Equipment designed to take liquid product from the bottom of a separator and to make reformate from it. Also known as a *stabilizer*.

Full Regenerative Reformer A class of reformer where four of five reformers remain operational, while the fifth is offline while the catalyst being regenerated. This process usually requires 20 to 30 hours before the fresh reactor comes on line.

Fugitive Emissions Portions of the process that escape from between static joints or dynamic parts of a piece of process equipment, which may or may not be acceptable. Usually fugitive emissions are regulated and monitored by government agencies.

Heavy Crude Oil The composition of crude oil that produces heating oil and gas oil.

Hydrocracking The process of cat cracking in the presence of hydrogen that permits the cracking of low quality light gas oil.

Hydrotreating A process that removes impurities from the process, which involves the use of catalysts, high temperatures and mixing hydrogen to the fluid.

Isomerization A process that converts paraffins to isoparaffins.

Isoparaffins A term for branched saturated hydrocarbons.

Joule-Thompson Expansion A process in an Olefins plant where C_2 and C_3 gases are used as a refrigerant to separate a number of petroleum products.

Light Crude Oil The composition of crude oil that produces gasoline, naphtha and kerosene.

Max Distillate Mode The regulation of balance between gasoline and distillate as seasonal demands dictate.

Naphthenes Alkylcyclohexanes and alkylcyclopentanes found in crude oil.

Needle Coke Coke characterized by a crystalline structure and is preferred in the manufacture of electrodes.

Octane Number A number that represents the equivalent percentage by volume of isooctane in a fuel.

Olefins Unsaturated hydrocarbons with one double bond, having the molecular formula C_nH_{2n} . They may be thought of as derivatives of ethylene.

Olefinic Light fragments of a carbon concentrated feed

Paraffins A term for saturated aliphatic hydrocarbons.

Pile The storage of dry sulfur.

Raffinate Portion of a treated stream that is not removed.

Recycling to Extinction Constant recycling of cycle oil until it eventually all reacts.

Refinery A process plant where crude oil is converted into petroleum products.

Refining A process designed to convert crude oil into useful petroleum products through a series of separation and chemical processes.

Reflux A process where the vapor is run through a cooler and reintroduced to a lower tray to assure purity and eliminate carry-over.

Reforming Conversion of naphtha into more volatile products of higher octane via simultaneous combination of polymerization, cracking, dehydrogenation and isomerization.

Regeneration The process of removing coke deposits on a catalyst so that it can be reused.

Regenerator A special vessel that uses heated air to promote regeneration.

Saturated Gas Plant A refining gas plant that collects gases from hydrocrackers, hydrotreaters and reformers.

Semi-regenerative Reformer A class of reformer where the catalyst had a life of about six months before deactivation took place and regeneration was necessary (requiring plant shutdown).

Severe Service A process characterized by one or more characteristics: extreme temperatures, erosion, corrosion, high pressure drops, high velocities, cavitation, and flashing.

Sidedraws Special piping that draws distilled product from portions of a column.

Sponge Coke A common form of coke used in the manufacture of electrodes and anodes, production of graphite, and a source for carbides.

Stabilizer Equipment designed to take liquid product from the bottom of a separator and to make reformate from it. Also known as a *fractionator*.

Steam Cracking A process in an ethylene plant that mixes steam with feed to promote cracking.

Thermal Cracking The process that breaks down hydrocarbon molecules into smaller compounds, which are usually olefinic in nature.

Vacuum Flashing A process that separates hydrocarbons into the straight residue cut.

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For more information, contact:

For more information about Flowserve Corporation, contact www.flowserve.com or call USA 972 443 6500

Manufacturing Facilities

Valtek Control Valves
1350 N. Mt. Springs Prkwy.
Springville, UT 84663
Phone 801 489 8611
Facsimile 801 489 3719

Valtek-Kammer Valve
1300 Parkway View Drive
Pittsburgh, PA 15205 USA
Telephone 412 787 8803
Facsimile 412 787 1944

Valtek-Kammer Ventile
Manderscheidstr. 19
45141 Essen, Germany
Telephone (49) 2 01 89 19 5
Facsimile (49) 01 891 9600

Valtek-Kammer Vannes
Allée du Quartz 1
CH-2300 La Chaux-de-Fonds
Switzerland
Telephone (41) 32 925 9700
Facsimile (41) 32 926 5422

Quick Response Centers

Valtek Houston
5114 Railroad Street
Deer Park, TX 77536 USA
Telephone 281 479 9500
Facsimile 281 479 8511

Valtek Philadelphia
104 Chelsea Parkway
Boothwyn, PA 19061 USA
Telephone 610 497 8600
Facsimile 610 497 6680

