# **Process Description**

Global demand for transportation fuels will continue to grow and this demand will be met largely by gasoline and diesel fuels. The fluid catalytic cracking (FCC) process continues to play a key role in an integrated refinery as the primary conversion process of crude oil to lighter products. In the next two decades, the FCC process will be likely used for biofuels and possibly for reducing CO<sub>2</sub> emissions. For many refiners, the cat cracker is the key to profitability because the successful operation of the unit determines whether or not the refiner can remain competitive in today's market.

Since the start-up of the first commercial FCC unit in 1942, many improvements have been made to enhance the unit's mechanical reliability and its ability to crack heavier, lower value feedstocks. The FCC has a remarkable history of adapting to continual changes in market demands. Tables 1.1 and 1.1A highlight some of the major developments in the history of the FCC process.

The FCC unit uses a "microspherical" catalyst that behaves like a liquid when it is properly fluidized. The main purpose of the FCC unit is to convert high-boiling petroleum fractions called *gas oil* to high-value transportation fuels (gasoline, jet fuel, and diesel). FCC feedstock is often the gas oil portion of crude oil that commonly boils in the 650°F+ to 1,050°F+ (330–550°C) range. Feedstock properties are discussed in Chapter 3.

Approximately 350 cat crackers are operating worldwide (102 in the United States), with a total processing capacity of over 14.7 million barrels per day [1]. Most of the existing FCC units have been designed or modified by six major technology licensors:

- 1. UOP (Universal Oil Products)
- 2. Kellogg Brown & Root—KBR (formerly The M.W. Kellogg Company)
- 3. ExxonMobil Research and Engineering (EMRE)
- 4. The Shaw Group Inc.
- 5. CB&I Lummus
- 6. Shell Global Solutions International.

Table 1.1: The Evolution of Catalytic Cracking—Pre FCC Invention.

1915	Almer M. McAfee of Gulf Refining Co. discovered that a Friedel-Crafts aluminum chloride
	catalyst could catalytically crack heavy oil. However, the high cost of catalyst prevented the
	widespread use of McAfee's process.

- 1922 The French mechanical engineer named Eugene Jules Houdry and a French pharmacist named E.A. Prodhomme set up a laboratory to develop a catalytic process for conversion of lignite to gasoline. The demonstration plant in 1929 showed the process is not economical. Houdry had found that fuller's earth, a clay containing aluminosilicate (Al<sub>2</sub>SiO<sub>6</sub>), could convert oil from lignite to gasoline.
- 1930 The Vacuum Oil Company invited Houdry to move his laboratory to Paulsboro, NJ.
- 1931 The Vacuum Oil Company merged with Standard Oil of New York (Socony) to form Socony-Vacuum Oil Company.
- 1933 A small Houdry unit processing 200 bpd of petroleum oil was commissioned because of the economic depression of the early 1930s. Socony-Vacuum could not support Houdry's work and granted him permission to seek help elsewhere. Sun Oil Company joined in developing Houdry's process.
- 1936 Socony-Vacuum converted an old thermal cracker to catalytically crack 2,000 bpd of petroleum oil using the Houdry process.
- 1936 Use of natural clays as catalyst greatly improved cracking efficiency.
- 1937 Sun Oil began operation of Houdry unit processing 12,000 bpd. The Houdry process used reactors with a fixed bed of catalyst and it was a semi-batch operation. Almost 50% of the cracked products were gasoline.
- 1938 With the commercial successes of the Houdry process, Standard Oil of New Jersey resumed research of the FCC process as part of the consortium that included five oil companies (Standard Oil of New Jersey, Standard Oil of Indiana, Anglo-Iranian Oil, Texas Oil, and Dutch Shell), two engineering construction companies (M.W. Kellogg and Universal Oil Products), and a German chemical company (I.G. Farben). This consortium was called Catalyst Research Associates (CRA), and its objective was to develop a catalytic cracking process that did not impinge on Houdry's patents. Two MIT professors (Warren K. Lewis and Edwin R. Gilliand) had suggested to CRA researchers that a low gas velocity through a powder might lift the powder enough to flow like liquid. Standard Oil of New Jersey developed and patented the first fluid catalyst cracking process.
- 1938 By 1938 Socony-Vacuum had 8 additional units under construction, and by 1940 there were
- 1940 14 Houdry units in operation processing 140,000 bpd of oil.

  The next step was to develop a continuous process rather than Houdry's semi-batch operation.

  Thus came the advent of a moving-bed process known as thermofor catalytic cracking (TCC), which used a bucket conveyor elevator to move the catalyst from the regenerator kiln to the reactor.
- 1940 M.W. Kellogg designed and constructed a large pilot plant at the Standard Oil Baton Rouge, Louisiana, refinery.
- 1941 A small TCC demonstration unit was built at Socony-Vacuum's Paulsboro refinery.
- 1943 A 10,000 bpd TCC unit began operation at Magnolia Oil Company in Beaumont, TX (an affiliate of Socony-Vacuum's Paulsboro refinery).
- By the end of World War II, the processing capacity of the TCC units in operation was about 300,000 bpd.

Table 1.1A: The Evolution of the FCC Process.

1942	The first commercial FCC unit (Model I upflow design)
	started up at the Standard of New Jersey Baton Rouge,
	Louisiana, refinery, processing 12,000 bpd.
1943	First down-flow design FCC unit was brought online. First
	TCC brought online.
1947	First Universal Oil Products (UOP)-stacked FCC unit was
	built. M.W. Kellogg introduced the Model III FCC unit.
1948	Davison Division of W.R. Grace & Co. developed
	microspheroidal FCC catalyst.
1950s	Evolution of bed cracking process designs.
1951	M.W. Kellogg introduced the Orthoflow design.
1952	Exxon introduced the Model IV.
1954	High alumina $(Al_2O_2)$ catalysts were introduced.
Mid-	UOP introduces side-by-side design.
1950s	
1956	Shell invented riser cracking.
1961	Kellogg and Phillips developed and put the first resid cracker
	onstream at the Borger, TX, refinery.
1963	The first Model I FCC unit was shut down after 22 years of
	operation.
1964	Mobil Oil developed ultrastable Y (USY) and rare earth
	exchanged ultrastable Y zeolite (ReY) FCC catalyst. Last TCC
	unit completed.
1972	Amoco Oil invented high-temperature regeneration.
1974	Mobil Oil introduced CO promoter.
1975	Phillips Petroleum developed antimony for nickel
	passivation.
1981	TOTAL invented two-stage regeneration for processing
	residue.
1983	Mobil reported first commercial use of ZSM-5 octane/
	olefins additive in FCC.
1985	Mobil started installing closed cyclone systems in its FCC
	units.
1994	Coastal Corporation conducted commercial test of
	ultrashort residence time, selective cracking (MSCC).
1996	ABB Lummus Global acquired Texaco FCC technologies.

Figures 1.1–1.9 contain sketches of typical unit configurations offered by the FCC technology licensors. Although the mechanical configuration of individual FCC units may differ, their common objective is to upgrade low-value feedstock to the more valuable products used for transportation and petrochemical industries. Worldwide, about 45% of all gasoline comes from FCC and ancillary units such as the alkylation unit.

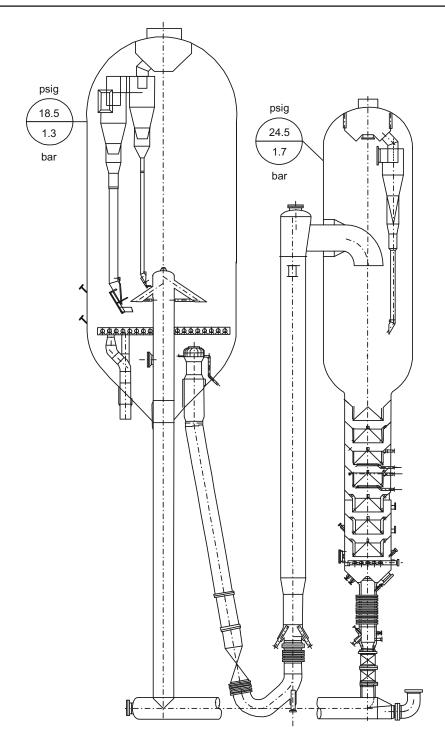


Figure 1.1: Example of a Model II cat cracker with enhanced RMS design internals.

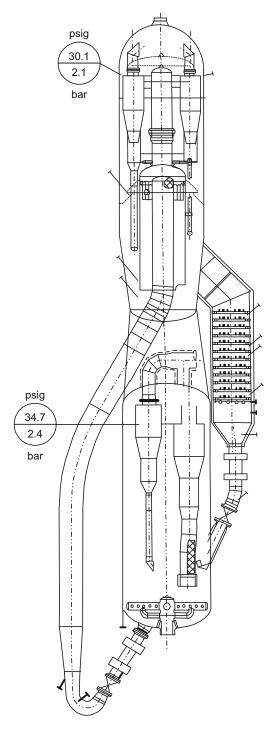


Figure 1.2: Example of a UOP stack design FCC unit.

Figure 1.3: Example of a Model IV design FCC unit.

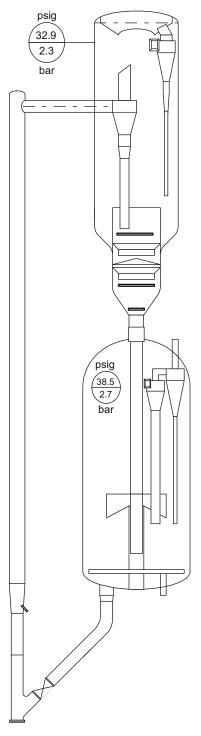


Figure 1.4: Example of KBR Orthoflow design FCC unit.

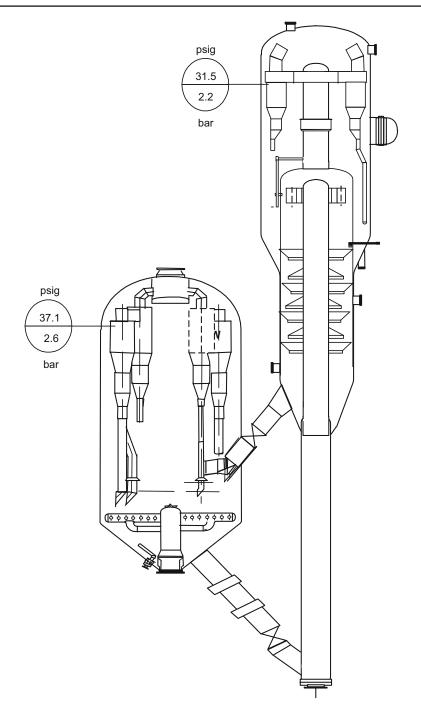


Figure 1.5: Example of a side-by-side design FCC unit.

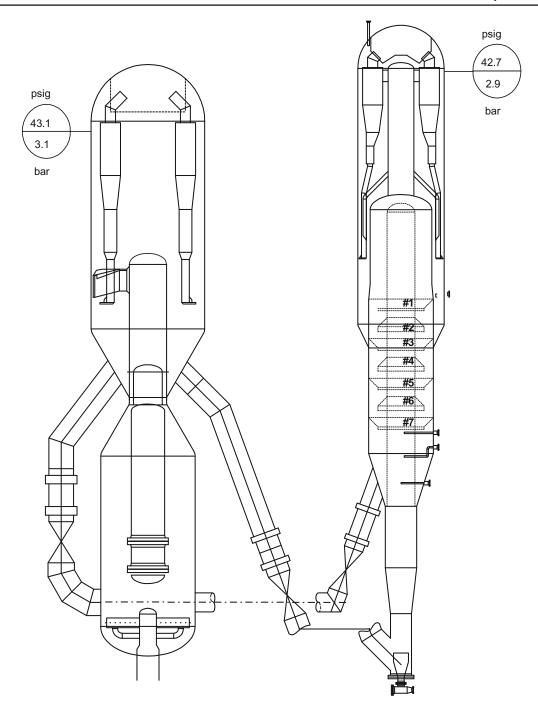


Figure 1.6: Example of a UOP high-efficiency design FCC unit.

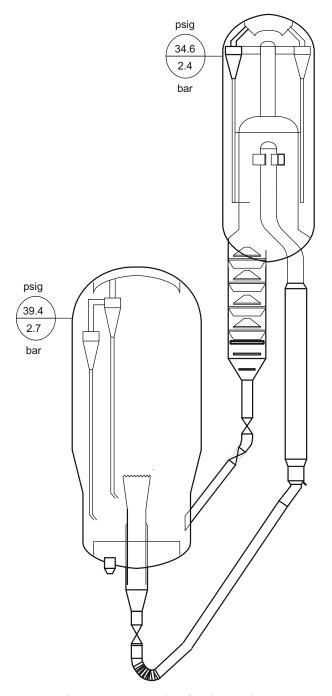


Figure 1.7: Example of a Flexicracker.

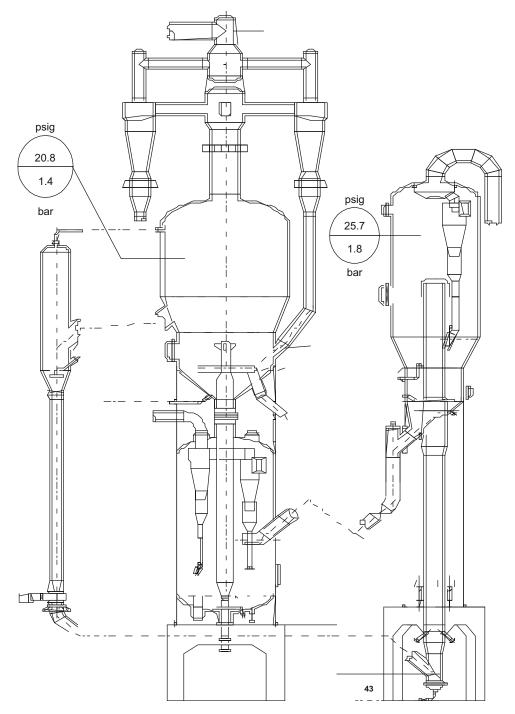


Figure 1.8: Example of The Shaw Group Inc. design FCC unit.

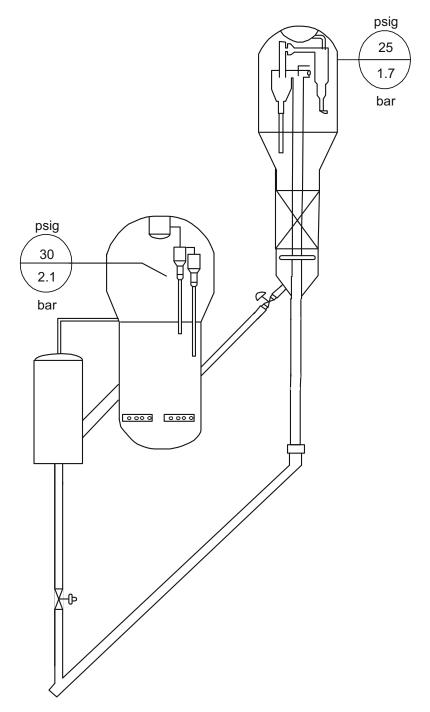


Figure 1.9: Example of Lummus Technology Inc. FCC unit.



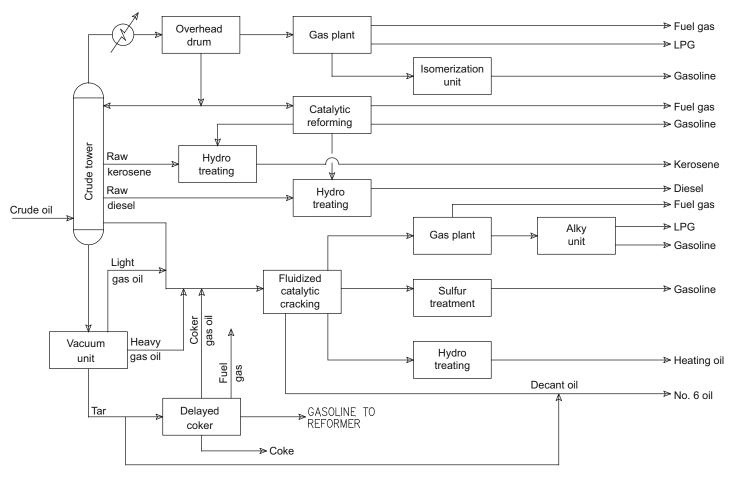


Figure 1.10: A typical high-conversion refinery.

Before proceeding, it is helpful to understand how a typical cat cracker fits into the refining process. A petroleum refinery is composed of several processing units which convert the raw crude oil into usable products such as gasoline, diesel, jet fuel, and heating oil (Figure 1.10).

The crude unit is the first unit in this refining process. Here, the raw crude is distilled into several intermediate products: naphtha, kerosene, diesel, and gas oil. The heaviest portion of the crude oil, which cannot be distilled in the atmospheric tower, is heated and sent to the vacuum tower where it is split into gas oil and residue. The vacuum tower bottoms (residue) can be sent to be processed further in units such as the delayed coker, deasphalting unit, visbreaker, or residue cracker, or is sold as fuel oil or road asphalt.

The gas oil feed for the conventional cat cracker comes primarily from the atmospheric column, the vacuum tower, and the delayed coker. In addition, a number of refiners blend some atmospheric or vacuum resid into their feedstocks to be processed in the FCC unit. The charge to the FCC unit can be fully hydrotreated, partially hydrotreated, or totally unhydrotreated.

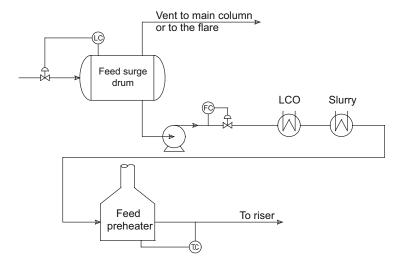
The FCC process is very complex. For clarity, the process description has been broken down into the following separate sections:

- Feed preheat
- Feed nozzles—riser
- Catalyst separation
- Stripping section
- Regenerator—heat/catalyst recovery
- Partial versus complete combustion
- Regenerated catalyst standpipe/slide valve
- Flue gas heat and pressure recovery schemes
- Catalyst handling facilities
- Main fractionator
- Gas plant
- Treating facilities.

#### Feed Preheat

Most refineries produce sufficient gas oil to meet the cat crackers' demand. However, for those refineries in which the gas oil produced does not meet the cat cracker capacity, it may be economical to supplement feed by purchasing FCC feedstocks or blending some residue. The refinery-produced gas oil and any supplemental FCC feedstocks are generally combined and sent to a surge drum that provides a steady flow of feed to the charge pumps. This drum can also separate any water or vapor that may be in the feedstocks.

In most FCC units, the gas oil feed from storage and/or from other units is preheated prior to reaching the riser. The source of this preheat is often main fractionator pumparound streams, main fractionator products, and/or a dedicated gas-fired furnace (Figure 1.11).



**Figure 1.11:** Typical feed preheat system (*FC* = *flow control*, *LC* = *level control*, *TC* = *temperature control*, *LCO* = *light cycle oil*).

Typical feed preheat temperature is in the range of 400–750°F (205–400°C). The feed is first routed through heat exchangers using hot streams from the main fractionator. The main fractionator top pumparound, light cycle oil (LCO) product, and bottoms pumparound are commonly used (Figure 1.11). Removing heat from the main fractionator is at least as important as preheating the gas oil feed.

The majority of FCC units use fired heaters to maximize the FCC feed preheat temperature. The gas-fired feed preheater provides several operating advantages. For example, in units where the air blower capacity and/or catalyst circulation is constrained, increasing the preheat temperature allows increased throughput. Additionally, for units in which deep hydrotreated feed is processed, the ability to increase the feed preheat temperature is an excellent option to control the regenerator bed temperature. The effects of feed preheat are discussed in Chapter 8.

#### Feed Nozzles-Riser

The reactor—regenerator is the heart of the FCC process. In today's cat cracking, the riser is the reactor (see Figure 1.12 for a typical riser Wye feed section).

Efficient contacting of the feed and regenerated catalyst is critical for achieving the desired cracking reactions. Feed nozzle(s) are used to atomize the feed with the help of dispersion or atomizing steam. Smaller oil droplets increase the availability of feed at the reactive acid sites on the catalyst. With high-activity zeolite catalyst, virtually all of the cracking reactions take place in 3 seconds or less.

In most FCC units, the feed nozzles are an "elevated" type, in which they are located about 15-40 ft (5-12 m) above the base of the riser. Depending on the FCC feed rate and riser diameter, the number of feed nozzles can range from 1 to 15.

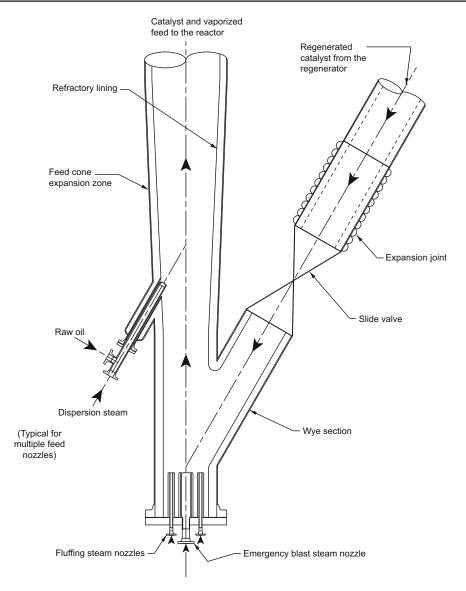


Figure 1.12: Typical riser Wye feed section.

The cracking reactions ideally occur in the vapor phase. Cracking reactions begin as soon as the feed is vaporized by the hot regenerated catalyst. The expanding volume of the vapors is the main driving force that is used to carry the catalyst up the riser.

The hot regenerated catalyst will not only provide the necessary heat to vaporize the gas oil feed and bring its temperature to the desired cracking temperature, but also compensate for the "internal cooling" that takes place in the riser due to endothermic heat of reaction.

Depending on the feed preheat, regenerator bed, and riser outlet temperatures, the ratio of catalyst to oil is normally in the range of 4:1 to 10:1 by weight. The typical regenerated

catalyst temperature ranges between 1,250°F and 1,350°F (677–732°C). The cracking or reactor temperature is often in the range of 925–1,050°F (496–565°C).

The riser is often a vertical pipe. Typical risers are 2 to 7 feet (61 to 213 cm) in diameter and 75 to 120 feet (23 to 37 meters) long. The ideal riser simulates a plug flow reactor, where catalyst and vapor travel the length of the riser, with minimum back mixing.

Some risers are fully external, in which they are mostly cold-wall design with 4- to 5-in. (10-13 cm) thick internal refractory lining, for insulation and abrasion resistance. The section of the riser that is internal to the reactor vessel is of a hot-wall design, often having 1-in. (2.5 cm) thick internal refractory lining. The material of construction for the cold-wall riser is carbon steel and low chrome alloy for the hot-wall design.

Risers are normally designed for an outlet vapor velocity of 40–60 ft/s (12–18 m/s). The average hydrocarbon and catalyst residence times are about 2 and 3 s, respectively (based on riser outlet conditions). As a consequence of the cracking reactions, a hydrogen-deficient material called "coke" is deposited on the catalyst, reducing catalyst activity.

## **Catalyst Separation**

After exiting the riser, catalyst enters the reactor vessel. In today's FCC operations, the reactor vessel serves as housing for the cyclones and/or a disengaging device for catalyst separation. In the early application of FCC, the reactor vessel provided further bed cracking, as well as being a device used for additional catalyst separation.

Nearly every FCC unit employs some type of inertial separation device connected on the end of the riser to separate the bulk of the catalyst from the vapors. A number of units use a deflector device to turn the catalyst direction downward. On some units, the riser is directly attached to a set of cyclones. The term "rough cut" cyclones generally refers to this type of arrangement. These schemes separate  $\sim 75-99.9\%$  of the catalyst from product vapors.

Most FCC units employ either single- or two-stage cyclones (Figure 1.13) to separate the remaining catalyst particles from the cracked vapors. The cyclones collect and return the catalyst to the catalyst stripper via the diplegs and flapper/trickle valves (Figures 1.14A and 1.14B). The product vapors exit the upper cyclones and flow to the main fractionator tower. The efficiency of a typical riser termination device and upper cyclone system is often 99.999+%.

It is important to separate catalyst and vapors as soon as they enter the reactor, especially if the cracking temperature is >950°F (510°C). If not, the extended contact time of the vapors with the catalyst in the reactor housing will allow for nonselective catalytic recracking of some of the desirable products. The extended residence time also promotes thermal cracking of the desirable products. These recracking reactions can be extensive if the reactor temperature is more than 950°F (510°C). Most refiners have modified their riser termination devices to minimize these reactions.



Figure 1.13: A typical two-stage cyclone system.

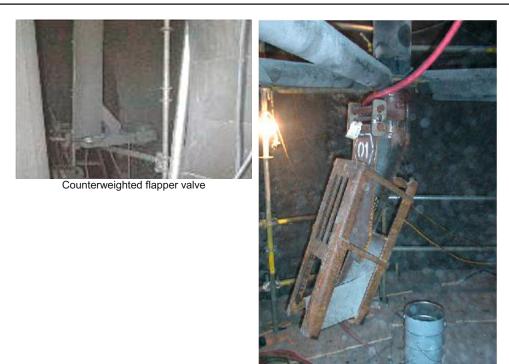


Figure 1.14A: Photos of a typical counterweighted flapper valve, and a secondary cyclone trickle valve.

Secondary cyclone trickle valve

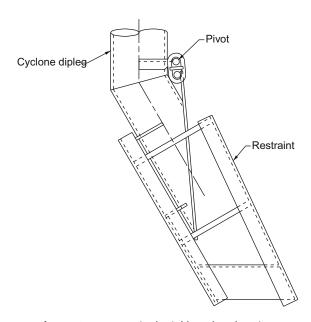


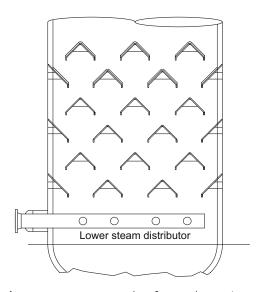
Figure 1.14B: Typical trickle valve drawing.

# **Stripping Section**

The "spent catalyst" entering the catalyst stripper has hydrocarbons that are adsorbed on the surface of the catalyst; there are hydrocarbon vapors that fill the catalyst's pores, and hydrocarbon vapors that are entrained with the catalyst. Stripping steam is used primarily to remove the entrained hydrocarbons between individual catalyst particles. The stripping steam does not often address hydrocarbon desorption or the hydrocarbons that have filled the catalyst's pores. However, cracking reactions do continue to occur within the stripper. These reactions are driven by the reactor temperature and the catalyst residence time in the stripper. The higher temperature and longer residence time allow conversion of adsorbed hydrocarbons into "clean lighter" products. Shed trays, disk/donut baffles, and structural packing are the most common devices in commercial use for providing contact between down-flowing catalyst and upflowing steam (for stripper example, see Figure 1.15).

An efficient catalyst stripper design provides the intimate contact between the catalyst and steam. Reactor strippers are commonly designed for a steam superficial velocity of about 0.75 ft/s (0.23 m/s) and a catalyst mass flux rate at approximately 700 lb/min/ft<sup>2</sup> (3,418 kg/min/m<sup>2</sup>). At too high a flux rate, the falling catalyst tends to entrain steam, thus reducing the effectiveness of stripping steam. A typical stripping steam rate is in the range of 2–5 lb of steam per 1,000 lb (2–5 kg per 1,000 kg) of circulating catalyst.

It is important to minimize the amount of hydrocarbon vapors carried over to the regenerator, but not all the hydrocarbon vapors can be displaced from the catalyst pores in the stripper. A fraction of them are carried with the spent catalyst into the regenerator.



**Figure 1.15:** An example of a catalyst stripper.

These hydrocarbon vapors/liquid have a higher hydrogen to carbon ratio than the "hard" coke on the catalyst. The drawbacks of allowing these hydrogen-rich hydrocarbons to enter the regenerator are as follows:

- Loss of liquid product: Instead of the hydrocarbons burning in the regenerator, they could be recovered as liquid products.
- Loss of throughput: The combustion of hydrogen to water produces 3.7 times more heat than the combustion of carbon to carbon dioxide. The increase in the regenerator temperature caused by excess hydrocarbons could exceed the temperature limit of the regenerator internals and force the unit to reduce the feed rate.
- Loss of catalyst activity: The higher regenerator temperature combined with the presence of steam in the regenerator reduces catalyst activity via destroying the catalyst's crystalline structure.

The flow of spent catalyst to the regenerator is often regulated by either a slide or plug valve (Figure 1.16A). The slide or plug valve maintains a desired level of catalyst in the stripper. In all FCC units, an adequate catalyst level must be maintained in the stripper to prevent reversal of hot flue gas into the reactor.

In most FCC units, the spent catalyst gravitates to the regenerator. In others, lift or carrier air is used to transport the catalyst into the regenerator. The uniform distribution of the spent catalyst is extremely critical to achieve efficient combustion that minimizes any afterburning and NO<sub>x</sub> emissions. Figure 1.16B shows an example of a properly designed spent catalyst distribution system, and Figure 1.16C shows an example of the spent catalyst entering the regenerator through the sidewall using a ski-jump distributor, which unfortunately does not provide uniform catalyst distribution.





Example of a slide valve

Example of a plug valve

**Figure 1.16A:** Example of a typical slide valve and a typical plug valve.

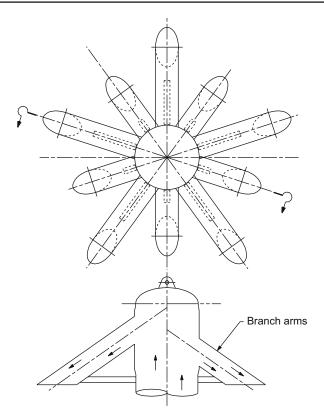


Figure 1.16B: Example of a spent catalyst distribution system (courtesy of RMS Engineering, Inc.).

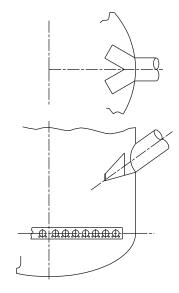


Figure 1.16C: Example of a hockey stick style catalyst distributor.

## Regenerator—Heat/Catalyst Recovery

The regenerator has three main functions:

- It restores catalyst activity.
- It supplies heat for cracking reactions.
- It delivers fluidized catalyst to the feed nozzles.

The spent catalyst entering the regenerator usually contains between 0.5 and 1.5 wt% coke. Components of coke are carbon, hydrogen, and trace amounts of sulfur and organic nitrogen molecules. These components burn according to the reactions given in Table 1.2.

Air provides oxygen for the combustion of this coke and is supplied by one or more air blowers. The air blower provides sufficient air velocity and pressure to maintain the catalyst bed in a fluidized state. In some FCC units, purchased oxygen is used to supplement the combustion air. The air/oxygen enters the regenerator through an air distribution system (Figure 1.17) located near the bottom of the regenerator vessel. The design of the air distributor is important in achieving efficient and reliable catalyst regeneration. Air distributors are often designed for a 1.0- to 2.0-psi (7-15 kPa) pressure drop to ensure positive air flow through all nozzles.

kcal/kg of C, H2, or S BTU/lb of C, H<sub>2</sub>, or S  $C + 1/2O_2$ CO 2,200 3,968 (1.1) $CO + 1/2O_2$  $CO_2$ 5,600 10,100 (1.2)7,820 14,100  $C + O_2$  $CO_2$ (1.3) $H_2 + 1/2O_2$  $H_2O$ 28,900 52,125 (1.4)S + xO $SO_x$ 2,209 3,983 (1.5)N + xO $NO_x$ (1.6)

Table 1.2: Heat of Combustion.





**Figure 1.17:** Examples of air distributor designs (courtesy of RMS Engineering Inc.).

In traditional bubbling bed regenerators, there are two regions: the *dense phase* and the *dilute phase*. At velocities common in these regenerators, 2–4 ft/s (0.6–1.2 m/s), the bulk of catalyst particles are in the dense bed, immediately above the air distributor. The dilute phase is the region above the dense phase up to the cyclone inlet and has a substantially lower catalyst concentration.

## Partial Versus Complete Combustion

Catalyst can be regenerated over a range of temperatures and flue gas composition with inherent limitations. Two distinctly different modes of regeneration are practiced: *partial combustion* and *complete combustion*. Complete combustion generates more energy and the coke yield is decreased; partial combustion generates less energy and the coke yield is increased. In complete combustion, the excess reaction component is oxygen, so more carbon generates more combustion. In partial combustion, the excess reaction component is carbon, all the oxygen is consumed, and an increase in coke yield means a shift from CO<sub>2</sub> to CO.

FCC regeneration can be further subdivided into low-, intermediate-, and high-temperature regeneration. In low-temperature regeneration (about 1,190°F or 640°C), complete combustion is impossible. One of the characteristics of low-temperature regeneration is that at 1,190°F, all three components (O<sub>2</sub>, CO, and CO<sub>2</sub>) are present in the flue gas at significant levels. Low-temperature regeneration was the mode of operation that was used in the early implementation of the catalytic cracking process.

In the early 1970s, high-temperature regeneration was developed. High-temperature regeneration meant increasing the temperature until all the oxygen was burned. The main result was low carbon on the regenerated catalyst. This mode of regeneration required maintaining, in the flue gas, either a small amount of excess oxygen and no CO or no excess oxygen and a variable quantity of CO. If there was excess oxygen, the operation was in full burn. If there was excess CO, the operation was in partial burn.

With a properly designed air/spent catalyst distribution system and potential use of CO combustion promoter, the regeneration temperature could be reduced and still maintain full burn mode of catalyst regeneration.

Table 1.3 contains a matrix summarizing various aspects of catalyst regeneration. Regeneration is either partial or complete at low, intermediate, or high temperatures. At low temperatures, regeneration is always partial, carbon on regenerated catalyst is high, and increasing combustion air results in afterburn. At intermediate temperatures, carbon on regenerated catalyst is reduced. The three normal "operating regions" are indicated in Table 1.3.

Operating Region Regenerator Partial Combustion Mode **Full Combustion Mode** Combustion Low temperature (nominally Stable (small afterburning); O2, CO, Not achievable 1,190°F/640°C) and CO2 in the flue gas Intermediate temperature Stable (with combustion promoter), Stable with combustion (nominally 1,275°F/690°C) tends to have high carbon on promoter regenerated catalyst High temperature (nominally Stable operation Stable operation 1,350°F/730°C)

Table 1.3: A Matrix of Regeneration Characteristics.

There are some advantages and disadvantages associated with full as compared with partial combustion:

- Advantages of full combustion:
  - Energy efficient
  - Heat balances at low coke yield
  - Minimum hardware (no CO boiler)
  - Better yields from clean catalyst
  - Environmentally friendlier
- Disadvantages of full combustion:
  - Narrow range of coke yields, unless a heat removal system is incorporated
  - Greater afterburn, particularly with an uneven air or spent catalyst distribution system
  - Low catalyst/oil ratio.

The choice of partial versus full combustion is dictated by FCC feed quality. With "clean feed," full combustion is the choice. With low-quality feed or resid, partial combustion, possibly with heat removal, is the choice.

## Regenerated Catalyst Standpipe/Slide Valve

During regeneration, the coke level on the catalyst is typically reduced to <0.10%. From the regenerator, the catalyst flows down a transfer line, commonly referred to as a standpipe. The standpipe provides the necessary pressure head to circulate the catalyst around the unit. Some standpipes are short and some are long. Some standpipes extend into the regenerator and employ an internal cone, and the top section is often called a *catalyst hopper*. In some units, regenerated catalyst is fed into an external withdrawal well hopper.

Standpipes are typically sized for a catalyst flux rate in the range of 150–300 lb/s/ft<sup>2</sup> (750–1,500 kg/s/m<sup>2</sup>) of circulating catalyst. In most short standpipes, sufficient flue gas is carried down with the regenerated catalyst to keep it fluidized. However, longer standpipes

will require external aeration to ensure that the catalyst remains fluidized. A gas medium, such as air, steam, or nitrogen, is injected at intervals along the length of the standpipe to achieve this. The catalyst flowing density in a well-designed standpipe is in the range of  $35-45 \text{ lb/ft}^3$  ( $560-720 \text{ kg/m}^3$ ).

The flow rate of the regenerated catalyst to the riser is commonly regulated by either a slide or a plug valve. The operation of a slide valve is similar to that of a variable orifice. Slide valve operation is often controlled by the reactor temperature. Its main function is to supply enough catalyst to heat the feed and achieve the desired cracking temperature. In the ExxonMobil Model IV (see Figure 1.3) and Flexicracker designs (see Figure 1.7), the regenerated catalyst flow is controlled by adjusting the pressure differential between the reactor and regenerator.

#### Regenerator Catalyst Separation

As flue gas leaves the dense phase of the regenerator, it entrains catalyst particles. The amount of entrainment depends largely on the flue gas superficial velocity in the regenerator. The larger catalyst particles,  $50-90 \mu m$ , fall back into the dense bed. The smaller particles,  $0-50 \mu m$ , are suspended in the dilute phase and carried into the cyclones.

Most FCC unit regenerators employ 2-20 pairs of primary and secondary cyclones. These cyclones are designed to recover catalyst particles >15  $\mu m$  diameter. The recovered catalyst particles are returned to the regenerator via the diplegs.

The distance above the catalyst bed at which the flue gas velocity has stabilized is referred to as the transport disengaging height (TDH). At this height, the catalyst concentration in the flue gas stays constant; none will fall back into the bed. The centerline of the first-stage cyclone inlets should be at TDH or higher; otherwise, excessive catalyst entrainment will cause extreme catalyst losses.

# Flue Gas Heat and Pressure Recovery Schemes

The flue gas exits the cyclones to a plenum chamber in the top of the regenerator. The hot flue gas holds an appreciable amount of energy. Various heat recovery schemes are used to recover this energy. In some units, the flue gas is sent to a CO boiler where both the sensible and combustible heat is used to generate high-pressure steam. In other units, the flue gas is exchanged with boiler feed water to produce steam via the use of a shell/tube or box-type heat exchanger.

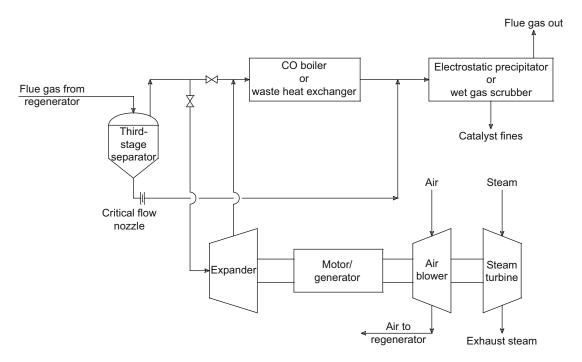
In most units without turbo expanders, the flue gas pressure is let down via a double-disk slide valve and an orifice chamber. Approximately one-third of the flue gas pressure is let down across the double-disk valve, with the remaining two-thirds via an orifice chamber. The orifice chamber is either a vertical or horizontal vessel containing a series of perforated plates, designed to maintain a reasonable pressure drop across the flue gas valve.

In some medium-to-large FCC units, a turbo expander can be used to recover this pressure energy. Associated with this pressure recovery, there is also about a 200°F (93°C) drop in the flue gas temperature.

To protect the expander blades from being eroded by catalyst, flue gas is first sent to a third-stage separator to remove the catalyst fines. Depending on the design, the third-stage separator, which is external to the regenerator, can contain a large number of small cyclones, swirl tubes, or several large cyclones. The third-stage separators are designed to separate 70–95% of the incoming particles from the flue gas.

A power recovery train (Figure 1.18) employing a turbo expander usually consists of four parts: the expander, a motor/generator, an air blower, and a steam turbine. The steam turbine is primarily used for start-up and often to supplement the expander to generate electricity.

The motor/generator works as a speed controller and flywheel; it can produce or consume power. In some FCC units, the expander horsepower exceeds the power needed to drive the air blower and the excess power is output to the refinery electrical system. If the expander generates less power than what is required by the blower, the motor/generator provides the power to hold the power train at the desired speed.



**Figure 1.18:** A typical flue gas power recovery scheme.

From the expander, the flue gas goes through a steam generator to recover thermal energy. Depending on local environmental regulations, an electrostatic precipitator (ESP) or a wet gas scrubber may be placed downstream of the waste heat generator prior to release of the flue gas to the atmosphere. Some units use an ESP to remove catalyst fines in the range of  $5-20 \,\mu m$  from the flue gas. Some units employ a wet gas scrubber to remove both catalyst fines and sulfur compounds from the flue gas stream.

# **Catalyst Handling Facilities**

The activity of catalyst degrades with time. The loss of activity is primarily due to impurities in the FCC feed and from thermal and hydrothermal deactivation mechanisms that occur in the regenerator. To maintain the desired activity, fresh catalyst is continually added to the unit. Fresh catalyst is stored in a fresh catalyst hopper and, in most units, is added automatically to the regenerator via a catalyst loader.

The circulating catalyst in the FCC unit is often called equilibrium catalyst or simply E-cat. Periodically, quantities of equilibrium catalyst are withdrawn and stored in the E-cat hopper for future disposal. A refinery that processes residue feedstocks can also use good-quality E-cat from a refinery that processes light sweet feed. Residue feedstocks contain large quantities of impurities, such as metals, and require high rates of fresh catalyst to maintain the desired activity. The use of a good-quality E-cat, in conjunction with fresh catalyst, can be cost-effective in maintaining low catalyst costs.

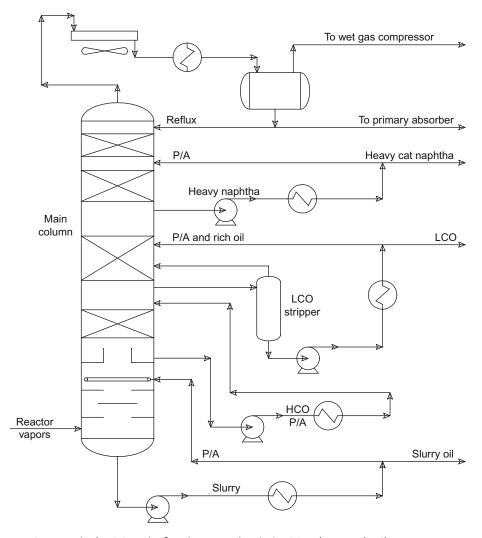
Even with proper operation of the reactor and regenerator cyclones, catalyst particles smaller than  $20 \,\mu m$  still escape from both of these vessels. In most FCC units, the catalyst fines from the reactor cyclones are sent with the slurry oil product into the storage tanks. Few units employ tertiary recovery devices (slurry settler, Gulftronics, Dorrclone, etc.), in which the recovered catalyst is recycled to the riser.

The residual catalyst fines from the regenerator flue gas are often removed through a flue gas scrubber, an ESP, or a properly designed third-/fourth-stage cyclone system.

### Main Fractionator

The purpose of the main fractionator, or main column (Figure 1.19), is to desuperheat and recover liquid products from the reactor vapors. The hot vapors from the reactor flow into the main fractionator near the base. Fractionation is accomplished by condensing and revaporizing hydrocarbon components as the vapor flows upward through trays and/or packing in the tower.

The operation of the main column is similar to the crude tower, but with two differences. First, the reactor effluent vapors must be cooled before any fractionation begins. Second, large quantities of gases will go overhead with the unstabilized gasoline for further separation.



**Figure 1.19:** A typical FCC main fractionator circuit ( $HCO = heavy \ cycle \ oil, \ P/A = pumparound$ ).

The bottom section of the main column provides a heat transfer zone. Shed decks, disk/donut trays, and grid packing are among some of the contacting devices used to promote vapor/liquid contact. The reactor vapor is desuperheated and cooled by several pumparound streams. The cooled pumparound also serves as a scrubbing medium to wash down catalyst fines entrained in the vapors.

Pool quench (see also Figure 13.12) can be used to maintain the fractionator bottoms temperature below the coking temperature, usually at about 680°F (360°C).

The recovered heat from the main column bottoms is commonly used to preheat the fresh feed, generate steam, serve as a heating medium for the gas plant reboilers, or some combination of these services.

The heaviest bottoms product from the main column is commonly called slurry, clarified, or decant oil (DO) (in this book, these terms are used interchangeably). The slurry oil is often used as a "cutter stock" with vacuum bottoms to make No. 6 fuel oil. High-quality slurry oil (low sulfur, low metals, low ash) can be used for carbon black feedstocks.

Early FCC units had soft catalyst and inefficient cyclones, with substantial carryover of catalyst to the main column, where it was absorbed in the bottoms. Those FCC units controlled catalyst losses in two ways. First, they used high recycle rates to return slurry to the reactor. Second, the slurry product was routed through slurry settlers, either gravity or centrifugal, to remove catalyst fines. A slipstream of FCC feed was used as a carrier to return the collected fines from the separator to the riser. Since then, improvements in the physical properties of FCC catalyst and in the reactor cyclones have lowered catalyst carryover. Most units today operate without separators. The slurry oil is sent directly to the storage tank. Catalyst fines accumulate in the tank and are disposed of periodically. Some units continue to use some form of slurry settler to minimize the ash content of the slurry oil.

Above the bottoms product, the main column is often designed for three possible sidecuts:

- 1. Heavy cycle oil (HCO), used as a pumparound stream, sometimes as recycle to the riser, rarely as a product
- 2. LCO, used as a pumparound stream, sometimes as absorption oil in the gas plant, stripped as a product for diesel/heating oil blending
- 3. Heavy naphtha, used as a pumparound stream, sometimes as absorption oil in the gas plant, and possible blending in the gasoline pool.

In many units, the LCO is the only sidecut that leaves the unit as a product. LCO is withdrawn from the main column and routed to a side stripper for flash control. LCO is often treated for sulfur removal prior to being blended into the heating oil pool. In most units, a slipstream of LCO, either stripped or unstripped, is sent to the sponge oil absorber in the gas plant. In other units, sponge oil is the cooled heavy naphtha.

HCO, heavy naphtha, and other circulating side pumparound streams are used to remove heat from the fractionator. They supply reboil heat to the gas plant and generate steam. The amount of heat removed at any pumparound point is set to distribute vapor and liquid loads evenly throughout the column and to provide the necessary internal reflux.

Unstabilized gasoline and light gases pass up through the main column and leave as vapor. The overhead vapor is cooled and partially condensed in the fractionator overhead condensers. The stream flows to an overhead receiver, typically operating at <15 psig (<1 bar). Hydrocarbon vapor, hydrocarbon liquid, and water are separated in the overhead drum.

The hydrocarbon vapors flow to the wet gas compressor (WGC). This gas stream contains not only ethane and lighter gases but also more than 95% of the C<sub>3</sub>'s/C<sub>4</sub>'s and about 10% of the naphtha. The phrase "wet gas" refers to condensable components of the gas stream.

The hydrocarbon liquid from the overhead receiver is split. Some is pumped back to the main column as reflux and some is pumped forward to the gas plant. Condensed water is also split. Some is pumped back as wash water to the overhead condensers and some is pumped away to treating. In some units, the sour water from the overhead receiver is also used as wash to the WGC discharge coolers.

### Gas Plant

The FCC gas plant (Figure 1.20) separates the unstabilized gasoline and light gases into:

- Fuel gas
- C<sub>3</sub>'s and C<sub>4</sub>'s
- Gasoline.

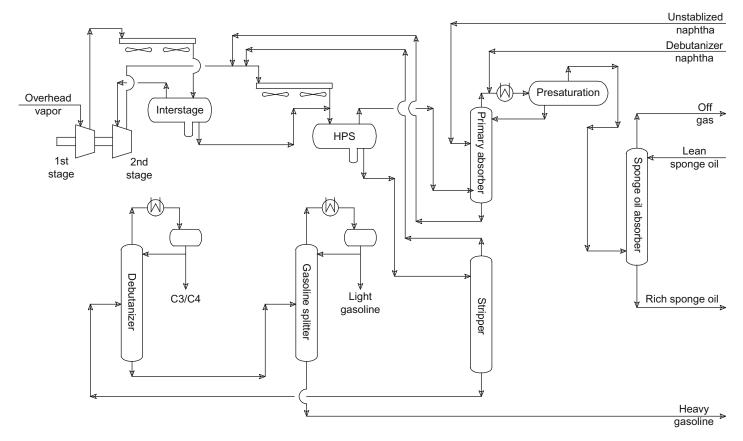
C<sub>3</sub>'s and C<sub>4</sub>'s (or debutanizer overhead products) include propane, propylene, normal butane, isobutane, and butylenes. Most refiners either alkylate the C3's/C4's or use a depropanizer tower to split C<sub>3</sub>'s from C<sub>4</sub>'s and process C<sub>4</sub>'s stream into the alkylation unit. Most FCC gas plants also include treating facilities to remove sulfur from these products.

The gas plant starts at the WGC. A two-stage centrifugal compressor is often employed. This type of compressor generally incorporates an electric motor, or a multistage turbine, that is typically driven by high-pressure steam. The steam is often exhausted to a surface condenser operating under vacuum. It should be noted that there are FCC units in which single-stage WGCs are employed.

In most two-stage systems, the vapors from the compressor's first-stage discharge are partially condensed and flashed in an interstage drum. The liquid hydrocarbon is pumped forward to the gas plant, either to the high-pressure separator (HPS) or directly to the stripper.

The vapor from the interstage drum flows to the second-stage compressor. The second-stage compressor discharges through a cooler to the HPS. Gases and light streams from other refinery units are often included for recovery of liquefied petroleum gas (LPG). Recycle streams from the stripper and the primary absorber also go to the HPS. Wash water is injected to dilute contaminants, such as ammonium salts, that can cause equipment fouling. This mixture is partially condensed and flashed in the HPS.

The vapor from the HPS flows to the primary absorber and the liquid is pumped to the stripper. The HPS is essentially a separation stage with an external cooler located between the primary stripper and absorber. In some units, they are a single tower.



**Figure 1.20:** A typical FCC gas plant (HPS = high-pressure separator).

### **Primary Absorber**

The HPS overhead vapor contains appreciable amounts of  $C_3$ 's and heavier components. The primary absorber recovers these components. The HPS vapor enters below the bottom tray and proceeds up the tower contacting absorption oil. Heavy components are absorbed in the oil.

Two sources of absorption oil are normally utilized in this tower. The first is the hydrocarbon liquid from the main fractionator overhead receiver. This stream, often called "wild," or unstabilized naphtha, enters the absorber a few trays below the top tray. The second absorbent is cooled debutanized gasoline, which generally enters on the top tray. It has a lower vapor pressure and can be considered a trim absorbent. The expression "lean oil" generally refers to the debutanized gasoline plus the unstabilized naphtha from the overhead receiver.

The absorption process is exothermic. To improve  $C_3+$  recovery, liquid from one or more of the middle trays is pumped through an intercooler and returned to the tray below. In some FCC units, the lean oil feed is chilled.

To enhance  $C_3+$  recovery, some units have installed presaturator drums that function as an additional absorption stage. In this operation, the cooled debutanized gasoline is mixed (presaturated) with the absorber overhead gas. The mixture is cooled and flashed in the presaturator drum. The liquid from this drum is then pumped to the top of the primary absorber.

## Sponge Oil or Secondary Absorber

The vapor from the primary absorber or the presaturator contains a small quantity of gasoline. The sponge oil or secondary absorber recovers this gasoline. "Sponge oil" is often stripped or unstripped LCO. It is used for final absorption of the dry gas stream. Instead of LCO, a few FCC units use cooled heavy naphtha from the main column as sponge oil.

The lean sponge oil enters the absorber on the top tray. The gas from the presaturator or from the primary absorber enters below the bottom tray. The rich sponge oil from the bottom is then returned to the main fractionator. The lean gas leaves the top of the absorber to an amine unit for  $H_2S$  removal prior to entering the refinery fuel gas system.

## Stripper or De-ethanizer

The HPS liquid consists mostly of  $C_3$ 's and heavier hydrocarbons; however, it also contains small fractions of  $C_2$ 's,  $H_2S$ , and entrained water. The stripper removes these light ends. The liquid enters the stripper on the top tray. The heat for stripping is provided by an external reboiler, using steam or debutanizer bottoms as the heat medium. The vapor from the reboiler rises through the tower and strips the lighter fractions from the descending liquid. The rich overhead vapor flows to the HPS via the condenser and is fed on to the primary absorber. The stripped naphtha leaves the tower bottoms and goes to the

debutanizer. Few de-ethanizer towers have dedicated water draw trays to remove the entrained water.

#### Debutanizer

The stripper bottoms contain  $C_3$ 's,  $C_4$ 's, and gasoline; the debutanizer separates the  $C_3$ 's and  $C_4$ 's from the gasoline. In some units, the hot stripper bottoms can be further preheated before entering the debutanizer. In a number of units, the stripper bottoms are sent directly to the debutanizer. The feed enters about midway in the tower. Debutanizer feed is always partially vaporized because the debutanizer operates at a lower pressure than the stripper. A control valve that regulates the stripper bottoms' level is the means of this pressure drop. As a result of this drop, part of the feed is vaporized across the valve.

The debutanizer separates the feed into two products. The overhead product contains a mixture of  $C_3$ 's and  $C_4$ 's. The bottoms product is the stabilized gasoline. Heat for separating these products comes from an external reboiler. The heating source is usually the main fractionator HCO or slurry. Steam can also be used.

The overhead product is totally liquefied in the overhead condensers. A portion of the overhead liquid is pumped and returned to the tower as reflux. The remainder is sent to a treating unit to remove  $H_2S$  and other sulfur compounds. The mixed  $C_3$ 's and  $C_4$ 's stream can then be fed to either an alkylation unit or is fed to a depropanizer tower where the  $C_3$ 's are separated from  $C_4$ 's. The  $C_3$ 's are processed for petrochemical feedstock and the  $C_4$ 's are alkylated.

The debutanized gasoline is cooled, first by supplying heat to the stripper reboiler or by preheating the debutanizer feed. This is followed by a set of air or water coolers. A portion of the debutanizer bottoms can be pumped back to the presaturator or to the primary absorber as lean oil. The balance is treated for sulfur and blended into the refinery gasoline pool.

## Gasoline Splitter

A number of refiners split the debutanized gasoline into "light" and "heavy" gasoline. This optimizes the refinery gasoline pool when blending is constrained by sulfur and aromatics. In a few gasoline splitters, a third "heart cut" is withdrawn. This intermediate cut is low in octane, and it is processed in another unit for further upgrading.

## Water Wash System

The cat cracker feedstock contains concentrations of organic sulfur and nitrogen compounds. Cracking of organic nitrogen compounds liberates hydrogen cyanide (HCN), ammonia (NH<sub>3</sub>), and other nitrogen compounds. Cracking of organic sulfur compounds produces hydrogen sulfide (H<sub>2</sub>S) and other sulfur compounds.

A wet environment exists in the FCC gas plant. Water comes from the condensation of process steam in the main fractionator overhead condensers. In the presence of H<sub>2</sub>S, NH<sub>3</sub>, and HCN, this environment is conducive to corrosion attack. The corrosion attack can be any or all of the following types [2]:

- General corrosion from ammonium bisulfide
- Hydrogen blistering and/or embrittlement
- Pitting corrosion under fouling deposits.

Ammonium bisulfide is produced by the reaction of ammonia and hydrogen sulfide [2]:

$$NH_3 + H_2S \rightarrow (NH_4)HS$$
  
 $MW = 17$ ,  $MW = 34$   
Weight ratio:  $NH_3/H_2S = 0.5$  (1.1)

Ammonium bisulfide is extremely corrosive to steel. The corrosion product is hydrogen gas and iron sulfide. The reaction is normally self-terminating because iron sulfide coats the metal surface with a protective film that inhibits further corrosion. However, if cyanide is present, the iron sulfide is removed and bisulfide corrosion is no longer self-terminating. Hydrogen cyanide (HCN) is formed in the riser from the reaction of ammonia (NH<sub>3</sub>) and CO. Ammonium cyanide is formed from the reaction of hydrogen cyanide (HCN) and ammonia (NH<sub>3</sub>). The ammonium cyanide will dissolve in a wet environment and ionize into cyanide and ammonium ions. The cyanide ion reacts with the insoluble iron sulfide to form a soluble ferrocyanide complex. This destroys the iron sulfide protective film and exposes fresh metal to further attack. As this corrosion proceeds, it produces hydrogen atoms which penetrate into the metal surfaces causing hydrogen blistering. This leads to stress corrosion cracking (SCC).

The chemical reactions are as follows:

1. Generation of hydrogen cyanide

$$CO + NH_3 \rightarrow HCN + H_2O \tag{1.2}$$

Formation of ammonium cyanide

$$HCN + NH_3(aq) \rightarrow NH_4CN(aq)$$
 (1.3)

Ionization in water

$$NH_4CN \to NH_4^+ + CN^-$$
 (1.4)

4. Cyanide corrosion

$$FeS + CN^{-} \rightarrow Fe(CN)_{6} + (NH_{4})_{2}S$$
 (1.5)

Ammonia can also react with hydrogen sulfide to form ammonium sulfide:

$$2NH_3 + H_2S \rightarrow (NH_4)_2S$$
  
 $MW \ 2NH_3 = 34$ ,  $MW \ H_2S = 34$ , (1.6)  
weight ratio  $2NH_3/H_2S = 1.0$ 

Ammonium sulfide is not corrosive, but it can precipitate. Under-deposit corrosion and pitting can occur.

Typically, sour water from the FCC contains a mixture of ammonium sulfide and ammonium bisulfide with an ammonia-to-hydrogen sulfide ratio between 0.5 and 1.0.

Most refiners employ continuous water wash as the principal method of controlling corrosion and hydrogen blistering. The best source of water is either steam condensate or well-stripped water from a sour water stripper. A number of refiners use ammonium polysulfate to neutralize hydrogen cyanide and to control hydrogen stress cracking.

In the gas plant, corrosive agents (H<sub>2</sub>S, HCN, and NH<sub>3</sub>) are most concentrated at high-pressure points. Water is usually injected into the first- and second-stage compressor discharges. The water contacts the hot gas and scrubs these agents. There are two common injection methods: *forward cascading* and *reverse cascading*.

In forward cascading (Figure 1.21), the water is normally injected into the discharge of the first-stage compressor and condenses in the interstage cooler. From the interstage drum, the

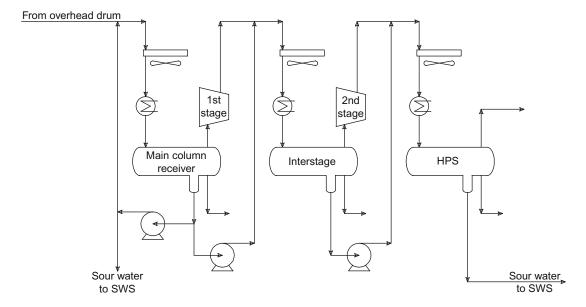


Figure 1.21: A typical forward cascading water wash system (SWS = sour water stripper).

water is pumped to the second-stage discharge, condenses in the cooler, and collects in the HPS. From the HPS, the water is then pressured to the sour water stripper (SWS).

In reverse cascading (Figure 1.22), fresh water is injected into the second-stage discharge. The water containing corrosive agents is pressured to the first-stage discharge and then back to the main fractionator overhead. From the overhead receiver, the water is then pumped to the sour water stripper. Reverse cascading requires one less pump, but a portion of cyanide captured in the second stage is released in the interstage, forming a cyanide recycle. Consequently, forward cascading is more effective in minimizing cyanide attack.

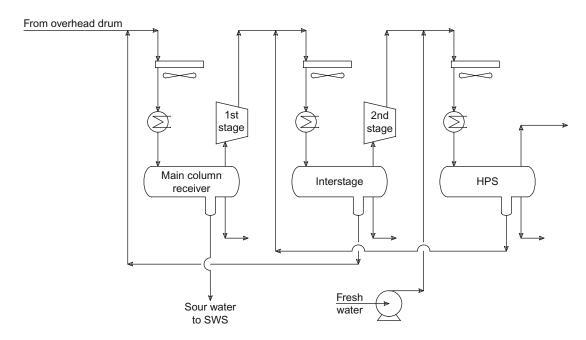


Figure 1.22: A typical reverse cascading scheme for water wash.

# **Treating Facilities**

The gas plant products, namely fuel gas, C<sub>3</sub>'s, C<sub>4</sub>'s, and gasoline, contain sulfur compounds that require treatment. Impurities in the gas plant products are acidic in nature. Examples include hydrogen sulfide (H<sub>2</sub>S), carbon dioxide (CO<sub>2</sub>), mercaptan (R—SH), phenol (ArOH), and naphthenic acids (R—COOH). Carbonyl and elemental sulfur may also be present in the above streams. These compounds are acidic.

Amine and caustic solutions are used to remove these impurities. The amine solvents known as alkanolamines remove both  $H_2S$  and  $CO_2$ . Hydrogen sulfide is poisonous and toxic. For refinery furnaces and boilers, the maximum  $H_2S$  concentration is normally about 160 ppm.

Amines remove the bulk of the  $H_2S$ ; primary amines also remove the  $CO_2$ . Amine treating is not effective for removal of mercaptan. In addition, it cannot remove enough  $H_2S$  to meet the copper strip corrosion test. For this reason, caustic treating is the final polishing step downstream of the amine units. Table 1.4 illustrates the chemistry of some of the important caustic reactions.

Table 1.4: Acid/Base Reactions Encountered Most Frequently by Oil Industry Caustic Treaters.

Carbon dioxide			
CO <sub>2</sub> + 2NaOH	$\rightarrow$	$Na_2CO_3 + H_2O$	
Hydrogen sulfide			
$H_2S + 2NaOH$	$\rightarrow$	$Na_2S + 2H_2O$	
Mercaptan sulfur			
RSH + NaOH	$\rightarrow$	$RSNa + H_2O$	
Naphthenic acid			
RCOOH + NaOH	$\rightarrow$	$RCOONa + H_2O$	
1			

#### Sour Gas Absorber

An amine absorber (Figure 1.23) removes the bulk of  $H_2S$  from the sour gas. The sour gas leaving the sponge oil absorber usually flows into a separator that removes and liquefies hydrocarbon from vapors. The gas from the separator flows to the bottom of the  $H_2S$  contactor where it contacts a countercurrent flow of the cooled lean amine from the regenerator. The treated fuel gas leaves the top of the  $H_2S$  absorber, goes to a settler drum for the removal of entrained solvent, and then flows to the fuel system.

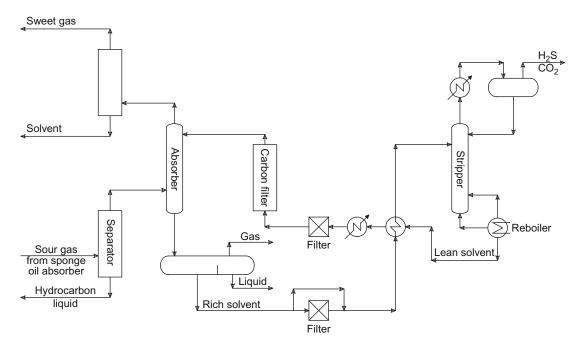
Rich amine from the bottom of the H<sub>2</sub>S contactor goes to a flash separator to remove dissolved hydrocarbons from the amine solution. The rich amine is pumped from the separator to the amine regenerator.

In the amine regenerator, the rich amine solution is heated to reverse the acid—base reaction that takes place in the contactor. The heat is supplied by a steam reboiler. The hot, lean amine is pumped from the bottom of the regenerator and exchanges heat with the rich amine in the lean-rich exchanger and a cooler, before returning to the contactor.

A portion of the rich amine flows through a particle filter and a carbon bed filter. The particle filters remove dirt, rust, and iron sulfide. The carbon filter, located downstream of the particle filters, removes residual hydrocarbons from the amine solution.

The sour gas, containing small amounts of amine, leaves the top of the regenerator and flows through a condenser to the accumulator. The sour gas is sent to the sulfur unit, while the condensed liquid is refluxed to the regenerator.

For many years, nearly all the amine units were using monoethanolamine (MEA) or diethanolamine (DEA). However, in recent years, the use of tertiary amines such as methyl diethanolamine (MDEA) has increased. These solvents are generally less corrosive and require less energy to regenerate. They can be formulated for specific gas recovery requirements.



**Figure 1.23:** A typical amine treating system.

## LPG Treating

The LPG stream containing a mixture of  $C_3$ 's and  $C_4$ 's must be treated to remove hydrogen sulfide and mercaptan. This produces a noncorrosive, less odorous, and less hazardous product. The  $C_3$ 's and  $C_4$ 's from the debutanizer accumulator flow to the bottom of the  $H_2S$  contactor. The operation of this contactor is similar to that of the fuel gas absorber, except that this is a liquid—liquid contactor.

In the LPG contactor, the amine is normally the continuous phase with the amine—hydrocarbon interface at the top of the contactor. This interface level controls the amine flow out of the contactor. (Some liquid/liquid contactors are operated with the hydrocarbon as the continuous phase. In this case, the interface is controlled at the bottom of the contactor.) The treated  $C_3/C_4$  stream leaves the top of the contactor. A final coalescer is often installed to recover the carryover amine.

#### Caustic Treating

Mercaptans are organic sulfur compounds having the general formula of R—S—H. As stated earlier, amine treating is not effective for the removal of mercaptan. There are two options for treating mercaptans. In each option, the mercaptans are first oxidized to disulfides. One option, extraction, dissolves the disulfides in caustic and removes them. The other option, sweetening, leaves the converted disulfides in the product. Extraction removes sulfur, sweetening just removes the mercaptan odor. Extraction is used for light products (up to light naphtha) and sweetening for heavy products (gasoline through diesel).

Both sweetening and extraction processes (Figure 1.24) commonly use caustic and catalyst. If the LPG and the gasoline contain high levels of  $H_2S$ , a caustic prewash is needed to protect the catalyst.

The sweetening process utilizes a caustic solution, catalyst, and air. Mercaptans are converted to disulfides in a mixing vessel or fiber film contactor. The reactions take place according to the following equations:

$$RSH + NaOH + catalyst \rightarrow RSNa + H_2O$$
 (1.7)

$$2RSNa + \frac{1}{2}O_2 + H_2O + catalyst \rightarrow RSSR + 2NaOH$$
 (1.8)

The mixture of caustic and disulfides is transferred to a settler. From the settler, the treated gasoline flows to a coalescer, sand filter, or wash water tower, before going to storage. The caustic solution is recirculated to the mixing vessel/fiber film contactor.

In the extraction process, the LPG from the prewash tower enters the bottom of an extractor column. The extractor is a liquid/liquid contactor in which the LPG is countercurrently contacted by a caustic solution. Another option is the use of a fiber film contacting device. The mercaptans dissolve in the caustic (Eq. (1.7)). The treated LPG leaves the top of the extractor and goes on to a settler, where entrained caustic is separated.

From the bottom of the extractor, the caustic solution, containing sodium mercaptide, enters the regenerator. Plant air supplies oxygen to react with the sodium mercaptide to form disulfide oil (Eq. (1.8)), which is insoluble in caustic. The oxidizer overhead stream flows to a disulfide separator. A hydrocarbon solvent, such as naphtha, washes the disulfide oils out of the regenerated caustic. The regenerated caustic is returned to the extractor and the solvent containing disulfide oil is disposed in other units.

## Summary

FCC is one of the most important conversion processes in a petroleum refinery. The process incorporates most phases of chemical engineering fundamentals, such as fluidization, heat/mass transfer, and distillation. The heart of the process is the reactor—regenerator, where most of the innovations have occurred since 1942.



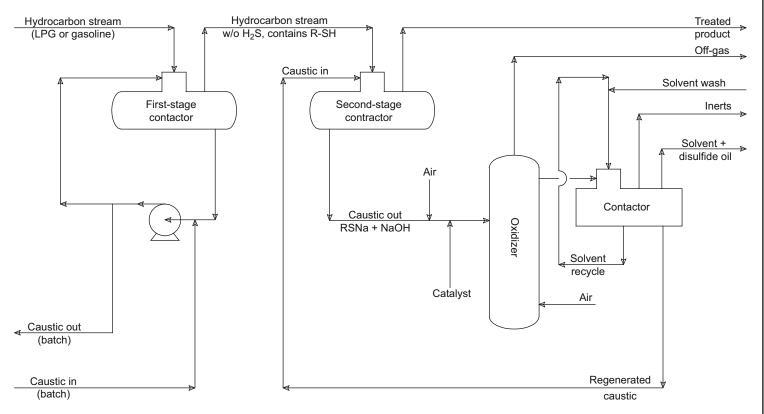


Figure 1.24: Caustic sweetening and extraction processes (adapted from Merichem Company—Houston, TX).

The FCC unit converts low-value, high-boiling feedstocks into valuable products such as gasoline and diesel. The FCC is extremely efficient, with only about 5% of the feed used as fuel in the process. Coke is deposited on the catalyst during the reaction and burned off in the regenerator, supplying all the heat for the reaction.

Products from the reactor are recovered in the main fractionator and the gas plant. The main fractionator recovers the heaviest products, such as LCO and DO, from the gasoline and lighter products. The gas plant separates the main fractionator overhead vapors into gasoline,  $C_3$ 's,  $C_4$ 's, and fuel gas. The products contain sulfur compounds and need to be treated prior to being used. A combination of amine and caustic solutions are employed to sweeten these products.

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- [2] Fluid Catalytic Cracking Information, Fluid catalytic cracking reference articles. <a href="http://www.canadaspace.com">http://www.canadaspace.com</a>