CATALYTIC CONVERSION PROCESSES
6.1.1 Principles and development

Introduction

After about 70 years of activity, at the beginning of the new millennium catalytic cracking still remains the principal process used to convert heavy oil fractions into lighter products, especially gasoline.

Historically, the distinction between simple-cycle refineries and conversion refineries is based on the absence or presence of catalytic cracking in the production cycle.

The first true catalytic process in the refining industry, cracking is still one of the most important catalytic processes in the petrochemical industry, both in terms of plantsize and the amount of catalyst.

The advent of cracking has significantly contributed to the understanding of the acid catalysis mechanisms that leads to the formation of carbocations starting from hydrocarbon molecules.

Compared to its predecessor (i.e. the thermal cracking process), catalytic cracking presents numerous advantages, including higher gasoline yields (≥50% in weight with respect to the feed), the higher quality of the gasoline produced and a lower production of gaseous, liquid and solid by-products (coke). The gaseous fractions can be used as feed for alkylation processes (see Chapter 4.3), for the production of methyl tert-butyl ether or MTBE (see Chapter 4.4) and for polypropylene plants; heavy liquid fractions (cycle oil) are excellent feedstocks for the production of carbon black (Fig. 1). The use of alkylates and ethers has been encouraged, from the last decade of the Twentieth century onwards, by the reduction of the aromatics and benzene content of commercial gasolines.

Typical feedstocks for catalytic cracking are the high boiling distillates obtained from vacuum distillation, and deasphalted or hydrogenated residues.

The most recent developments in the process also allows the partial feed of atmospheric residues, albeit mixed with the distilled feedstock, since the process takes place in the vapour phase; moreover, residues deactivate the catalyst more rapidly.

Thanks to its versatility and capacity for continuous renewal and development, catalytic cracking has long withstood ‘competition’ from other conversion processes, especially hydrocracking (see Chapter 6.2).

It cannot be ruled out that cracking’s predominant role among catalytic processes will be downscaled, due to changing market requirements (lower demand for gasoline with respect to other fuels), the need to obtain sulphur-free products directly, and to the establishment of processes capable of converting residues directly. However, catalytic cracking will remain a fundamental process in the refining industry for many years to come.

Development of the processes

Despite some earlier attempts to improve the thermal process with the addition of various substances (which cannot always be described as catalysts), it was only in the 1930s that catalytic cracking became commercially important, thanks to the work of Eugène Houdry (see Chapter 1.1).

The first unit, equipped with three fixed bed reactors, came on line in the United States in 1936; the catalyst consisted of a natural clay based on montmorillonite. In the same year, the first plant was built to supply ‘activated earths’ (with acid) to the catalytic plants and, in 1940, the Houdry Corporation started up a plant for the production of synthetic aluminium-silicates.
The fixed bed process was difficult to manage at that time since the three reactors alternated reaction phases with regeneration phases, with intermediate purging. The process remained complex and demanding despite an increase in the number of reactors (six) and the introduction of electrical cycle timers to control the opening and closing of all the valves in the various circuits (oil, vacuum, air and steam). Motivated by the war, experiments began to introduce moving bed plants (TCC, Thermofor Catalytic Cracking) and fluid bed plants (FCC, Fluid Catalytic Cracking), which came on line in the United States almost simultaneously in the years 1942-43.

In moving bed reactors, the catalyst was initially moved using mechanical bucket elevators, and subsequently with air; this allowed for the continuous regeneration of the catalyst, leading to improved yields and product quality. The same benefits were obtained by fluidizing the bed with the vaporized feed (in the reactor) and with air (in the regenerator).

The catalyst consisted of spheres approximately 3 mm in diameter, and microspheres (powder) for the TCC and FCC processes, respectively.

After competing for several decades, the fluid bed technology supplanted the moving bed process so that, already at the end of the Twentieth century, TCC units were extremely rare.

The FCC process, in turn, has undergone continuous development over the years, maintaining it constantly up-to-date. One of the most important developments was the introduction in the early 1960s of zeolite catalysts (able to ‘select’ the reacting molecules), which considerably revitalized the process.

The improved efficiency and stability of catalysts has led to the elimination of the traditional reactor and the introduction of the riser reactor; more efficient catalyst regeneration systems have also been developed. A further step forward was made possible thanks to catalysts, again zeolites (ZSM-5), able to improve the octane number of the gasolines produced, and to the introduction of a series of new additives and passivators.

### Catalytic cracking reactions

The relatively high process temperatures (>450°C) lead to the formation of free radicals and to thermal reactions. These reactions have low selectivity and produce light gas molecules, such as methane and ethane, and lead to the formation of olefins.

Although the latter may be precursors to the formation of carbocations, thermal reactions should be limited by operating at temperatures which are as low as possible.

Catalytic cracking reactions include isomerization, the \( \beta \)-scission of paraffins, dehydrogenation, hydrogen transfer and various types of condensation reactions. The main reactions, according to the various classes of hydrocarbons, are summarized in Table 1.

Catalysts of acid type promote the formation of carbocationic intermediates rather than free radicals, improving yields and selectivity.

Carbocations may form starting from an olefin, in the presence of Brønsted acid sites in the catalyst, or by the protonation of a paraffin or naphthene:

\[
\begin{align*}
R_1 - C & \rightarrow R_2 + H^+ \\
R_1 - C & \rightarrow R_2 + H^+ \\
R_1 - C & \rightarrow R_2 + H^+ \\
R_1 - C & \rightarrow R_2 + H^+
\end{align*}
\]

The first of these mechanisms is universally accepted and, in comparison with others, is significantly faster. However, the hypothesis that carbocations may also be formed starting from
Lewis-type sites, present on the catalyst together with Brønsted sites, is also commonly accepted:

\[ R_1\text{-}C\text{-}C\text{-}R_2\text{+L} \rightarrow R_1\text{-}C\text{--CH_3+}\text{CH_2--CH_2\text{--CH_2--CH_2--CH_2}}_\text{--R_2} \]

Since they are deficient in electrons, Lewis-type sites can stabilize one of the hydrogens in the H- form, and form the complementary carbocation. The carbocations that form on the surface of the catalyst tend to isomerize towards the more stable form (from a primary to secondary to tertiary carbocation); in the latter state, the carbon containing the charge is linked to three other carbon atoms. With reference to a paraffin chain, after the formation of the carbon ion, there are various possibilities. The first is isomerization towards a more stable form; the second, endothermic, involves the rupture of the C—C bond in the \( \beta \) position with respect to the charge, forming an olefin and an unstable paraffinic carbocation, which subsequently isomerizes:

\[ R_1\text{-}CH_2\text{-CH_2--CH_2--CH_2--CH_2--R_2} \rightarrow R_1\text{-}CH_2\text{+CH_2--CH_2--CH_2--CH_2} \]

The probability of \( \beta \)-scission increases if the configuration of the original carbocation is favourable (tertiary or secondary, rather than primary). There are also other possibilities: the carbocation frees a proton and turns into an olefin, or saturates by taking a proton from the catalyst’s active site, or reacts with an olefin to alkylate it.

Olefins behave in a comparable way, with the difference that they crack much faster, given their higher tendency to form carbocations; however, they may also oligomerize and cyclize, contributing, alongside aromatics, to the formation of coke.

The \( \beta \)-scission mechanism leads to a preferential rupture of the bonds inside the molecule; non-condensible gases such as methane, ethane and ethylene, which would be formed by the rupture of terminal bonds, are thus only present in small quantities, in contrast to what occurs in thermal processes. The olefins that form have 3 or 4 carbon atoms and are excellent feedstocks for the processes downstream (see again Fig. 1).

However, the formation of olefins is on average lower than that predicted by the mechanisms described above. This is due to exothermic reactions involving the transfer of hydrogen from cycloalkane donor molecules to unsaturated molecules, with the formation of aromatic compounds and paraffins.

This reaction is probably as important as the rupture of the naphthene ring, with the formation of isoalkanes.

The reactivity of the naphthene ring increases with the degree of substitution, in other words the potential for forming tertiary carbocations on the ring. Only the longer side-chains are broken; the methyl and ethyl groups are generally unaffected, given the high

<table>
<thead>
<tr>
<th>HYDROCARBONS</th>
<th>SCHEMATIC STRUCTURE</th>
<th>MAIN REACTIONS</th>
<th>MAIN PRODUCTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffins</td>
<td></td>
<td>Rupture of the molecule in different points: difficult rupture of C—C bonds</td>
<td>Paraffins and olefins with at least 3 or 4 C atoms; small quantities of methane</td>
</tr>
<tr>
<td>Naphthenes</td>
<td></td>
<td>Rupture of the ring and side chains</td>
<td>Paraffins and olefins; small quantities of aromatics</td>
</tr>
<tr>
<td>Naphthene-aromatics</td>
<td></td>
<td>Opening of the naphthene ring; rupture of the side chains of the aromatic rings</td>
<td>Paraffins, olefins and aromatics</td>
</tr>
<tr>
<td>Aromatics without side chains</td>
<td></td>
<td>Negligible cracking</td>
<td>Coke</td>
</tr>
<tr>
<td>Aromatics with side chains</td>
<td></td>
<td>Rupture of side chains</td>
<td>Olefins and aromatics</td>
</tr>
<tr>
<td>Olefins</td>
<td></td>
<td>Rupture of the chains at various points</td>
<td>Branched olefins; paraffins; diolefins</td>
</tr>
</tbody>
</table>
formation energy of the corresponding ions. In this case, a ring with 5 carbon atoms may isomerize to the more reactive ring with 6 carbon atoms.

The above discussion also applies to the dealkylation of aromatics, whose ring is extremely stable and is not ruptured; however, it may be involved in condensation reactions with the formation of coke. Methyl aromatics may undergo disproportionation; thus, benzene and xylene can be made from toluene.

**The formation of coke**

The term coke is used to describe the material deposited on the catalyst during the process, and oxidized during the regeneration phase, producing the energy needed for the cracking reactions. It consists of a series of components with a high carbon content (≥90%), mainly in the form of condensed aromatic rings. Its composition depends on the type of feed, the content of contaminants (such as V, Ni, and Fe, which catalyze the dehydrogenation reactions), the nature of the catalyst and the operating conditions. Like its composition, the mechanism of coke formation is complex and involves cyclization and polycondensation reactions starting from precursors such as olefins, diolefins and aromatics. These reactions, though not encouraged by the conditions adopted in current processes (high temperatures and low pressures), may occur anyway. The polyaromatic compounds formed are resistant to cracking, and gradually accumulate in the heavy liquid fractions and on the catalyst.

**Catalysts**

As seen above, the catalytic cracking mechanism involves the formation of carbocations and is activated by acid functions.

In the earliest processes, the catalysts were essentially natural clays (aluminium-silicates) activated with an acid treatment and then calcinated. This treatment had the aim of creating acid centres, responsible for catalytic activity, by replacing the alkaline and alkaline-earth ions saturating the negative charges.

The clay most widely used was montmorillonite, which can be described with the general formula:

\[ \text{Si}_{8}\text{Al}_{4}\text{O}_{20}(\text{OH})_{4}\cdot n\text{H}_{2}\text{O} \]

Silica and alumina, taken separately, do not have acid properties; however, if the alumina is dispersed within a silica matrix, strong acidity can be observed. Silica consists of SiO\(_4\) tetrahedrons; substituting a silicon atom with an aluminium atom is accompanied by the formation of a negative charge, which must be balanced; if this is done by a proton (rather than, for example, a sodium ion), the result is a strongly acidic material:

![Catalyst structure](image)

Nevertheless, silica-alumina based catalysts have two types of acidity linked to the aluminium atom: Lewis acidity, characteristic of a tricoordinate Al (capable of acquiring a pair of electrons to form the stable octet), and Brønsted, or protonic acidity. During heating, protonic acidity tends to become Lewis acidity; this, in turn, tends to turn into protonic acidity due to the action of small quantities of water.

The need for greater control over chemical composition and morphology led, as early as the 1930s, to the appearance of synthetic catalysts (silica-alumina gel), obtained using spray drying processes; these had a more regular physical form and improved performance.

However, the genuine revolution occurred during the mid-1960s with the introduction of catalysts based on zeolites (faujasite).

Unlike the natural aluminium-silicates previously used, which were amorphous, zeolites are porous crystalline materials whose properties are governed and defined principally by their chemical composition and crystalline structure, consisting of a three-dimensional grid with regular pores. Chemically, these are also aluminium-silicates with negative charges on the tetrahedrons \([\text{AlO}_{3}]^-\); therefore, they must contain positive external M ions (e.g. H\(^+\), Na\(^+\), K\(^+\), Ca\(^{++}\), Mg\(^{++}\), etc.) to balance the charge of the anions. These materials can be described with the general formula:

\[ M_x(\text{AlO}_2)_y(\text{SiO}_2)_z\cdot z\text{H}_2\text{O} \]

If M is a monovalent positive cation, \(u=x\); if it is bivalent, \(u=x/2\).

The cations are positioned near the anions in the crystal tunnels, whose diameters range in natural minerals, from 0.25 nm (sodalite) to around 0.8 nm (faujasite).

Although zeolites exist as natural minerals, synthetic products are now used for catalysis.

Zeolites are acid catalysts, but are often considered separately, given their unusual properties and, in particular, their ability to carry out shape-selective catalysis: the size and shape of the internal cavity determine those of the products, whereas the diameter of the pore determines the type of molecules which can enter them.
Zeolites are often classified on the basis of the Si-Al ratio (Table 2); this ratio is equal to or greater than one.

The fact that the \([\text{AlO}_4]^-\) group in zeolites of the Linde ‘A’ and ‘X’ types is an unstable site to acid attack, in the presence of steam at high temperatures, created the basis for the synthesis of products with a lower Al content.

The Linde ‘Y’ zeolite, with a Si/Al ratio of between 1.5 and 3.0, and the same structural and skeletal typology as Linde ‘X’ (and identical to the rare natural zeolite faujasite), was introduced in 1964 and immediately became the preferred product for industrial processes.

The basic unit of faujasite is the sodalite cage, consisting of 24 (SiO₄) or (AlO₄) tetrahedrons; depending on how the basic units are joined, two different structures can be obtained: the Linde ‘A’ type zeolite and the Linde ‘X’ or ‘Y’ type zeolite (Fig. 2). In all cases, a three-dimensional grid of intercommunicating tunnels containing larger cavities (or cages) inside is obtained; the diameter of the pores is determined in part by the type of cation, which balances the structure’s negative charges. These are thus highly porous structures, within which gas molecules can circulate.

Table 2. Classification of zeolites on the basis of the Si/Al ratio

<table>
<thead>
<tr>
<th>Si/Al Ratio</th>
<th>Types</th>
<th>Origin</th>
<th>Å</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low (1.0-1.5)</td>
<td>Linde ‘A’</td>
<td>Synthetic</td>
<td>3-5</td>
<td>Unstable at high T and to acid attack</td>
</tr>
<tr>
<td></td>
<td>Linde ‘X’</td>
<td>Synthetic</td>
<td>7-8</td>
<td>Low resistance to steam</td>
</tr>
<tr>
<td>Medium (1.5-5.0)</td>
<td>Faujasite</td>
<td>Natural</td>
<td>7-8</td>
<td>Rare in nature</td>
</tr>
<tr>
<td></td>
<td>Linde ‘Y’</td>
<td>Synthetic</td>
<td>7-8</td>
<td>Like faujasite but more stable; for cracking and isomerization</td>
</tr>
<tr>
<td></td>
<td>Mordenite</td>
<td>Synthetic</td>
<td>6-7</td>
<td>Different structure</td>
</tr>
<tr>
<td>High (6-100)</td>
<td>ZSM-5</td>
<td>Synthetic</td>
<td>5-6</td>
<td>Highly selective</td>
</tr>
<tr>
<td></td>
<td>Silicalite</td>
<td>Synthetic</td>
<td>5-6</td>
<td>Basically siliceous, hydrophobic</td>
</tr>
</tbody>
</table>

The linear dimensions of the broadest cages are about 1.15-1.20 nm; the ‘entrance windows’, however, are extremely small in Linde ‘A’ type zeolites, and wider in Linde ‘X’ and ‘Y’ type zeolites (see again Table 2 and Fig. 3); this property makes it possible to use Linde ‘A’ type zeolites as molecular sieves for small molecules, whereas Linde ‘X’ and ‘Y’ type zeolites, which allow larger molecules to pass through them (naphthenes, branched hydrocarbons etc.), are ideal for the cracking process.

When the zeolites are synthesized, the negative charges are neutralized by sodium ions, which are then exchanged with ammonium ions or the ions of rare earths (Ce³⁺, La³⁺); during calcination, the NH₄⁺ ions are turned into ammonia and H⁺ ions, which create the necessary protonic acidity, while the rare earths contribute to both Brønsted-type and Lewis-type acidity:

\[
\begin{align*}
\text{H}^+ & \quad \text{Brønsted-type acid site} \\
\text{Ce (OH)} & \quad \text{Lewis-type acid site}
\end{align*}
\]

The exchange with rare earths confers greater acidity; the result is an increase in conversion and a decrease in octane quality (Fig. 4).

Fig. 2. Cubic-octahedral unit of sodalite (A), structure of Linde ‘A’ type (B) and ‘X’ and ‘Y’ type zeolites (C).
Increasing the Si/Al ratio leads to greater thermal stability and a higher resistance to steam, fundamental properties for cracking catalysts given the significant use of steam (stripping during the transitions from reactor to regenerator and vice versa) and the high temperatures in regeneration.

Ultrastable zeolites, up to 1,000°C (such as UltraStable 'Y' zeolites or USY) are also made with a hydrothermal treatment, moving Al towards positions which are no longer reticular.

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### Fig. 3. Structure of synthetic Linde ‘Y’ faujasite with the formula Na₅₆[(AlO₂)₅₆(SiO₂)₁₃₆]250 H₂O, giving a partial indication of the acid sites, the position of the oxygen (yellow circles) and the non-reticular cations (red circles).

### Table 3. Selectivity of some Linde ‘Y’-type zeolites to different products

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>USY</th>
<th>REUSY</th>
<th>REHY</th>
<th>REY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Saturated C₃-C₄</td>
<td>High</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Low</td>
</tr>
<tr>
<td>C₃-C₄ olefins</td>
<td>High</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Low</td>
</tr>
<tr>
<td>Coke/conversion</td>
<td>Very low</td>
<td>Very low</td>
<td>Low</td>
<td>Moderate</td>
</tr>
<tr>
<td>Gasoline</td>
<td>Moderate</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Octane yield</td>
<td>High</td>
<td>Moderate</td>
<td>Low</td>
<td>Low</td>
</tr>
</tbody>
</table>

**Activity vs feedstocks**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>USY</th>
<th>REUSY</th>
<th>REHY</th>
<th>REY</th>
</tr>
</thead>
<tbody>
<tr>
<td>340-480°C</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>&gt;480°C</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Low</td>
<td>Low</td>
</tr>
</tbody>
</table>

**USY** = ultrastable Y zeolite  
**REUSY** = ultrastable Y zeolite containing rare earths  
**REHY** = Y zeolite containing rare earths and hydrogen  
**REY** = Y zeolite containing rare earths
components: cohesion between the microspheres of the catalyst is ensured by silica-alumina gel; kaolin or a similar material has the function of dispersing heat (during regeneration) and acts as macroporous material for diffusing and precracking the reagents.

The use of selective matrices (SAM, Selective Alumina Matrix) is especially important in processes that are also fed with a significant quantity of residue (30-50%) in addition to heavy distillates (O’Connor et al., 1991), as shown in the example given in Fig. 5.

Various additives are dispersed in the matrix, particularly alumina, with the aim of promoting the cracking activity of specific catalysts destined for the treatment of particularly heavy feedstocks; other additives can be added as separate microspheres.

Among the additives, it is worth mentioning combustion promoters (from CO to CO₂); aluminium and magnesium compounds to fix sulphur oxides in the form of sulphates (in the regenerator), releasing them as H₂S in the reactor and in the strippers; and passivators to neutralize the action of vanadium and nickel.

Fig. 6 shows the structure of a typical cracking catalyst.

The structure of cracking catalysts makes it easy to see how these can be deactivated by potentially basic compounds (Na or compounds containing nitrogen) and by the metals present in the feed, which in the long run lead to permanent deactivation.

Specifically, vanadium is oxidized to V₂O₅ in the regenerator and may form vanadates of rare earths, in addition to catalyzing dehydrogenation (under cracking conditions).

Nickel is a far stronger dehydrogenator than vanadium, and thus encourages the formation of coke; the addition of organometallic compounds of antimony and bismuth partially neutralizes this effect with the formation of intermetallic compounds.

The formation of coke, which, as seen above, originates from various secondary dehydrogenation, condensation and polymerization reactions, leads to the gradual obstruction of the active centres of the catalyst, which loses activity and must therefore be regenerated by the combustion of the deposit and recycled into the reactor.

In the cracking process, the catalyst performs at least three functions (see below): activator for cracking reactions, support for coke, heat transporter; all occurs under extremely severe conditions since it continuously circulates in high friction zones (fluid bed) and high velocity zones (cyclones, riser: 20-30 m/s). Furthermore, every 8-10 minutes, the catalyst passes from a reducing atmosphere at about 500°C (riser-stripper) to an oxidizing atmosphere at 700-800°C (regenerator).

**Thermodynamic aspects**

An accurate thermodynamic analysis of catalytic cracking would require the acquisition of data on the hydrocarbons and other compounds contained within the heavy fractions that feed the process; this is impossible. It may be useful to refer to some typical, simpler hydrocarbons in order to roughly define the thermodynamic aspects of the process.
Table 4 (Raseev, 2003) shows the heats of reaction and entropy variations for some typical cracking reactions involving paraffins, olefins, cycloalkanes and aromatics under typical cracking conditions (i.e. about 500°C and pressures slightly above atmospheric pressure).

The differences between the various possible reactions of an individual hydrocarbon series are not significant. With the exception of secondary condensation and polymerization reactions (which are not desired, but occur anyway) and isomerizations, typical cracking reactions (i.e. the rupture of carbon-carbon bonds and dehydrogenation) are all endothermic.

Isomerizations are weakly exothermic ($\Delta H$ between $-4$ and $-20$ kJ/mol).

Overall, the cracking process is thus endothermic, with values of the reaction $\Delta H$ moderately influenced by the type of catalyst, and generally in the range of 900 to 1,000 kJ/kg (Pekediz et al., 1997).

Approximate thermodynamic calculations, based on simplified expressions of free energy, show that the balance which leads to a paraffin and an olefin starting from a generic paraffin

$$C_{m+n}H_{2(m+n)+2} \rightleftharpoons C_mH_{m+2} + C_nH_{2n}$$

moves to the right at temperatures above 300°C (Giavarini, 1999).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H^{0\circ}_\text{800 K}$ (kJ/mol)</th>
<th>$\Delta S^{0\circ}_\text{800 K}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{8}H\textsubscript{14} $\rightleftharpoons$ C\textsubscript{3}H\textsubscript{8} + C\textsubscript{5}H\textsubscript{6}</td>
<td>79.13</td>
<td>140.50</td>
</tr>
<tr>
<td>C\textsubscript{20}H\textsubscript{42} $\rightleftharpoons$ C\textsubscript{3}H\textsubscript{8} + C\textsubscript{17}H\textsubscript{34}</td>
<td>79.09</td>
<td>139.70</td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{12} $\rightleftharpoons$ 2C\textsubscript{3}H\textsubscript{6}</td>
<td>77.79</td>
<td>140.49</td>
</tr>
<tr>
<td>C\textsubscript{20}H\textsubscript{40} $\rightleftharpoons$ 2C\textsubscript{10}H\textsubscript{20}</td>
<td>77.75</td>
<td>143.18</td>
</tr>
</tbody>
</table>
Industrial processes must therefore operate at higher temperatures (above 450 °C), at which it can be assumed that the cracking reactions are complete.

A similar calculation, referring to the transition from cyclohexane to benzene, gives a temperature above 550 °C.

As such, under the conditions adopted in industrial processes (470-520 °C and pressures slightly above atmospheric pressure), thermodynamic aspects limit the decomposition of alkanes to alkenes in the gas phase.

The same can be said for the rupture of the side chains of naphthene and aromatic rings, whose conversions are determined by the relative kinetics. Again in the gas phase, the cracking of naphthene rings, which is less favoured thermodynamically than that of aromatic rings, preferably occurs in rings with 5 terminals, whereas in rings with 6 terminals dehydrogenation is favoured (Raseev, 2003).

The decomposition of non-cyclic heteroatomic compounds (which also contain sulphur, nitrogen or metals) does not have thermodynamic limitations.

If the aim is to obtain isomers with a high octane number (exothermic reactions), the process should take place at the lowest possible temperatures, compatible with cracking reactions (endothermic).

It is more difficult to describe the reactions that occur on the chemiadsorbed layer in the catalyst and lead to the formation of coke. Under process conditions, the polymerization of alkenes and other condensation reactions are not favoured: these can take place only in the liquid phase or on the surface of the catalyst; in the gas phase, they can occur only at very high pressures (Raseev, 2003).

The formation of compounds with a high molecular weight (by polymerization, condensation, dehydrogenation) takes place inside the cages and pores, where they cannot be desorbed (given their size) from the catalyst, leading to the formation of coke.

In the regenerator, the coke deposited on the catalyst is oxidized to reactivate it and to supply heat to the process. The heat of combustion of the coke depends on its hydrogen content and the CO₂/CO ratio in the combustion gases; the H₂ content generally falls within the interval 4-10%.

Table 5 (Raseev, 2003) shows the heats of combustion of cokes with different H/C ratios and different CO₂/CO ratios in the fumes.

The thermal balance, based on two opposite energy exchanges, depends mainly on the quality of the feed: for ‘easy’ feeds with a low Conradson carbon content, such as vacuum gas oils, the coke yield may be insufficient to balance the requirements of the unit, whereas for residues, the energy produced by the regenerator is excessive and some of it must be disposed of.

The heat $Q_{\text{cat}}$ (kJ/h) transferred to the catalyst in the regenerator can be expressed by the equation (Bonifay and Marcilly, 2001):

$$Q_{\text{cat}} = \Delta_{\text{coke}} \cdot W_{\text{cat}} \cdot Q_{\text{coke}} \cdot R$$

where: $\Delta_{\text{coke}}$ (kg of coke/kg of catalyst) is the difference, referring to the unit of weight of the circulating catalyst, between the weight of the coke deposited on the catalyst (from the reactor) and the weight of the residual coke on the catalyst (from the regenerator); $W_{\text{cat}}$ (kg of catalyst/h) is the weight flow rate of the catalyst in circulation; $Q_{\text{coke}}$ (kJ/kg of coke) is the combustion heat of the coke; $R$ is the efficiency of combustion in the regenerator, in other words, the ratio of heat absorbed by the catalyst to heat produced by the combustion of the coke. $Q_{\text{cat}}$ is an extremely important parameter that depends on the properties of the feedstock and those of the catalyst. For heavy feedstocks, such as residues, it is thus important to choose catalysts characterized by low $\Delta_{\text{coke}}$ values, to reduce problems of overheating; if there is an energy deficit (lighter feedstocks), a catalyst with high $\Delta_{\text{coke}}$ should be used.

### Table 5. Thermal effects of coke combustion (kJ/kg of coke) (Raseev, 2003)

<table>
<thead>
<tr>
<th>CO₂/CO RATIO IN THE FUMES</th>
<th>CONTENT (% in weight) OF HYDROGEN IN THE COKE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.0</td>
</tr>
<tr>
<td>0</td>
<td>14,590</td>
</tr>
<tr>
<td>1</td>
<td>24,075</td>
</tr>
<tr>
<td>2</td>
<td>27,215</td>
</tr>
<tr>
<td>4</td>
<td>29,745</td>
</tr>
<tr>
<td>10</td>
<td>31,820</td>
</tr>
</tbody>
</table>
As a rough indication, a 0.1% increase in $\Delta_{\text{coke}}$ may lead to variations of 20°C or more in the regenerator.

**Kinetic aspects**

A complete analysis of the process should also take into consideration both the phenomena of the diffusion of the reagents and the products, and the gradual decrease in the activity of the catalyst, in systems with an extremely high number of unknown components such as heavy petroleum fractions; this is thus extremely complex.

Among the first attempts was that of Voorhies (1945), who correlated mean conversion on a stationary bed with the feed rate and the contact time. The following expression for the kinetic constant $k$ was then proposed:

$$K = \frac{w}{\ln \left( \frac{1}{1-x} \right)}$$

where $w$ is the volume flow rate and $x$ the conversion rate.

A more recent method for obtaining a kinetic representation involves grouping the molecules and considering ‘pseudoreactions’ between groups or lumps of components (Fig. 7; Lee et al., 1989).

It is assumed that the constant refers to second order kinetics for gas oil and first order kinetics for gasoline.

A series of equations (Ancheyta-Juarez and Murillo-Hernandez, 2000) takes into consideration the function of the deactivation of the catalyst, kinetic parameters and the variations in yields over time.

The kinetic parameters thus obtained can be used as starting values for estimating the kinetic constants of models with more than four lumps.

The combustion reaction (regeneration phase) is assumed to be of the first order with respect to both carbon and oxygen (Bonifay and Marcilly, 2001):

$$r = k_e \frac{e^{-E/RT}}{[C] [O_2]}$$

where $r$ is the reaction velocity, $[C]$ is the concentration of carbon in the catalyst, $[O_2]$ the partial pressure of the oxygen, $T$ the absolute temperature, $E$ the activation energy, $R$ the gas constant and $k$ the kinetic constant.

Combustion in a real process is far more complex than that shown in the schematic equation given above. However, the expression does allow for a rough estimate of the time required to reach a given reduction of the coke in the catalyst; in turn, this time depends exponentially on the temperature, which thus determines the size of the regenerator.

**The development of fluid bed technologies**

Current catalytic cracking processes are all fluidized bed processes (FCC, Fluid Catalytic Cracking) using powder catalysts (20-50 m).

Regeneration takes place continually, with some of the catalyst being sent from the reactor to the regenerator, and then from the regenerator to the reactor (Fig. 8). Some of the heat serves to compensate for the strongly endothermic nature of cracking, and some exits with the fumes in the form of sensitive heat; a third part (any excess) can be recovered in cooling coils or preferably in external exchangers. As already mentioned, the partial use of residues increases the production of coke and the excess heat produced by its combustion. The production of coke generally ranges from 3 to 5% in weight of the feedstock.
The catalyst is maintained under fluidized bed conditions by the vaporized hydrocarbon phase (in the reactor) and by air (in the regenerator). The movement of the catalyst between these two sections takes place by a gravity or pressure differential; this movement can be controlled by varying the apparent density of the catalyst with the intake of steam or air.

Steam also functions as a stripping fluid during the transitions from the oxidizing phase (regenerator) to the purely hydrocarbon phase of the reactor. The need to use large quantities of steam at high temperatures explains the constant efforts made to improve the thermal stability and the stability to water of zeolite catalysts.

The heat required for the process decreases as a function of the degree of conversion since at low conversion rates strongly endothermic reactions involving the rupture of the C—C bond predominate, whereas at high conversion rates, exothermic condensation and polymerization reactions become significant.

The combustion temperature needed to regenerate the catalyst is usually 100-200°C higher than that of the cracking process.

Depending on the conditions, especially as a function of the excess of air, combustion may be more or less complete, with the formation of CO₂ or CO; combustion to CO allows for a better control of temperature, but makes it essential to install a system (CO boiler) for the subsequent oxidation of CO to CO₂.

In addition to the deposition of coke (reversible deactivation), the catalyst is also poisoned by the deposition of metals and basic compounds; it also undergoes mechanical erosion and the alteration of porosity. Some of it is therefore continuously purged, with the addition of fresh catalyst.

There are various versions of the cracking process, which differ in terms of the relative positions of the reactor and the regenerator, and their shape.

These technologies have always evolved constantly, starting from the installation of the first FCC unit in 1942 in Baton Rouge (Louisiana, USA).

Historically, the pioneers of these processes include Standard Oil (later Esso and then Exxon Mobil), which through a series of developments created the well-known Model IV in 1952, and then the various versions of Flexicracking; this group also includes UOP (Universal Oil Products), which as early as 1945 introduced the version with a reactor and regenerator side by side, and which currently also offers processes for residues and for deep conversion (see Chapter 7.2).

Fig. 9 shows a diagram of Esso’s Model IV, the first to introduce ‘U’ piping for the transfer of the catalyst. Weighed down by the coke, the spent catalyst falls towards the bottom of the reactor where it is stripped

**Fig. 9.** The historic Model IV FCC by Esso.
with steam and then transported to the regenerator. From the regenerator, the regenerated (lighter) catalyst is separated by ‘skimming’ from above and sent back to the reactor, whose temperature is regulated by the flow rate of the hot catalyst. This movement is facilitated by maintaining a slight pressure difference between the reactor and regenerator, and by varying the intake of air into the piping leading back into the regenerator (increasing the amount of air decreases the density, thus slowing the circulation of the catalyst). The two-stage cyclones on the regenerator and reactor cycle have the function of capturing the particles of catalyst entrained in the effluent vapours and gases; the diagram shows only one, but in fact there are at least six or eight.

In the later Flexicracking process, introduced in 1979, Exxon positioned the ‘reactor’ above the regenerator, with an external vertical riser (riser reactor).

**Fig. 10** shows a classic scheme by Kellogg (Orthoflow F) equipped with two regeneration zones and an external tubular reactor. As said earlier, the introduction in the 1960s of far more active catalysts led to the elimination of the catalytic bed, since the reactions took place already in the piping (riser). The various riser cracking technologies differ in terms of the shape and positioning of the riser (outside or inside the regenerator).

If the system is fed with particularly heavy feedstocks, an exchanger to recover heat from the fluid catalyst may be included.

The circulation of the catalyst is controlled by special valves linked to the temperature control system. Worth noting, again in Fig. 10, is the connector at right angles on the upper part of the riser, equipped with a ‘cap’, which can be easily replaced since it is subjected to the erosion caused by the catalyst. It should be remembered that these plants, since they must operate at high temperatures, are protected internally by fire-proof materials, which are easily eroded.

Other companies, in addition to those named above, have developed viable cracking processes; these include Stone & Webster, the Institute Français du Pétrole (Axens), and Shell (Shell Global Solutions).

The times required for the various phases in a typical process are roughly as follows:

- Residence time of the catalyst: in the riser <3 s; in the stripper ≤2 min; in the regenerator 6-10 min.
- Residence time of the hydrocarbons in the riser <1.5 s.

The most recent developments of the process have aimed at reducing the contact time between catalyst and hydrocarbon vapours, in order to limit non-selective *post-riser cracking*; this can be done by separating the vapours from the catalyst with the installation of ‘prestripping’ cyclones at the exit from the riser reactor (McAuley and Dries, 2001). This expedient leads to higher yields, lower $\Delta$coke and cracking which is more selective for gasolines and light olefins.

The coexistence of a combustion phase and a phase consisting of hydrocarbon vapours, where the only barrier is represented by the steam strippers and the catalyst transfer piping, makes the whole process extremely delicate; the instrumentation and safety systems must therefore be adequate.

The effluent from the cracking reactor contains a wide range of products (*Table 6*); therefore, it must be fractionated in a plant with characteristics similar to
those of the topping column (see Chapter 2.2), with the difference that the feed is not a liquid-vapour mixture, but a superheated vapour, which must therefore be cooled rather than heated as in topping. Some of the residue and the heavy distillate from the main distillation column is usually recycled to the reactor to increase conversion yields.

The cracking of residues

Although many normal FCC units are often partially fed with residues, the direct cracking of residues is possible only in purposely-designed units, and when the content of metals (especially Ni and V) and Conradson carbon does not exceed specific values (e.g. 30 ppm and 5-10% in weight, respectively). Feedstocks that are especially rich in these components must first be hydrogenated (hydrocracking/hydrofining).

The units for treating residues are equipped with special exchangers to cool the catalyst; these exchangers must be able to work in a particularly erosive environment. The high C/H ratio of the feedstock leads to the production of larger amounts of coke on the catalyst and, consequently, to an increased production of heat in the regenerator.

The feedstock injection systems must also be appropriate, as must the types of catalysts, particularly ‘robust’ with respect to contaminants and capable of pretreating large-sized molecules in the matrix.

UOP’s MSCC process (MilliSecond Catalytic Cracking) involves charging the feedstock perpendicularly to the descending flow of the catalyst (Fig. 11). The reaction products and the catalyst are transported horizontally through the reaction zone towards the separator. The riser reactor is thus also eliminated (see Section 6.1.2).

Other techniques have been developed (for example, by IFP-SWEC-Total) based on the regeneration of the catalyst in two separate stages (Bonifay and Marcilly, 2001). In the first stage, 60-70% of the coke is burned at low temperature in a deficiency of air to give CO; in the second stage, the combustion of the remaining coke is completed in an excess of air. The gases rich in CO from the first stage must be sent to a boiler (CO boiler) in which high-pressure steam is generated. The CO boiler is also characteristic of other FCC processes.
which are not necessarily devoted to residues; the combustion of CO makes it possible to work at lower temperatures in the regenerator, to the benefit of catalyst life and of safety. However, the investments required for the unit are higher.

**Deep conversion processes**

Adopting more severe operating conditions (high conversion temperatures with low contact times and low partial pressures) and the use of shape-selective catalysts allow the process to produce larger quantities of olefins, when these are required by specific market conditions. The early years of the Third millennium, like those immediately preceding it, have seen a strong increase in the consumption of propylene for the production of polypropylene, an extremely versatile polymer with one of the highest growth rates. Propylene is also supplied by thermic cracking plants, whose principal product is ethylene (see Chapter 10.5).

Estimates made at the beginning of this millennium attributed about 30% of the worldwide production of propylene to catalytic cracking processes. However, since refineries were not yet well integrated with petrochemical plants, only about 50% of the propylene made in refineries was used for petrochemical productions. Over the years, the FCC process has revealed itself to be extremely flexible; although it is aimed mainly at the production of gasolines, the process has frequently been managed in order to maximize other products, such as LPG and olefins. In the immediate future, the FCC process is likely to play a greater role in petrochemical productions, at the expense of the production of gasoline.

Specially designed Deep Catalytic Cracking (DCC) units may, if fed with paraffinic feedstocks, supply over 25% in weight of propylene. The Stone & Webster/Sinpec unit can operate so as to maximize propylene or iso-olefin yields (Refining […], 2002). UOP’s Petro FCC unit is described in Section 6.1.2.

The layout of a DCC unit is essentially similar to that of a conventional FCC with a riser reactor. Aside from the catalyst, the differences concern the choice of operating variables, the severity and the design of the gas plant. Table 6 compares the typical yields of a DCC plant with those of an FCC unit.

**Operating variables**

Before examining the impact of the main operating variables on the cracking process, it is worth reviewing the concepts of conversion and recycling.

In general, it is assumed that all products with a molecular weight similar to the feedstock have not undergone conversion. Traditionally, all products that boil above 220°C are considered heavy fractions; this temperature can be considered the end boiling point of gasoline. Conversion can thus be defined as follows:

\[
C\% = 100(1 - \frac{Q_{pes}}{Q_{alim}})
\]

where \(Q_{pes}\) and \(Q_{alim}\) are the volume flow rates of heavy products and the liquid feedstock respectively.

The products are classified as dry gases, Liquefied Petroleum Gas or LPG (\(C_1\) and \(C_2\)), gasoline, light cycle oil (LGO, Light Cycle Gas Oil), heavy cycle oil (HCGO, Heavy Coker Gas Oil), residue (decant oil) and coke.

Decant oil, sometimes considered alongside HCGO, is highly aromatic and suitable for producing black carbon.

If conversion is too high (>76-81%, depending on the type of feedstock) some of the gasoline produced is transformed into lighter products and coke by secondary cracking reactions, with a consequent decrease in gasoline yields.

Conversion is influenced by: a) the type of feed; b) the activity of the catalyst; c) the amount of coke on the regenerated catalyst \(\Delta \alpha_{cok}\); d) the reaction temperature; e) the flow rate of the combined feed; f) the oil/catalyst ratio; g) the nebulization vapour of the feedstock.

The oils (LGO and HCGO) obtained from cracking are fairly resistant to subsequent conversions due to their prevalently aromatic nature; however, if partially recycled to the reactor, they produce an additional quantity of gasoline, increasing yields as compared with a process without recycling.

The recycling ratio \(R\) is defined by the ratio of cycle oil to fresh feed \((R = \frac{Q_{ric}}{Q_{alim}})\); the total volume fed to the reactor is thus \(Q_{alim} + Q_{ric}\).

An example will help to clarify the concept of recycling. Suppose that 100 m³/h of liquid feedstock is sent to the reactor, with a conversion of 60% without recycling; thus, remembering the conversion equation, 40 m³/h of non-converted oil is obtained. If 20 m³/h of non-converted residual oil is recycled to the reactor, the feed to the reactor must be lowered to 80 m³/h, and the recycling ratio will be 25%. Suppose, for the sake of simplicity, that conversion is identical for the fresh feedstock and for the cycle oil (although in practice this is not the case) and remembering that recycling is a closed loop inside the reaction section, the net production of heavy oil exiting the bottom of the column will be 20 m³/h rather than 40 m³/h, and conversion will thus rise to 75% rather than 60%, since \(C = 100\left[1 - \left(\frac{20}{80}\right)\right] = 75\%\).

Even assuming that the cracking of the cycle oil is half that of the fresh feedstock, the increase in conversion \((15/2 = 7.5\%)\) is still significant.
The main variables of catalytic cracking that influence conversion are the quality of the feedstock, the temperature of the reactor, the pressure of the reactor, the space velocity, the catalyst/oil ratio and the rate of recycling.

The main variables of the regenerator are the flow rate of air, the temperature and the pressure difference from the reactor. The entire process is also affected by the coke balance.

**Quality of the feedstock**

As already noted, cracking feedstocks containing mostly aliphatic and naphthenic hydrocarbons is much easier and more selective than cracking aromatic feedstocks. Within an individual class of compounds, the greater or lesser predisposition towards cracking depends on molecular weight: high boiling paraffins are the easiest to treat; cycle oils, rich in polyaromatics, give low gasoline yields, even though they are high boiling fractions. Olefins promote the formation of coke and aromatics act as precursors. Sulphur and nitrogen compounds are partially decomposed with the production of H₂S and NH₃; the gasolines and gas oils obtained must nevertheless be desulphurized with subsequent treatments. Ammonia tends to neutralize the acidity of the catalyst. High sulphur contents increase SO₂ emissions during regeneration.

Organometallic compounds tend to release heavy metals (V, Ni, Fe) under cracking conditions, depositing them on the catalyst and reducing its activity; they (especially nickel) may also trigger dehydrogenation reactions, leading to a higher production of light products and coke. Vanadium also causes sintering phenomena. The difficulty of treating residues results from their high metal contents.

Other problems linked to the treatment of residues include: the high concentration of asphaltenic compounds that deactivate the catalyst too quickly (due to the formation of coke); the presence of alkaline metals, such as Na and K, which permanently neutralize the acid sites of the zeolite; and the fact that a large proportion of the feed does not vaporize under normal cracking conditions. If these residues derive from hydrotreating processes (such as hydrocracking), these problems are significantly reduced.

**Temperature of the reactor**

The feed is preheated to 300-400°C to vaporize as large a quantity as possible and to lower the catalyst/oil ratio. The cracking temperature usually ranges from 480 to 550°C; this influences the reaction velocity, which almost doubles every 80°C. Increasing the temperature thus increases conversion, and therefore the amount of gasoline, gas, LPG and coke. Above a given conversion level, the gasoline yield decreases and its octane number increases, due to the higher olefins and aromatics content.

The temperature is defined by the enthalpic content of the combined feed and the amount of hot catalyst in the riser; it is varied by regulating the intake of catalyst. The temperature is the most important variable since this controls the progress of the process and the thermal balance between reactor and regenerator.

**Pressure of the reactor**

The total pressure of the process is only slightly above atmospheric pressure; the regenerator is generally at a higher pressure than the reactor. In the usual interval of values (1.5-3.5 bar), the effect of the partial pressure of the vaporized hydrocarbon feedstock on conversion and selectivity is extremely small.

An increase in pressure leads to a decrease in the octave number, given the lower production of olefins; at low-pressure values, a modest increase encourages the contact between oil and catalyst, as well as conversion and the formation of coke.

**Space velocity**

The space velocity in itself is not particularly significant; it varies even if the flow rate of the feed (understood as the sum of fresh feed and cycle oil) remains constant, since the amount of catalyst in the reactor may vary. In any case, it must be expressed in terms of weight and not volume (Weight Hourly Space Velocity, WHSV) given the variability of the volume of catalyst in the fluid phase: \( \text{WHSV} = \frac{\text{weight of feed}}{\text{weight of catalyst in the reactor}} \).

The circulation of the catalyst may be varied by increasing or decreasing the pressure in the regenerator.

Experience has shown that the best results using modern catalysts are obtained with extremely short contact times: a very few seconds (or fractions of a second) in the riser are sufficient to convert almost totally the non-aromatic portion of the feed. With short contact times, gasoline yields increase, limiting secondary cracking phenomena (overcracking); the formation of coke is also decreased.

**Catalyst/oil ratio**

This is defined as the ratio of the unit weight flow-rate of the circulating catalyst to the weight flow-rate of the feedstock to the reactor.

The amount of catalyst in circulation depends on the thermal balance of the reaction section. At constant temperature, any variation in the temperature of the feed leads to a variation in the catalyst/oil ratio. If the
temperature of the feedstock is low, the ratio increases but vaporization worsens; if the temperature of the feedstock is too high, the ratio decreases, with a consequent decrease in cracking reactions.

A variation in the temperature of the regenerated catalyst also leads to changes in the catalyst/oil ratio: if it decreases, the ratio increases to maintain the reactor at the predetermined temperature. An increase in the catalyst/oil ratio, given an identical reaction temperature, leads to an increase in conversion, coke and aromatics.

Recycle rate

An increase in the recycle rate causes a decrease in the residual oil from the plant and an increased deposition of coke; as a consequence, the temperature of the regenerator increases and the circulation of the catalyst decreases. The amount of oil to be recycled depends on the working conditions: the more severe these are, the smaller the amount of oil to be recycled.

Before the advent of zeolite catalysts, high recycling ratios were adopted to compensate for the low selectivity of the catalyst.

Temperature of the regenerator

Generally speaking, the temperature of the regenerator (700-750°C) is not controlled directly, but depends on the conditions in the reactor, the quality of the feedstock and the amount of air. The upper temperature limit depends on the thermal resistance of the catalysts and the materials used in the regenerator.

The heavier the feedstock, the greater the production of coke, with the consequent increased development of heat during regeneration; the amount of catalyst needed in the reactor is thus lowered; the lower circulation of catalyst limits conversion.

Low temperatures due to a lower coke content, by contrast, increase the amount of circulating catalyst.

References


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6.1.2 Industrial technologies

UOP Fluid Catalytic Cracking (FCC) and related processes

The UOP (Universal Oil Products) licensed catalytic cracking processes include the Fluid Catalytic Cracking (FCC) process, the Resid FCC (RFCC) process, the MilliSecond Catalytic Cracking (MSCC) and the PetroFCC process. The above processes convert gas oil and heavier streams into lighter, more valuable products via high-temperature catalytic cracking. A fluidized catalyst system is used to facilitate catalyst and heat transfer between the reactor and regenerator. The system is heat-balanced: the combustion of coke in the regenerator provides all of the heat necessary for the reactor. The main products from the processes include:

a) light gas: primarily H₂, C₁, and C₂s (normally an undesirable by-product of thermal cracking), where ‘s’ means saturated hydrocarbon;

b) LPG (Liquefied Petroleum Gas): C₃s and C₄s, including light olefins valuable for alkylation or petrochemical production (the PetroFCC process targets maximum light olefin production);

c) gasoline: C₅/₁₁₀₀ high octane component for gasoline pool or light fuel;

d) LCO (Light-Cycle Oil): light-cycle oil blend component for diesel pool or light fuel;

e) HCO (Heavy-Cycle Oil): optional heavy-cycle oil product for fuel oil or cutter stock;

f) CLO (Clarified Oil): clarified oil or slurry for fuel oil (potential carbon black feedstock);

g) coke: by-product consumed in the regenerator to provide reactor heat demand.

Based on conventional and proven technology, the FCC process features Optimix feed distributors, the Vortex Separation System (VSS) riser termination device, AF-spent-catalyst-stripping technology and a combustor style regenerator. Catalyst coolers, the RxCat technology and selective recycle can be added to increase flexibility for feed and product demands.

The feedstock to the FCC unit is typically VGO (Vacuum Gas Oil), but can also include many other heavy streams, such as straight run gas oil, coker gas oil, hydrocracked gas oil and deasphalted or demetallized oil. Some residuum can be fed, up to 4 wt% Conradson carbon.

The RFCC process uses similar reactor technology as the FCC process and is targeted for residual feeds containing over 4 wt% of Conradson carbon. A two-stage regenerator with catalyst cooling is typically used to control the higher coke production and resulting heat.

Mechanically similar to a conventional FCC, the PetroFCC process incorporates additional reaction severity along with the RxCat technology, Optimix feed distribution, AF spent catalyst stripping technology and VSS technology to enhance light olefin and/or aromatics production. Depending on the feedstock, propylene yields of 20-25 wt% are possible; paraffinic feed stocks and hydrocracked gas oils facilitate light olefin selectivity.

Developed by BARCO and licensed exclusively by UOP, the MSCC process reactor technology utilizes an ultra-short contact time in a proprietary design contact zone, without the use of a conventional reactor riser. It can be applied to all feeds, but its advantages grow when resid feeds are being processed.

The FCC processes

Feed distribution system

The cracking process starts with the injection of feed to the riser. Radially installed Optimix distributors are an integral part of UOP’s feed distribution system. Unlike other systems still using dense-phase feed injection, one of the features that differentiates the Optimix feed distribution system is the acceleration zone below the Optimix distributors produces a moderate catalyst density to achieve good penetration and mixing of the atomized feed spray. Other benefits of the Optimix feed distribution system include reduced dry gas and Δ_coke (delta coke, see Section 6.1.1) as well as increased gasoline yield.

The newest generation of Optimix feed distributors allows for the processing of VGO quality feeds with a reduction in steam consumption of 50% or more, compared with previous generations of feed distributors.
In every case, regardless of the feed quality or processing severity, a uniform and controlled catalyst environment and proper feed distribution are key factors for good mixing and quick vapourization of the raw oil feed in the FCC reactor riser. For this reason, UOP’s feed distribution technology is focused on both the catalyst environment into which the feed is injected and the feed distributor itself. UOP’s catalyst acceleration zone at the base of the reactor riser establishes a uniform catalyst environment of moderate velocity and density prior to feed injection. Optimix feed distributors, the heart of the UOP feed system, are used to atomize the feed and inject it into the conditioned catalyst in the reactor riser.

The base of the riser, commonly referred to as the wye section, is a very turbulent zone where the flow of regenerated catalyst changes direction and moves up the riser. It is important that the catalyst moves evenly up the riser prior to feed injection in order to minimize backmixing and the inefficient contact of the feed and catalyst. UOP’s feed distribution system injects either steam and/or dry gas at the base of the wye to accelerate the catalyst to a moderate velocity and to achieve an even, plug-flow catalyst distribution at a moderate density. This uniform and moderate density enhances penetration and quick vapourisation of the feed. Commercial unit performance testing has confirmed the benefits of the acceleration zone, with conversions over 80% by volume and naphtha yields over 66% by volume.

During testing, gamma scans were used to measure the resulting catalyst density profiles through the acceleration zone and up beyond the feed injection point. The catalyst density in the acceleration zone can vary between 15 and 20 lb/ft³, depending on the amount of acceleration media used. Within 1.5 ft diameters downstream of the feed injection point, the density decreases to approximately 5 lb/ft³. This confirms that the feed is vapourized very rapidly and efficiently by the moderate density catalyst phase. Density maps also show that the Optimix feed distribution system facilitates an even plug-flow regime in the riser both before and after the feed injection point.

The Optimix feed distributor is a sophisticated mechanical device that efficiently atomizes the raw-oil feed. Only a small amount of steam (0.5–3.0 wt% based on fresh feed) is required for good atomization and distribution of the feed through the use of an innovative three-stage atomization technique. One of the most important features of the Optimix feed distributor is that atomization occurs close to the distributor’s tip and prevents drop coalescing and pulsating flow.

The Optimix feed distributor tip generates a uniform, flat, fan spray pattern. This flat spray pattern is generated using a series of special orifices. These orifices (instead of larger slots) are designed and oriented to create the flat fan for each installation based on the feed quality, feed rate and riser dimensions. The spray pattern of the Optimix feed distributor generates a very uniform spray, containing small oil droplets with a narrow range of droplet sizes. The Optimix feed distributor generates a controlled spray angle, even at 50% turndown, to provide complete coverage of the reactor riser’s cross sectional area. In the vertical direction, the flat fan pattern remains thin, facilitating quick and uniform feed vapourization for superior yields and selectivity. Each Optimix feed distributor is individually designed and tested for each specific installation. This allows UOP to design the distributors in order to provide full riser coverage at moderate pressure drop and exit velocities, which avoids catalyst attrition and riser erosion problems. It also allows the maximum reuse of existing feed system equipment.

Maintenance and inspection requirements of the Optimix feed distributors are nearly non-existent. The Optimix feed distributor’s tip is of cast material, which provides improved resistance to erosion. In addition, UOP uses Dur-O-Lok couplings to facilitate easy replacement of the internal and external components, should the refiner’s processing objectives or operating capacity change substantially.

Separation technology (VSS and VDS)

The patented Vortex Separation System (VSS) for internal riser reactors and the Vortex Disengager Stripper (VDS) for external riser reactors represent state-of-the-art riser termination technology. Both systems have critical pre-stripping features and offer the highest post-riser hydrocarbon containment available in the industry. These systems capture the vapour-catalyst mixture at the outlet of the riser and efficiently separate the catalyst without allowing the vapour to enter the reactor vessel. The vapour stream is fed into cyclones for final clean up. Over 99.5% of the vapours pass through the disengager/cyclone system without entering the reactor. In this way, post-riser
cracking is virtually eliminated, resulting in an improved product distribution. Benefits include reduced dry gas, reduced Δ_coke, increased olefinicity, increased gasoline yield and reduced clarified oil yield.

UOP’s Vortex separation technology is the latest in a long line of fluid catalytic cracking riser termination improvements for more effective separation of the catalyst and hydrocarbon phases in the FCC reactor. UOP offers two options: the VDS design and the VSS design.

No riser termination device contains 100% of the hydrocarbon vapours flowing to it. Containment refers to the amount of hydrocarbon vapour that exits the primary separation device without spending time in the reactor vessel. In all systems, the catalyst flows into a primary separation device, either cyclonic or inertial. Most of the captured vapours quickly pass out of the device and into downstream, secondary cyclones. As a rule, fluidizing gas must be entrained in the catalyst stream exiting the primary separation device. These vapours escape into the reactor/stripper vessel. In the dilute phase of the reactor, the hydrocarbon vapours spend an extended period in the presence of catalyst and high temperature. Overcracking of this hydrocarbon vapour leads to higher dry gas production and loss of selectivity.

UOP’s Vortex separation technology minimizes the vapour passing into the reactor vessel to provide the greatest reaction selectivities. In other words, this technology maximizes hydrocarbon containment, which can exceed 99%. In addition to achieving rapid separation and high containment, UOP’s Vortex separation technology also provides a termination device that is flexible to operational changes and tolerant in upset conditions.

In direct-connected cyclones and other cyclonic separation systems, considerable hydrocarbon vapours escape the cyclone environment and enter the reactor vessel. The gas that keeps the catalyst fluidized travels down the cyclone diplegs with the catalyst. Since almost the entire catalyst circulation travels through the primary cyclone diplegs, the gas phase carried with it can amount to 5-6 wt% of the feed. As a result, a cyclonic system without pre-stripping can achieve only 94-95% hydrocarbon containment at best. When released into the stripper or reactor vessel, the remaining hydrocarbon content can spend 30 seconds or more in direct contact with hot, active catalyst. A substantial amount of this material eventually leaves the reactor as light ends, condensed ring aromatics and coke on the catalyst.

To capture and recover the useful products in this hydrocarbon stream and prevent overcracking, some form of pre-stripping of the catalyst is needed before it discharges into the reactor. To strip flowing catalyst effectively, the downward velocity of the catalyst must be less than the bubble rise velocity within the fluidized catalyst phase. The velocity difference is necessary so that the hydrocarbon gas phase can rise out of the catalyst phase and be removed quickly from the system. To minimize the stripping diluent (in most cases, steam), a dense phase of catalyst is desirable. A dense catalyst phase also reduces interstitial volume by effectively ‘squeezing’ gas from the catalyst. UOP’s efforts were focused on converting the catalyst stream, flowing down the dipleg, into a slower moving dense phase so that the pre-stripping step could be accomplished. These efforts resulted in the Vortex separation technology.

The first commercial application of Vortex separation technology suited smaller stacked reactor systems that are easily revamped to an external riser. This design is known as the VDS design. A single VDS system is fitted at the end of an external side-entry riser. Although the VDS system uses the same principles of centrifugal separation as a cyclone, it functions somewhat differently and has a special section at the base to slow catalyst flow and form a dense phase. Stripping steam is injected at the base of this chamber, below the dense phase of catalyst. The stripped hydrocarbons rise up into the disengager and exit through the gas tube with the rest of the vapour phase. A set of secondary cyclones is connected to the vapour outlet to complete the catalyst separation.

In the VSS design, the catalyst-vapour mixture travels up the reactor riser through the center of the chamber and exits through special disengaging arms. These arms generate a centrifugal flow pattern that separates the catalyst from the vapour inside the chamber. The flow mechanism is similar to that of traditional cyclone inlet horns. The catalyst falls and forms a dense phase at the base of the chamber, where it is pre-stripped prior to flowing into the reactor stripper. The stripped hydrocarbon vapours are fully contained in the chamber and exit with the rest of the riser effluent vapours to the secondary
cyclones. The only hydrocarbon lost to the reactor vessel is that which accompanies the small amount of catalyst disengaged by the cyclones. In both the VSS and VDS systems, hydrocarbon rising from the stripper vessel is captured in the chamber and is prevented from spending excessive time in the surrounding reactor space. The overall hydrocarbon containment for this system exceeds 99%.

Compared to other riser termination systems offered today, the VSS and VDS systems reduce the potential for non-selective post-riser cracking. The calculated post-riser residence time of the hydrocarbon phase within the chamber is less than one second. By creating a dense phase of catalyst and stripping it within the primary separation device, the hydrocarbon ‘leaking’ into the reactor vessel is minimized. In comparison, the dilute phase stripping of other systems is flawed because the interstitial volume is difficult to displace (i.e. the catalyst downward velocity exceeds the stripping bubble rise velocity). UOP’s Vortex separation technology has successfully overcome the shortcomings of earlier systems, while maintaining operating flexibility.

For larger units and units with internal risers, the VDS design has some mechanical drawbacks. For these layouts, UOP developed the VSS design. The VSS design retains hydrocarbon containment and pre-stripping characteristics of the VDS system; it is compact to fit into the widest possible range of reactor styles and sizes and has a lower investment cost than the VDS system.

**Spent-catalyst-stripper**

UOP’s riser termination systems incorporate a pre-stripping zone. The design achieves superior contacting and stripping efficiency. Vapours from the stripper enter the riser termination device and do not spend any time inside of the reactor vessel. A combination of pre-stripping and primary zone stripping, with due attention to catalyst residence time, provides the best possible catalyst stripping. UOP’s AF (Advanced Fluidization) stripping technology has resulted in increased hydrocarbon displacement efficiency, even at very high catalyst flux rates (over 120,000 lb/h/ft²).

Many of today’s state-of-the-art FCC units utilize UOP’s advanced technologies, such as Optimix feed distributors and VSS riser termination devices. An outcome of the enhanced catalytic cracking from these technologies is increased catalyst circulation. As a result, the spent-catalyst-stripper frequently operates well above the original catalyst flux design value, which can compromise hydrocarbon displacement efficiency and unit performance. AFspentcatalyststripping technology was developed not only to improve the FCC unit yield performance, but also its catalyst circulation (hydraulic) performance.

The spentcatalyststripper is a very important element of the FCC unit. Its duty is to strip the entrained and adsorbed hydrocarbons from the spent catalyst before it enters the regenerator vessel. These hydrocarbons are commonly referred to as coke on catalyst. In general, four different types of coke can be associated with the spent catalyst: catalytic coke, contaminant coke, additive coke and cat-to-oil coke. Catalytic, contaminant and additive coke are functions of the feed quality, catalyst type, and operating severity, and do not present much improvement opportunity for the catalyst stripper. However, cat-to-oil coke is entrained, strippable hydrocarbon, which is directly linked to the catalyst circulation rate. This type of coke is strongly impacted by the stripper performance.

AF stripper technology was developed during a three-year optimization program that included computational fluid dynamic modelling and extensive cold flow modelling work. The cold flow modelling effort tested numerous commercial and experimental tray designs at a wide range of fluxes (up to 140,000 lb/h/ft²), and a wide range of stripping media rates. These efforts made it quite clear that optimal stripper performance is a result of proper control of the stripping media to ensure maximum use of the stripper’s cross sectional area.

The outcome of this optimization program was the AF stripper tray, grid, and packing technology. All styles bring improved performance by creating a superior fluidization and contacting regime throughout the entire stripper vessel (Fig. 1).

**Catalyst cooler**

Catalyst coolers are relatively easy to add to all styles of regenerators. The dense-phase, low-velocity shell-and-tubetype cooler was pioneered by UOP in the 1980s for operation on heavy feeds, where high Δ_T,reg would cause excessive regenerator temperatures. The UOP catalyst cooler uses bayonet-style tubes and generates medium- or high-pressure saturated steam. Benefits include reduced regenerated
catalyst temperature, higher catalyst/oil ratio, the ability to process heavy feeds and better yields.

Many refiners are choosing to process lower cost, residual feed stock components in their FCC units. The conversion of these heavier feeds to lighter, more valuable products results in a higher operating temperature in the regenerator. Removing this heat not only retains the catalyst’s effectiveness, but also increases the catalyst/oil ratio for better yields, improved product selectivity and enhanced profitability.

The key features of the UOP catalyst cooler include the following:

- Vertical heat transfer surface provides uniform heat transfer and catalyst contact with the tube bundle, and reduces localized stresses resulting from uneven temperature distributions.
- Variable heat-removal capacity facilitates FCC unit operation when raising the temperature of the reactor and regenerator during start-ups. When necessary, the cooler can even be shut down and effectively isolated while the FCC unit continues to operate.
- Mechanical reliability is achieved through dense-phase operation with low catalyst velocity to reduce erosion.
- The cooler shell is separate from the regenerator vessel, which provides ultimate revamp flexibility plus easy, quick cooler maintenance or bundle replacement during turnarounds.

Three different styles of catalyst coolers (flow-through, back-mix and hybrid) have been designed and commercialized to accommodate a wide range of heat removal duties as well as physical and plot space constraints.

The UOP FCC catalyst cooler (Fig. 2) is an external vertical shell-and-tube heat exchanger. The catalyst flows over the entire cross sectional area of the tube bundle in the dense phase. UOP’s air lance distribution system ensures uniform air distribution within the tube bundle and a uniform heat transfer coefficient. The generation of steam (up to 850 psi) from the circulating water is used to remove heat from the regenerated catalyst.

Three different styles of catalyst coolers

Fig. 1. Spent-catalyst-stripper with AF trays (courtesy of UOP).

Fig. 2. UOP FCC catalyst cooler.
All of these features provide a reliable and flexible operation to enhance profitability and deliver an attractive return on investment.

**Catalyst recycle (RxCat technology)**

Good catalyst circulation is a key factor in FCC unit reliability. An innovative technology is used to recycle carbonized catalyst back from the reactor to the feed contacting zone (Fig. 3), taking advantage of inherent activity of modern catalysts that are not really ‘spent’ when leaving the reactor. The result is a much higher catalyst/oil ratio than is possible via a heat balanced regenerator. RxCat is intended for existing low Δc operation, where cold regenerators can become a problem and for those operations where increased light olefin yield is desired. Regenerator temperature increases when the RxCat design is applied. Benefits include very low dry gas and improved overall yield selectivity. RxCat technology is an integral part of UOP’s PetroFCC process.

The recycled carbonized catalyst is mixed with the regenerated catalyst in a mixing vessel (M×R chamber) at the base of the riser. Since the recycle of this carbonized catalyst back to the riser is a heat balance neutral process, the catalyst circulation rate up the riser can be varied widely without increasing the coke yield. Essentially, RxCat technology breaks the link between catalyst circulation and coke yield. The result is a much higher catalyst/oil ratio than is possible via the normal heat balanced operation. The use of RxCat technology provides significant advantages:

- It allows much shorter contact times to be used, thereby reducing olefin oligimerization and hence olefin loss.
- It allows the reactor riser to operate with relatively cool inlet catalyst temperatures, as the regenerated catalyst is mixed with the cooler carbonized catalyst, while maintaining an elevated riser outlet temperature.
- It provides more catalytic reaction sites in the reaction zone. Practical benefits include: increased conversion, improved product selectivity (gasoline and propylene increase), reduced dry gas yield, increased throughput and process flexibility.

**Oil selective recycle**

Selective recycle is the application of once-through recycles of CLO, HCO, LCO or naphtha to reduce undesirable products and to improve yields in selective products. A separate reaction zone prevents products from commingling with riser effluent. Selective recycle is suitable for low-severity distillate operations. Benefits include improvement in selective yields (e.g. gasoline + LCO) and reduction in undesirable product (e.g. CLO in distillate operations).

**Combustor and regenerator**

Introduced in the late 1970s, UOP’s combustor regenerator uses a fast-fluidized combustion zone to achieve the best coke burning and full combustion of CO to CO₂. Benefits include full combustion without the use of a promotor, minimum afterburn, lowest carbon on regenerated catalyst, no possibility of spent catalyst bypassing the regeneration zone and lower catalyst inventory.

The two-stage regenerator is used in units where full combustion would result in excessive regenerator temperatures (e.g. RFCC). The upper regenerator (first stage) operates in partial combustion, while the lower regenerator (second stage) operates in full combustion, with flue gas and excess O₂ rising into the upper regenerator. The two-stage regenerator has only one flue gas line, which exits from the upper vessel. Catalyst cooler (or coolers) is included in the design for control of combustion heat. Benefits include clean catalyst from the second stage (less than 0.05% carbon on regenerated catalyst) and the
ability to process heavy and contaminated residues (up to 10 wt% Conradson carbon).

A power recovery system recovers usable energy (in the form of electricity from the regenerator flue gas) and typically uses it to drive the main air blower. Economic justification depends on local power costs. UOP’s Third Stage Separator (TSS) technology is employed to protect rotating equipment and reduce emissions.

**The PetroFCC process for petrochemical feedstock production**

The PetroFCC process targets the production of petrochemical feedstocks rather than fuel products. The new process, which utilizes a uniquely designed FCC unit, can produce very high yields of light olefins and aromatics when coupled with an aromatics complex (Fig. 4).

Driven by an increased demand for polyethylene and polypropylene, future demand is expected to increase for petrochemical feedstocks, particularly the light olefins and especially propylene. The additional propylene produced from the increase in steam-cracker ethylene production is expected to be insufficient to meet the demand, and thus propylene from other sources will be required. Although its principal function has been to produce gasoline, the FCC unit is frequently operated to maximize other products, such as distillates or LPG. The LPG mode can be considered a step towards a petrochemical mode of operation since it provides enhanced yields of the petrochemical feedstocks. However, to be considered a major component in the petrochemical complex, an FCC style unit must produce substantially greater quantities of these light olefins, produce other petrochemical feedstocks of interest, and minimize or eliminate the yield of gasoline and heavier liquid fuels. This is the targeted area for the PetroFCC process.

The PetroFCC process starts with a uniquely designed FCC unit and is capable of producing a product slate, in liquid volume, of 35% propylene, 12% ethylene, 20% butylenes, and 20% of benzene and paraxylene. This is a substantial increase in the yield of petrochemicals compared to a conventional FCC unit. The catalyst section of the PetroFCC process uses a high-conversion, short-contact time reaction zone that operates at elevated reactor riser outlet temperatures and low partial pressures. It also incorporates a relatively high level of a shape selective zeolite catalyst additive with selected standard FCC catalyst as the balance. The PetroFCC process incorporates Optimix feed distribution system, VSS Vortex separation technology, AF-spent-catalyst-

![](image)

**Fig. 4.** UOP’s PetroFCC complex. C₂, ethane; C₃, propane; C₄ = , ethylene; C₅ = , propylene.
stripping technology and RxCat technology to enhance light olefin and/or aromatics production. RxCat is a key differentiating technology of the PetroFCC process when compared to alternative technology.

The components of PetroFCC technology can also be applied to existing FCC units that process more conventional VGO-based feedstocks and desire incremental propylene yield improvement. The extent of this light olefin yield improvement is usually dependent on the limitations in the existing light ends recovery section of the FCC.

**Propylene recovery unit**

Propylene recovery from refinery streams is increasingly used to supply downstream users with polymer-grade propylene for petrochemical applications. To meet polymer-grade specifications, the stream must be concentrated to a minimum of 99.5% propylene and be essentially free of diolefins and acetylenic species. Incorporating proprietary UOP process equipment, UOP’s Propylene Recovery Unit (PRU) allows the refiner to recover polymer-grade propylene in the most economic manner available today (Fig. 5).

About 30% of world propylene production for the petrochemical industry currently is contained in FCC and RFCC by-product streams. The UOP PRU gives the refiner the opportunity to cost-effectively upgrade the low-value C₃/C₄ by-product to high-value polymer-grade propylene. Additionally, the PRU can be used to upgrade existing refinery-grade and chemical-grade propylene to polymer grade.

The PRU configuration depends on the feed expected to be processed in the unit. Assuming that the feed is the C₃/C₄ by-product from an FCC, the feed would first be depropanized and then de-ethanized. De-ethanizer overhead is typically sent to the refinery fuel gas system, while the destination of the depropanizer bottoms is refinery specific. The C₃ splitter then fractionates propane and propylene; propane is sent from the bottom of the column to storage, while the propylene is taken overhead and sent downstream for further processing. This is a difficult separation, historically requiring two towers to accommodate the high reflux and a large number of distillation trays. However, the PRU has three proven technological advantages that allow the fractionation to be accomplished in a single tower, significantly reducing capital investment:

- UOP’s MD (Multiple Downcomer) distillation trays, which can be installed with minimum tray spacing, enable the reduction of both tower height and diameter without sacrificing product purity.
- UOP’s High Flux tubing installed in the reboiler/condenser reduces the size of that exchanger by promoting greater heat transfer efficiency.
- A heat pump compressor system functions as both the reboiler and the condenser. This reduces the overall equipment count and significantly lowers the fractionation pressure.

The combination of these technologies results in the most economic separation of propylene from propane available.

If necessary, propylene is further processed to remove carbonyl sulphide (COS) in a solvent system. After drying in an adsorbent chamber, the propylene stream is treated to remove trace amounts of arsine, phosphate, and antimony (and other metals, if present). The resulting product meets industry specifications for polymer-grade propylene.

**The MilliSecond Catalytic Cracking (MSCC) process**

Catalytic cracking continues to be the cornerstone of most petroleum refineries. It has proven to be one of the most efficient processes available for the conversion of gas oils and residue into lighter, more valuable hydrocarbons. Recent developments in the FCC unit design have focused on reducing the contact time between the catalyst and the hydrocarbon vapour. Improvements in riser termination devices have led to significant decreases in post-riser residence time and post-riser cracking. The benefits of shorter catalyst and oil contact times have been lower dry gas yields, lower Δ_{copol} on catalyst and more selective cracking to gasoline and light olefins. An innovative reaction system has been developed to extend the capabilities of short contact time by eliminating the reactor riser altogether. The MSCC design has proved to be a robust and easy-to-operate system that can provide distinct yield and process advantages when compared to traditional FCC reactor systems.

The MSCC reactor design is a novel departure from traditional riser systems. In the MSCC, feed is injected perpendicular to a down-flowing curtain of catalyst (Fig. 6). Reaction products move across the reaction zone and are quickly separated from the catalyst in a primary separation device.
Following the primary separation device, the remaining catalyst is further separated in a single stage of external cyclones. The reactor vapours are then carried over to the main column section of the MSCC complex. The combination of rapid catalyst-vapour separation and a small-volume reaction zone allows to maximize catalytic reactions and minimize thermal reactions. This leads to a notable reduction in undesired secondary reactions and a more selective product slate. The MSCC process also incorporates a unique approach to spent catalyst stripping. Due to the position of the reactor relative to the regenerator, it is possible to take a stream of hot catalyst from the regenerator and inject it directly into the stripper. The hot catalyst acts to increase the stripper temperature and thus the stripping efficiency. The increased stripping efficiency leads to higher liquid volume recovery and lower hydrogen content in the coke. The result is a lower regenerator temperature and a higher catalyst/oil ratio.

With the incentive to process more residues in the FCC feed, refiners are being forced to operate their FCC units at a greater severity to maintain yields and conversion. However, this can have an adverse effect on the product selectivity: in fact, an increase in reaction severity of a riser FCC unit will concern all of the feed, including the material that is easily converted. The latter will have the tendency to overcrack and to produce dry gas and coke. The MSCC unit design makes it possible to utilize two reaction zones. The primary reaction zone, with its inherent short contacting time between the catalyst and the hydrocarbon, is the basis of the improved selectivity and lower $\Delta_{\text{coke}}$. The secondary reaction zone, which takes place in the more severe hot stripping section, provides the conversion of the more refractory components of the feed. This allows effective conversion of MSCC feed, while avoiding the potential for overcracking in a typical riser FCC unit running at high severity.

Fig. 5. UOP’s Propylene Recovery Unit (PRU).

Fig. 6. MSCC reactor.
The MSCC unit expands on the modern FCC unit’s ability to handle a variety of complex catalytic cracking reactions by further controlling hydrogen transfer and dehydrogenation. The increased control of these reactions is an important consideration since hydrogen transfer reduces the olefinicity of the LPG components (valuable alkylation and petrochemical feedstocks), while dehydrogenation allows heavier components to form coke on the catalyst.

**Bibliography**


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