

7

Industrial Catalytic Cracking

7.1 FEED SELECTION AND PRETREATMENT

Since the 1970s, the basic feedstock for catalytic cracking has been crude oil vacuum distillate. Depending on the conjuncture and market demands for fuel oils, visbreaking or coking distillate as well as deasphalted oil were also used as feed. In very rare cases a portion of the straight-run gas oil was included in the catalytic cracker feed.

The increase of the price of crude oil starting in the 1970s and the increase of gasoline consumption led to the trend of converting crude as completely as possible to motor fuels. Thus, residual fuel was replaced by natural gases, hydroelectric, and nuclear energy, and sometimes even with coal. This situation led to the extension and even the general use of catalytic cracking and to a significant increase in the amounts of vacuum residue processed by visbreaking and coking. Concomitantly important investments were made in hydrocracking units as tools for the complete conversion of vacuum residue into light products.

The situation changed fundamentally in the middle of the 1980s. The difference between the price of residual fuel and of gasoline, which was 125 \$/t at the beginning of the 1980s dropped within a few years to 20 \$/t. Concomitantly, the difference between the cost of the light and heavy crude oils decreased from 50–60 \$/t to 12 \$/t.

In these conditions the investments for new hydrocracking units became non-profitable and it became necessary to find other less expensive solutions for the complete conversion of residues to light products.

The solution adopted was to use as feed to the catalytic cracking units, straight run residue, initially as supplement to the traditional feeds and subsequently by itself.

The direct cracking of the straight run residue required the development of catalysts with adequate characteristics, and of units capable of burning the much larger amounts of coke which form now on the catalyst.

The use in catalytic cracking of the mentioned feeds accentuates the importance of ensuring the lowest possible concentrations of heavy metals, especially of Ni

and V, and of Conradson carbon, in order to make the process economically feasible.

The following sections will discuss the requirements set for the selection of the feed and the pretreatment processes used for obtaining raw materials of the specified quality.

7.1.1 Vacuum Distillation of Straight Run Residue

The two current trends, i.e., to produce vacuum cuts with 565°C end point, and to increase the production of heavy crude oils with high Conradson carbon values and high Ni and V concentrations, made it necessary to improve the vacuum distillation columns.

The procedures considered depend to a large extent on the characteristics of the processed crude oil. Thus, the process and constructive recommendations mostly refer to the processing of crude oils of a specified quality [1–3]. However, the reported information allows one to draw conclusions concerning recent developments and future trends.

The evaluation of the quality of a vacuum distillate intended as feed for catalytic cracking is made by using, besides the standard analyses and the true boiling points (TBP) curve, the distribution curves for Conradson carbon and the concentrations of nickel and vanadium. The curves showing the distribution of nickel for three typical crude oils, are shown in Figure 7.1 [2].

A detailed analysis of the effect of various process solutions on the quality of the vacuum distillate used as feed for catalytic cracking was made by S. W. Golden and G. R. Martin [1].

The main characteristics of the two vacuum columns used are represented in Figures 7.2a and 7.2b, in which the numbers of theoretical plates for each specific section of each column are indicated.

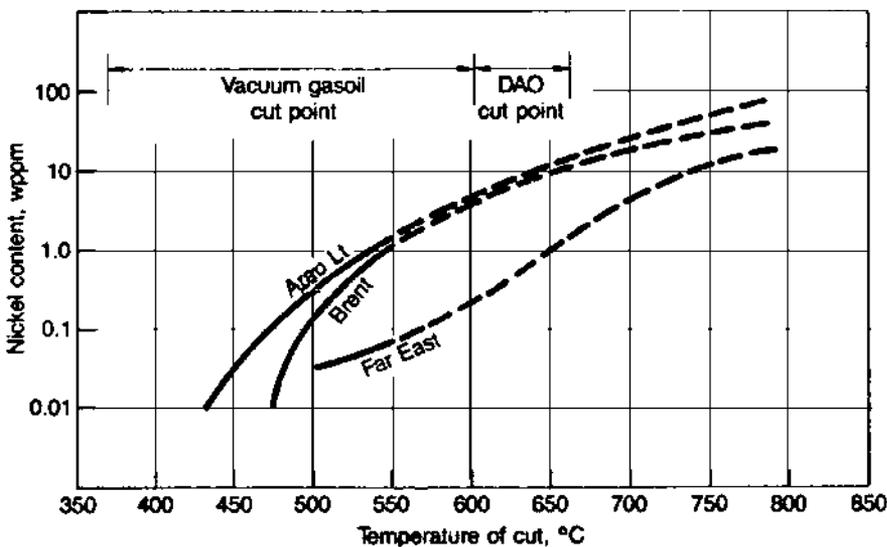


Figure 7.1 Nickel distribution for three representative crude oils. (From Ref. 2.)

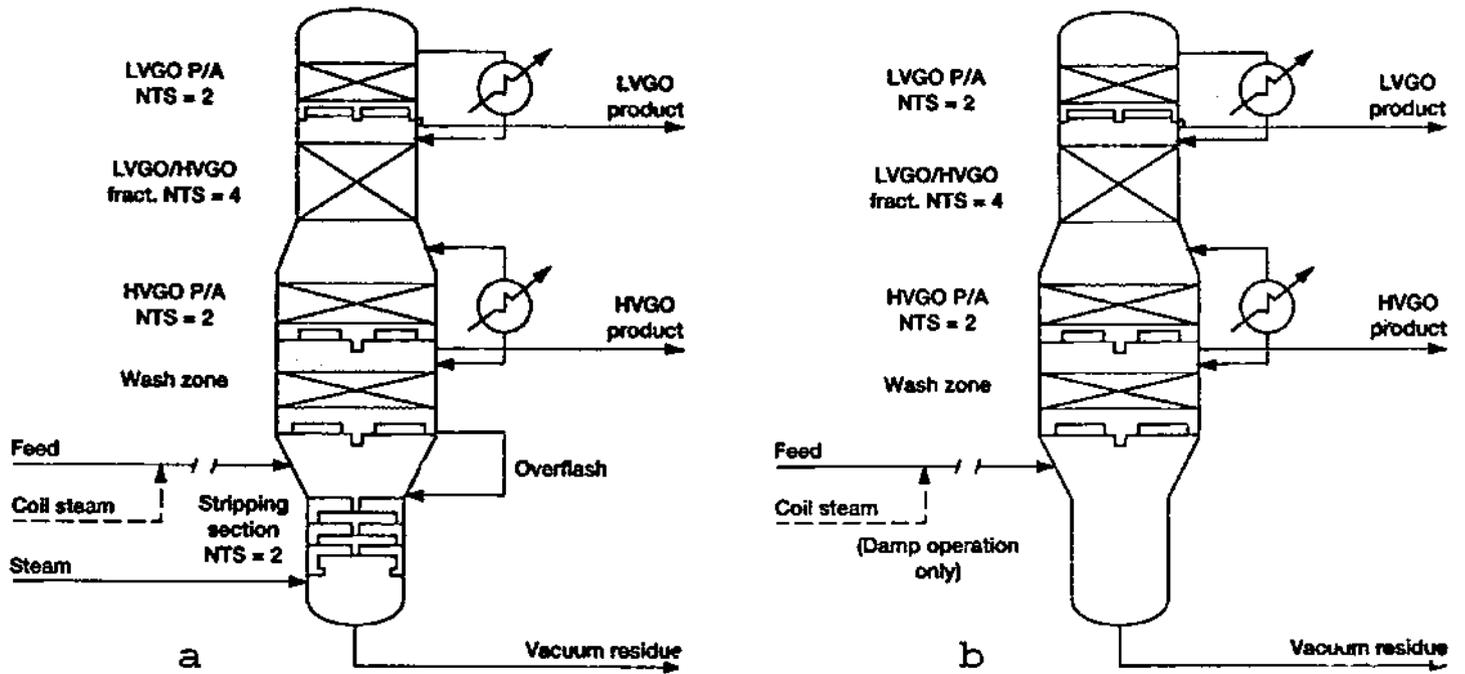


Figure 7.2 Typical vacuum columns configuration for catalytic cracking feed preparation. (a) Wet and damp (with stripping) operation mode. (b) Dry and damp (no stripping) operating mode. (From Ref. 1.)

The light distillate, obtained as the top product in the two columns, had in all cases an end point (TBP method) of 390°C and was used as component for the Diesel fuel. Only the heavy distillate obtained was used as feed for catalytic cracking.

For a feed having the characteristics:

Initial TBP	360°C
Density	0.9965
Molecular mass	505
Conradson carbon	8.3 wt %
Nickel	28 ppm

The feed was processed in four operating conditions reported in Table 7.1.

In all cases the feedrate used was 6.65 m³/s and the internal reflux in the separation section between the distillates, provided with 4 theoretical trays, was 0.98 m³/s. The recovered light distillate was 0.82 m³/s in all cases.

The concentrations of vanadium, nickel, and Conradson carbon of the heavy distillate destined to the catalytic cracking, depending on its final value for the four operating conditions, are plotted in the Figures 7.3a, b, and c.

The best results correspond to operating condition 4 and to an end point TBP of 569°C. The product obtained in these conditions was used in the studies that followed.

The variables were the number of theoretical trays in the stripping zone of the residue and the overflash in volume % of the feed. For three sets of operating conditions, the distillate with the end point of 569°C was redistilled and the content of metals and coke were plotted against the % distilled (see Figure 7.4a, b, c) [1].

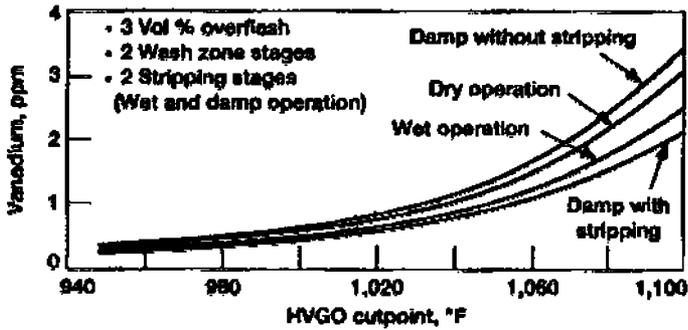
Attempts to reduce from 3 to 2 or to 1 the number of washing stages, keeping the overflash at 3%, led to a substantial increase in metal content, especially of vanadium, in the distillate. This proved that 3 wash stages were necessary.

The contacting efficiency achieved by the materials used for the trays of the washing zone is also important. The height equivalent to a theoretical plate (HETP) was found to be for:

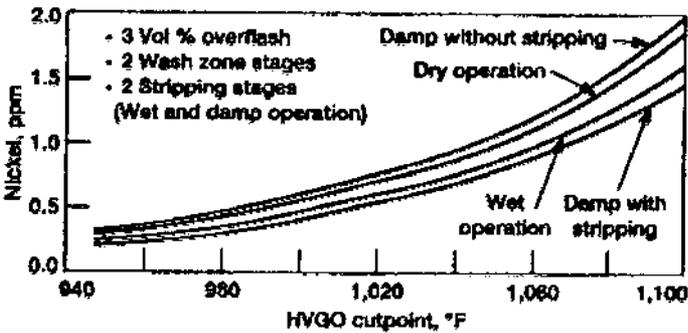
High efficiency metallic mesh	65–200 cm
Random packing	125–150 cm
Ordered packing	100–120 cm

Table 7.1 Conditions for Four Modes of Column Operation

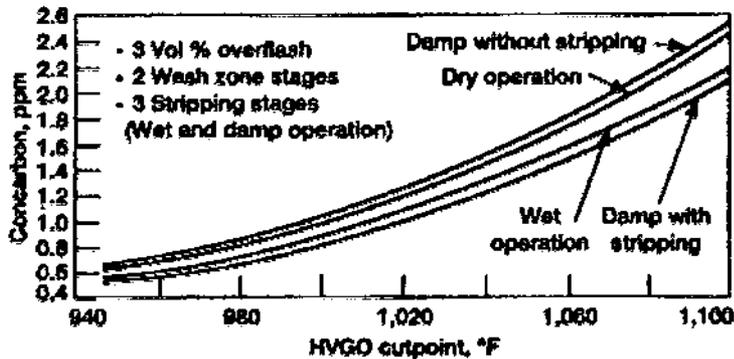
Conditions	1	2	3	4
Operating conditions	Dry	Wet	Damp no stripping	Damp w/stripping
Column type Fig. 7.2 a or b	b	a	b	a
Steam:				
coil (t/h)	—	1.34	2.86	1.34
stripping	—	1.82	—	1.82
Top pressure (mm Hg)	8	50	20	20
Flash zone pressure (mm Hg)	18	66	35	35
Overflash (%)	3	3	3	3



(a)



(b)



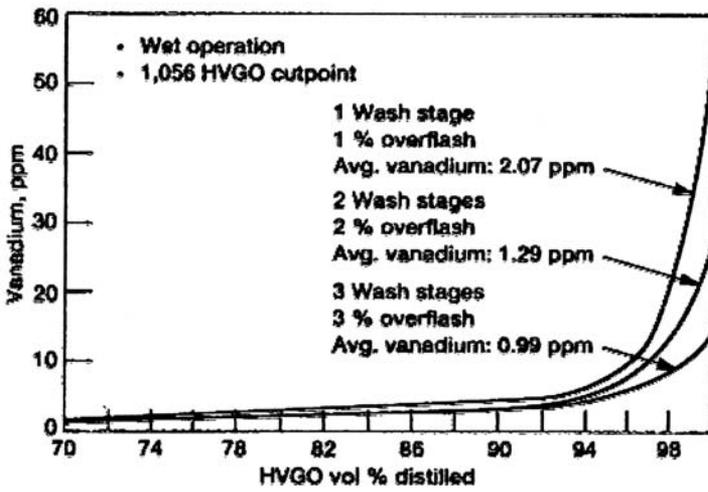
(c)

Figure 7.3 Effect of operation on HVGO. (a) vanadium, (b) nickel, (c) Conradson carbon. Content—variable mode of operation. (From Ref. 1.)

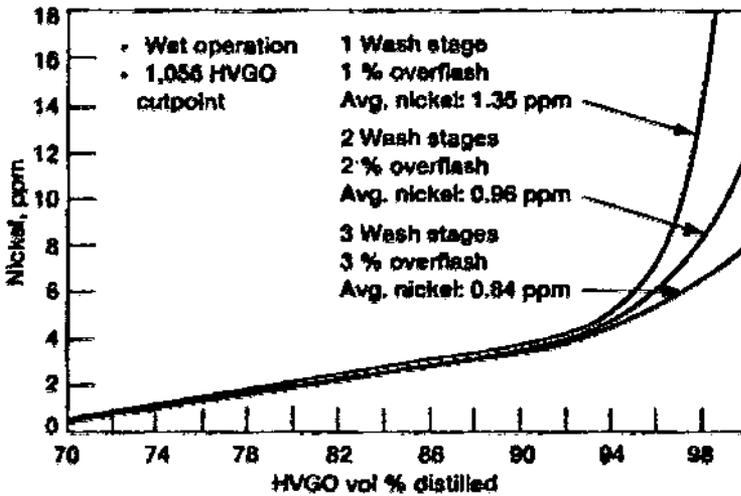
The efficiency of a fractionating plate was found to be equivalent to 0.25 theoretical plates.

The operating conditions that were finally selected were:

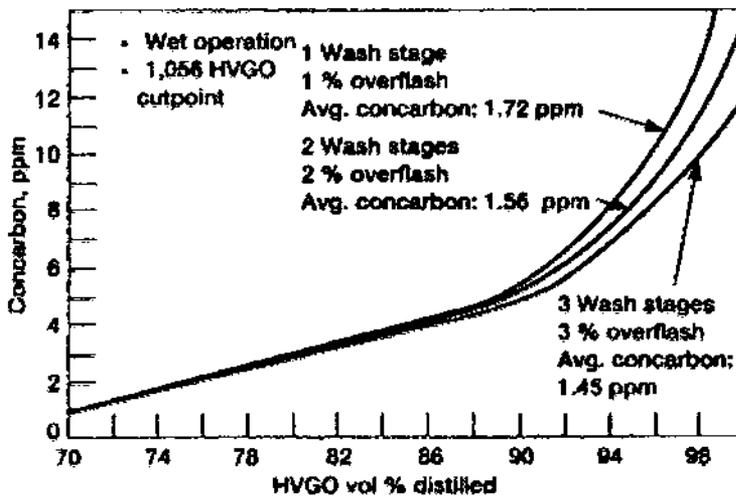
Operating conditions	No. 4 in Table 7.1
The end TBP of the heavy distillate	575°C
Overflash	3.0 vol %
Theoretical plates in the washing zone	2



(a)



(b)



(c)

Figure 7.4 Contaminants distribution in HVGO for operating conditions in Fig. 7.2. (a) Vanadium, (b) nickel, (c) Conradson carbon.

The results obtained in these conditions:

20.9% vol. of the feed as heavy distillate, containing:

0.85 ppm Ni

1.15 ppm V

1.5 ppm coke

Besides the problems of the number of theoretical trays in each section of the column, of the side reflux, and of the residue stripping, the measures taken for decreasing the formation of a fog of liquid drops in the vaporization zone of the column are also important. Fog formation is favored by the high inlet velocity (about 90 m/s) of the feed. From this point of view, the tangential inlet of the feed stream in the column is recommended, since it favors the separation of the liquid drops under the effect of the centrifugal force, and of other constructive means implemented in the design of the vaporization zone [4].

7.1.2 Processing of the Vacuum Residue

At the beginning of this chapter, several processes were indicated for obtaining catalytic cracking feedstocks from vacuum residues: visbreaking, coking, deasphalting with lower alkanes, and also hydrocracking. Several synergies between fluid catalytic cracking and hydroprocessing were also mentioned [77].

The main issues concerning the processes of visbreaking and coking were discussed in [Chapter 4](#) and those of hydrocracking in [Chapter 11](#).

The deasphalting process applied here is different from the “classical” propane deasphalting used for producing lubricating oils, since it uses higher alkanes and results in significantly higher yields of deasphalted product. As shown in [Table 7.2](#), the content of Ni, V, and coke in the deasphalted product increases with the molecular weight of the alkane solvent [5]. The data of this table are orientative only, since the yields and the metal content in the deasphalted product is to a large extent

Table 7.2 Deasphalting of Arabian Light Vacuum Residue

Characteristics and yields	Feed	Deasphalted with		
		C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂
Density (d ₄ ¹⁵)	1.003	0.935	0.959	0.974
Viscosity at 100°C, cSt	345	34.9	63	105
Conradson carbon (wt %)	16.4	1.65	5.30	7.90
Asphaltenes (insoluble C ₇) (wt %)	4.20	<0.05	<0.05	<0.05
Nickel (ppm)	19	1.0	2.0	7.0
Vanadium (ppm)	61	1.4	2.6	15.5
Sulfur (wt %)	4.05	2.55	3.30	3.65
Nitrogen (ppm)	2,875	1,200	1,950	2,170
Yields, wt %	100	45.15	70.10	85.50

Source: Ref. 5.

depending on the properties of the crude oil from which the vacuum distillate was obtained and on the particularities of the deasphalting process.

Overall, the product from the classical propane deasphalting mixed with the respective vacuum distillate may be submitted without other treatments to the catalytic cracking in classical plants. The deasphalted product obtained from butane deasphalting may be submitted directly to the catalytic cracking in mixture with vacuum distillate only in units designed for processing a heavy feed, whereas the product from pentane deasphalting needs to be hydrofined prior to catalytic cracking.

It is to be remarked that mixtures of light alkane hydrocarbons are often used as solvents. Besides the C_3 – C_5 alkanes, light gasolines containing no aromatic hydrocarbons may be used as deasphalting solvents.

The selection of the type of deasphalting unit depends on the hydrocarbons used. It is recommended that the plant should use supercritical conditions for the recovery of the solvent (as in the ROSE process) that lead to important energy savings. The detailed examination of the performance of various deasphalting units is beyond the framework of this book.

A comparison between the results obtained by the catalytical cracking of the vacuum distillate by itself and in mixture with the products from visbreaking, coking, or deasphalting is given in [Table 7.3](#). In the same table also the yields obtained by direct cracking of straight run residue with or without previous hydrofining are also given. These processes will be discussed in the next chapter.

7.1.3 Direct Use of the Straight Run Residue

The use of this feed became possible after catalytic crackers with two-step regenerators were developed. Such units can burn much larger amounts of coke than the earlier ones and have means for recovering the excess heat produced in the regenerator. Also, catalysts with better tolerance towards contaminating metals were developed.

The use of the straight run residue as feed for the catalytic cracking and the necessity for its pretreatment depend upon the level of coke and especially of metal content. The limits accepted as guiding values are given in [Table 7.4](#) [7–9].

Results obtained in the direct cracking of the straight run residue are compared with those of a distillate in [Table 7.5](#).

The large amounts of metals present on the equilibrium catalyst make compulsory the use of passivators, especially of antimony. The passivation leads to an increase by about 4% of the gasoline/conversion ratio and to a decrease by about 16% of the deposited coke. The reduced extent of the secondary reaction catalyzed by the metals (dehydrogenation, demethylation etc.) leads to a decrease by about 45% of the hydrogen and by about 25% of the amount of C_1 – C_2 hydrocarbons produced.

Quite different technologies were obtained by the combination of the catalytic cracking of residues with the contacting in a “riser” system of the feed with an inert solid material, heated to high temperatures by the burning of the deposited coke—the ART [9,10] and 3D [11] processes.

These processes achieve in fact a coking on a heat carrier, in a riser system, at very short contact time and high temperatures. The presence of butadiene in the

Table 7.3 Yields by Different Catalytic Cracking Feeds for Arabian Light Crude

Products (vol %)	Vacuum distillate	Vacuum + visbreak. distillates	Vacuum + cracking distillates	Vacuum distillate + deasphalt. oil	Atmospheric residue	
					without hydrofining	with hydrofining
Liquified gases	2.2	2.2	2.3	2.6	2.6	2.8
heavy gasoline	4.6	4.8	4.8	4.1	3.5	3.6
gasoline	48.9	49.6	52.7	56.7	58.9	65.1
jet fuel	6.3	6.2	6.2	6.2	6.3	6.3
diesel gas oil	20.4	21.6	27.4	20.6	24.1	25.1
Total motor fuels	82.4	84.4	93.4	90.2	95.4	102.9
Products (wt %)						
residual fuels	23.2	20.9	5.5	15.2	8.7	3.9
coke production	—	—	5.3	—	—	—
coke burnt in the regenerator	1.8	1.8	1.8	3.0	4.5	2.9
Total heavy products	25.0	22.7	12.6	18.2	13.2	6.8

Source: Ref. 6.

Table 7.4 Feed Pretreatment as Function of Metal and Coke Content

Ni+V ppm	Conradson carbon wt %	Recommended pretreatment
< 30	5–10	Without pretreatment
30–150	10–20	Hydrofining
> 150	> 20	Coking

Source: Refs. 7–9.

reaction products in the case of the ART process [9] proves that the reaction temperature exceeds 600–650°C.

In the ART process, the entire amount of asphaltenes present in the feed, 95% of the organometallic compounds and 30–50% of those with sulfur and nitrogen are destroyed, without any effect on the hydrogen contained in the hydrocarbons. The amount of coke deposited on the support called ARTCAT and burnt in order to reheat it, represents 80–90% from the Ramsbottom carbon, compared to 130–170% for the traditional coking. The sulfur is eliminated mainly as SO₂ and SO₃ together with the flue gases.

After the contacting in the riser and the separation of ARTCAT the products are cooled by injection of a cold liquid and separated by fractionation. The recovered gasoline contains 50% alkenes, has an octane number of 70 F₂ and 80 F₁. The fraction distilling above 343°C, which goes into the feed of the catalytic cracking

Table 7.5 Results of Direct Cracking of Primary Residue and a Distillate

	Distillate	Residue
Feed		
density, d_{15}^{15}	0.8927	0.9267
Ramsbottom coke, wt %	0.11	5.1
Ni, ppm	—	4.6
V, ppm	—	10.5
Yields: conversion, vol %	75.7	74.4
hydrogen, Nm ³ /m ³ liquid feed	0.135	0.455
C ₁ + C ₂ , Nm ³ /m ³ liquid feed	0.765	1.26
alkenes, C ₃ + C ₄ , vol %	11.8	14.0
alkanes, C ₃ + C ₄ , vol %	9.0	4.4
gasoline, vol %	60.1	56.5
light GO, vol %	13.6	16.0
column bottom, vol %	10.7	10.6
coke, wt %	4.6	11.7
Equilibrium catalyst (ppm)		
nickel	177	4290
vanadium	426	5490

Source: Ref. 8.

or of the hydrocracking, is similar to a vacuum distillate. The process makes possible the conversion of very heavy vacuum residues and even of the natural bitumens [9]. A portion of the ARTCAT is consumed in the process.

The solid inert contact material used in the 3D process [11] is not consumed in the process. It allows the processing of very heavy feeds having densities of the order 0.975, and containing about 43% components with boiling temperatures above 540°C and 10.7% Conradson carbon. Since it contains 2.6% S and 440 ppm metals, the product resulting from the contacting requires a preliminary hydrofining before being submitted to catalytic cracking.

A 3D industrial plant with a capacity of 500,000 t/year was started in 1989 [11].

The catalytical cracking of the liquid product obtained by the recovery of crude oil by means of underground combustion is to some extent similar to the above processes. Raseev et al. studied the cracking of such a feed, with the following characteristics [11]:

Density	$d_4^{20} = 0.9274$
Characterization factor	$K = 11.4$
Molecular mass	$M = 347$
Metals content	8.9 ppm

The comparative tests performed in a catalytic cracking unit with fixed bed of catalyst showed that this feed was similar to a coking distillate.

7.1.4 Feed Hydrofining

The hydrofining of the feed can significantly improve the performance of the catalytic cracking [12,13,77,78].

A systematic study was published [13] on the efficiency of the hydrofining of heavy distillates in mixture with gas oils from coking and visbreaking. Table 7.6 shows the improvements of the feed quality and yields, and the decrease in the SO₂ emissions that were obtained in different working conditions. These data were obtained for heavy distillates obtained from U.S. and Canadian crudes, which are similar to distillates obtained from Saudi Arabian and Russian crudes. To these distillates 20% by weight of coking gas oil was added.

Straight run residues may also be hydrofined prior to catalytic cracking. Such a combination of the processes was performed for the first time in 1981 in the Sweeny, Texas and Borger, Texas, refineries with good results. The efficiency of such treatment, especially concerning the decrease of the yield of hearth fuel and of coke is shown in Table 7.3.

The economic efficiency of these treatments depend upon the difference between the cost of gasoline and that of the straight run residue, and on the source and the cost of hydrogen. All factors must be analyzed case by case.

As general guideline, the hydrofining of the residue used as feed for catalytic cracking is recommended if the nickel and vanadium content is comprised between 30–150 ppm, and the Conradson carbon is between 10–20%.

For feeds exceeding these limits, special coking processes are recommended with very short contact times—ART and 3D—as described in the final part of Section 7.1.3.

Table 7.6 FCC Results from Untreated and Treated Feeds Using Hydrotreater/FCC

HT severity operating conditions	Untreated	Low severity		Moderate severity	
	max. naphtha	max. naphtha	max. diesel	max. naphtha	max. diesel
Feedstock					
dens., g/cm ³	0.9123	0.8866	0.8927	0.8745	0.8805
sulfur, w ppm	17,500	100	178	33	53
nitrogen, w ppm	1,050	140	185	8	10
UOP K index	11.75	11.96	12.10	12.12	12.27
VAPB, °C	416	376	433	376	437
Products (wt %)					
dry gas	4.0	2.9	1.8	3.1	2.0
LPG	14.0	16.6	9.8	19.4	11.4
gasoline	46.2	55.9	36.6	58.6	38.5
LCO	20.0	13.6	43.3	11.2	41.7
decant oil	9.8	4.7	4.4	3.3	3.3
coke	6.0	4.6	2.6	3.4	2.0
Sulfur (wppm)					
gasoline	2,700	6	—	<3	—
gas oil	27,400	146	—	70	—
decant oil	33,700	443	—	156	—
SO ₂ emission, g/kg of feed	4.235	0.109	—	0.037	—

Source: Ref. 13.

The hydrofining of the distillates is applied in a large number of catalytic cracking units. An important result is the almost complete reducing of SO₂ emissions to the atmosphere, a very important factor for the protection of the environment [78].

7.2 PROCESS HISTORY, TYPES OF UNITS

7.2.1 Fixed Bed and Moving Bed Units

The catalytic cracking process on aluminosilica catalysts was implemented commercially for the first time by F. J. Houdry and Socony Vacuum Oil Co. with a fixed bed of catalyst in cyclic operation in a unit having a processing capacity of 320 m³/day.

The unit, which started operation on April 6, 1936 in the Paulsboro, New Jersey refinery, was provided with 3 reactors. This ensured, by means of an automatic valve system, a cyclic operation: 10 min reaction and 10 min regeneration, separated by 5 min of stripping.

Besides the technical difficulties in operation, including the removal of the regeneration heat, the process had the major disadvantage of continuous change of the effluent composition along the cycle. The conversion decreased strongly as the amount of coke deposited on the catalyst increased.

In order to eliminate this disadvantage, Socony Vacuum Co. developed a unit with a moving bed of catalyst, the Thermoform Catalytic Cracker (TCC) in Figure 7.5, and simultaneously the Houdry process with moving bed shown in Figure 7.6. As shown in the two figures, the difference between the two processes consists in separate vessels or in a unique body for the reactor and the regenerator.

Initially, the catalyst was shaped as 3 mm pellets while subsequent particles were of spherical shape with the same diameter. The elevator system used at the beginning was replaced in 1949 by pneumatic transport for the used catalyst, which permitted high catalyst/feed ratios and later on, the processing of heavier feeds. In Figure 7.7, the device located at the basis of the transport is sketched, which makes possible changing the contact ratio by acting on the flowrate of injected primary air.

Operating data for a Thermoform unit was given in Table 7.7 [14]. They refer to the processing of a gas oil from mid-Continent crude, having $d_4^{20} = 0.8984$, 50% distillation at 400°C, characterization factor $K = 11.9$. Two catalysts were used:

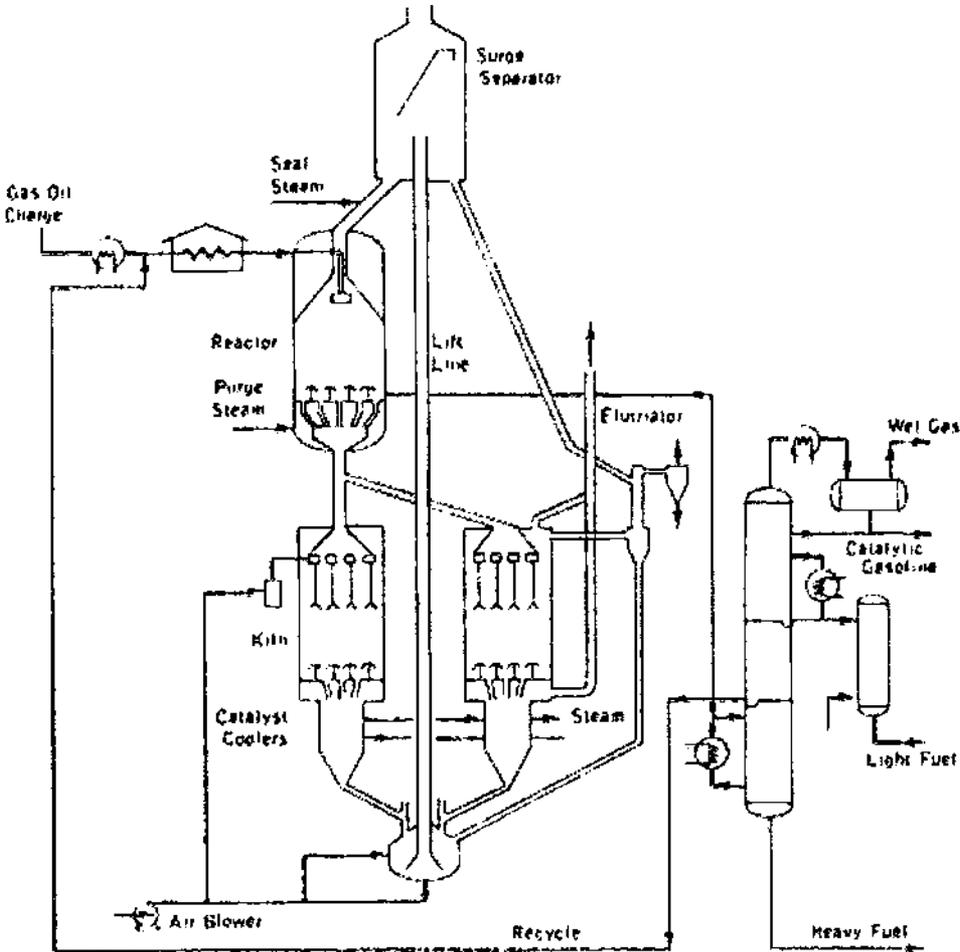


Figure 7.5 Socony Vacuum Thermoform Catalytic Cracker.

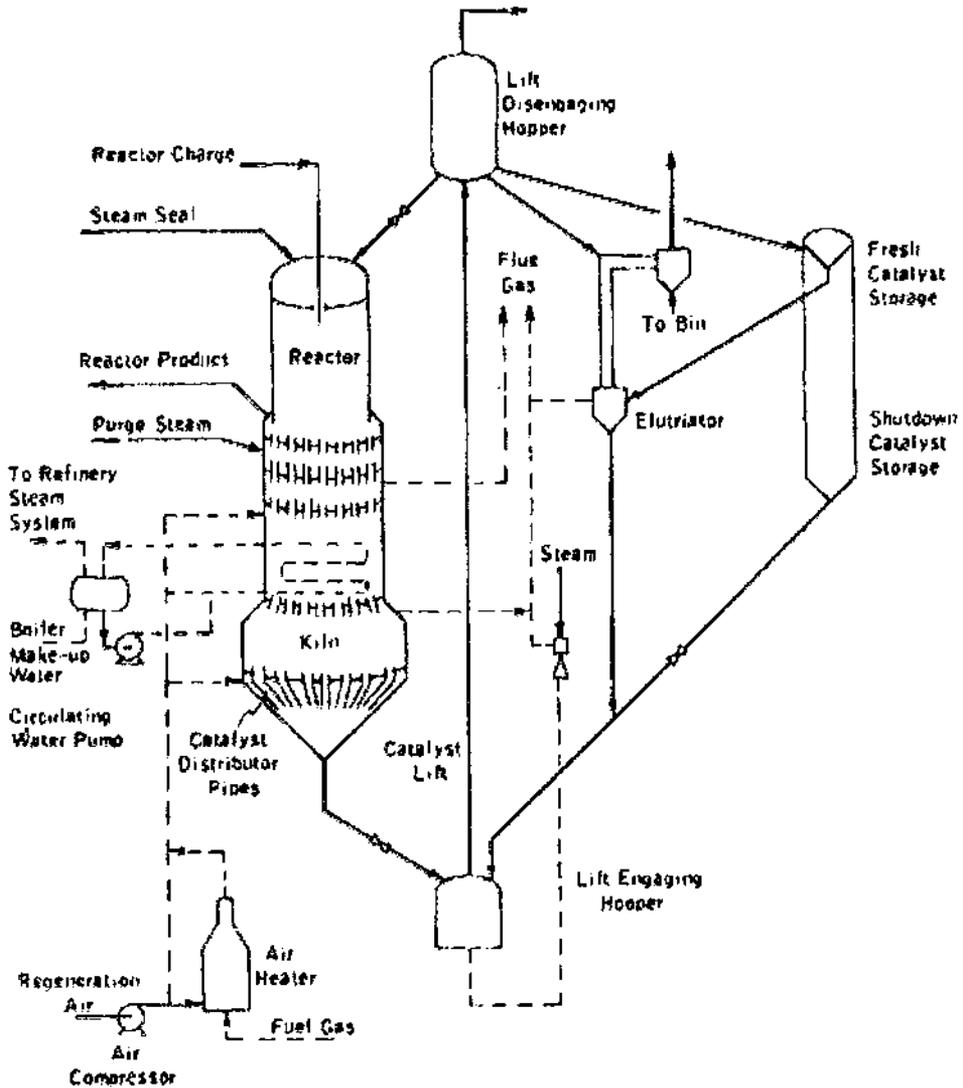


Figure 7.6 Houdry Moving Bed Catalytic Cracker.

3A—classical catalyst with a high content of Al_2O_3 and Durahead 5—a zeolite catalyst.

Other publications [15] supply similar comparisons between the operations with classical and zeolite catalysts.

The performance of the units improves at higher catalyst/feed ratios, as the mean coke content on the catalyst decreases and the mean activity increases. Thus, at a contact ratio of 5.5 the coke content on the catalyst at the inlet of the regenerator is of 1.1 wt % and the residual coke on the catalyst going to the reactor is of 0.05 wt %. The inability to further increase the contacting ratio was one of the reasons why units with fluidized bed became preferred. Indeed, depending on the unit capacity,

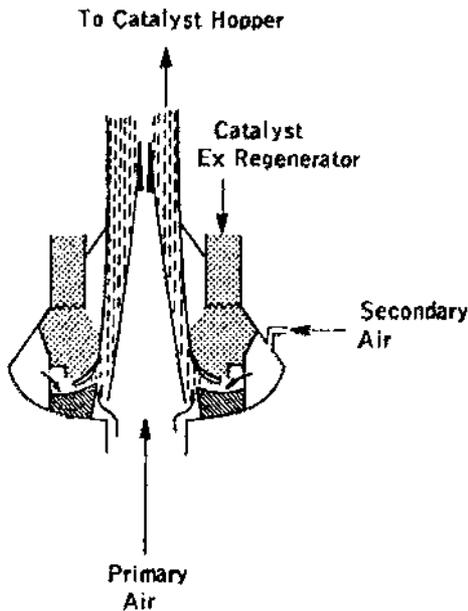


Figure 7.7 The bottom of a pneumatic transport system.

the amount of catalyst circulating through the system reached amounts of 200–1000 t/hour, which lead to high catalyst losses by erosion as well as by wear of the equipment and of the pneumatic transport system.

In addition, the burning of the coke deposited on the granules being a relatively slow process led to a residence time of about 1 hour for the catalyst in the regenerator.

Table 7.7 Operating Data of a Typical Thermoform Plant

Catalyst	A3	D5
Catalyst consumption, kg/day	750	350
fresh feed, m ³ /day	922	918
reactor temperature, °C	495	510
contacting ratio catalyst/feed	1.43	1.33
conversion, vol %	65.1	72.6
Yields		
combustion gas, wt %	6.0	6.4
oligomerization feed, vol %	16.5	17.5
gasoline, vol %	46.3	57.3
gas oil, vol %	21.9	18.0
decant oil, vol %	7.6	7.0
coke, wt %	7.6	7.0
octane F1 unblended	—	93.6

Source: Ref. 14.

The sizes of the reactor also became important. The reactor for a unit of 1 million t/year has a diameter of 5 m and a height of the catalyst bed of 4–5 m.

For all these reasons and other technical difficulties, the capacity of the plants with moving bed did not exceed 1.5 million t/year and they were or are gradually being replaced by fluidized bed units.

More details on this process, its various variations, examples of performance data and its estimation, and design methods for the reactor–regenerator system are presented in an earlier work of the author [4] and in other studies [16–18].

7.2.2 “Classical” Fluid Bed Units

The first catalytic cracking unit in fluidized bed was started in May 1942 at the Baton Rouge refinery of Standard Oil Co. as a result of a conjugated effort of a great number of American petroleum companies, determined by the state of war. For the same reason, in a relatively short time, the number of the units in the U.S. increased considerably. The processing capacities in the occidental countries reached the following values:

Year	m ³ /day
1945	160,000
1950	270,000
1960	830,000
1970	1320,000
1978	1575,000

In 1995 in the U.S. alone, the number of the units exceeds 350 and the processing capacity is over 1,600,000 m³/day.

The first catalytic cracking unit, called Model I, is characterized by the ascending circulation of the catalyst through the reactor and the regenerator, together with the reaction products, and the flue gases respectively. The separation of the catalyst is performed in external cyclone systems (see Figure 7.8). The plant had a processing capacity of 2400 m³/day and required 6000 tons steel, 3200 m pipes, 209 control instruments, and 63 electromotors. A complete description of these beginnings was made by A. D. Reichle [17].

Only 3 Model I units were ever built, being followed by the Model II, characterized by the internal placement of the cyclones, fluidization in dense phase, and descendent pipes for catalyst transport at its exit from the reactor and regenerator (see Figure 7.9). These solutions decreased the diameter of the reactor and the regenerator and the necessary amount of metal. The first Model II unit was started at the end of 1942, also in the Baton Rouge refinery, where several months before the operation of the Model I unit was started.

The Model II units were reproduced in the former Soviet Union under the name of A-1 and then B-1. A type B-1 unit was installed in the Onesti Refinery in Romania.

The Model III unit differs from Model II by the location at the same level of the reactor and of the regenerator, which required the use of a higher pressure for the

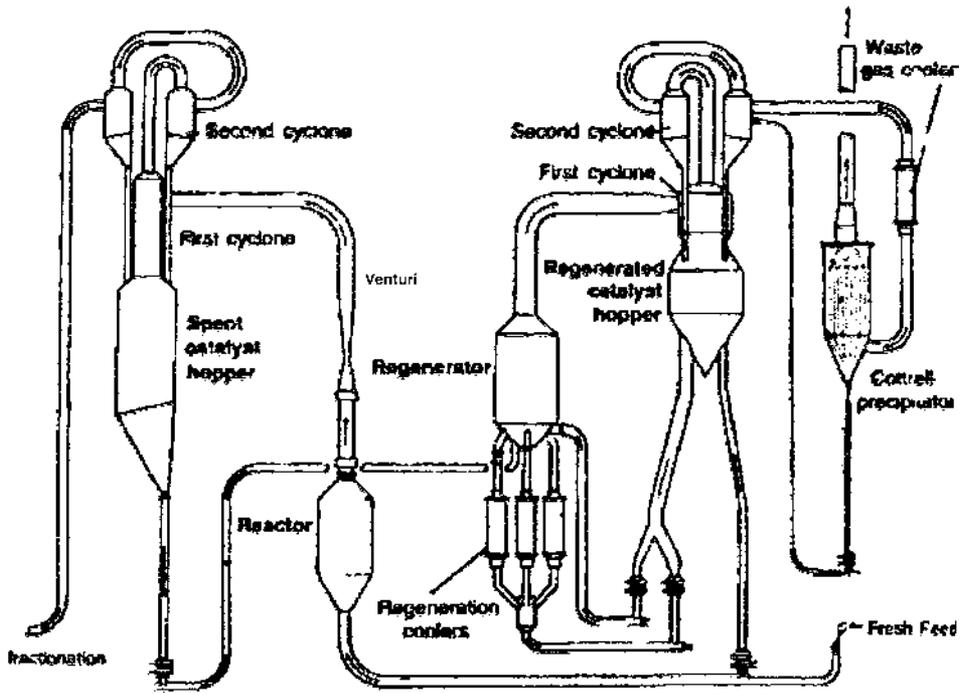


Figure 7.8 Catalytic cracking Model I.

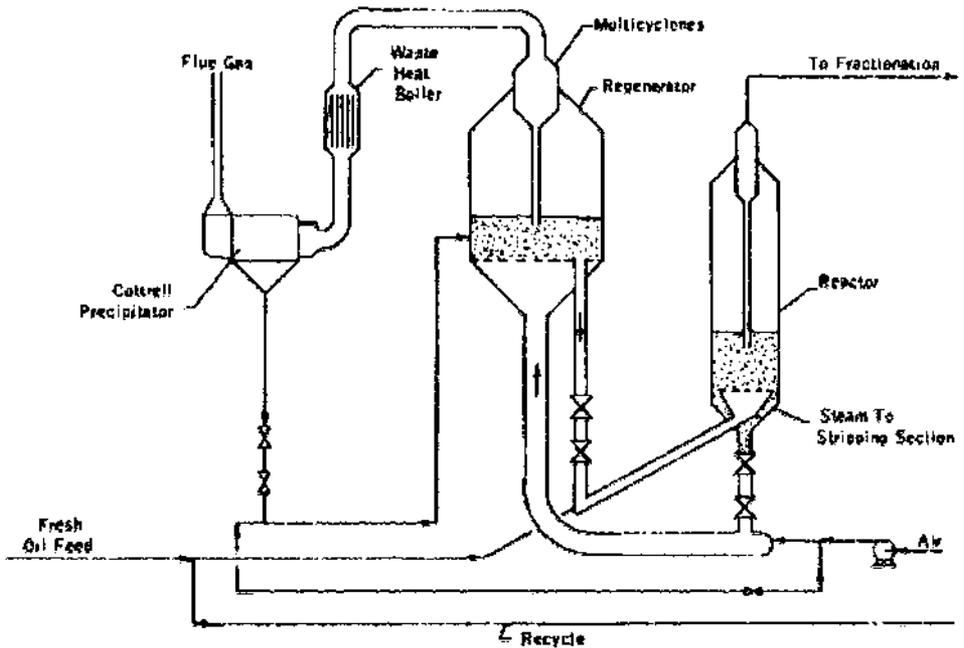


Figure 7.9 Catalytic cracking Model II.

regeneration air. Higher pressure became possible due to improved compression equipment.

The Model IV developed in 1952 made important progress over the previously described units. A number of units of this type are still in operation, including the Esso refinery in Port-Jérôme (France). A detailed description of these units and of the exploitation experience is given in the monograph published by Decroocq et al. [20].

The unit is characterized by the location at the same level of the reactor and of the regenerator and the transportation of the catalyst between the two vessels in dense phase through semicircular pipes. The dense phase in these pipes is maintained by injections of air and steam respectively.

The circulation sense of the solids is determined by steam and air injections respectively (see Figure 7.10). They produce a diluted phase of a lower volume density in the ascending portions of the transport pipes above the valves.

A similar transport system is used also in some fluid coking units and was presented in the final part of Section 5.3.5. Figure 5.8 and Eqs. (5.69–5.72) give the conditions that ensure correct circulation.

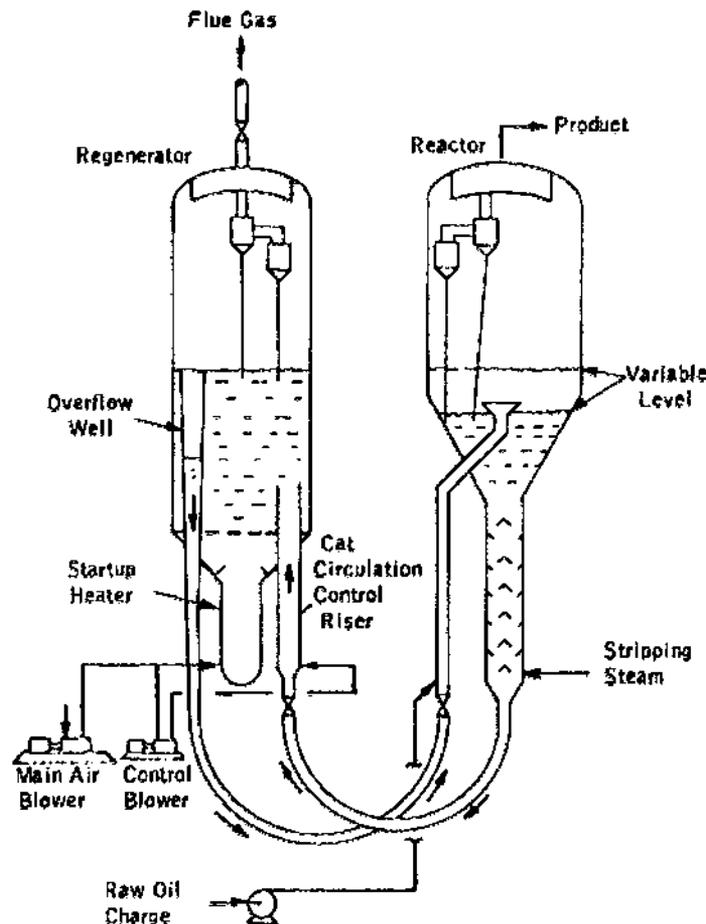


Figure 7.10 Exxon Model IV.

Another characteristic of this unit is the increase of the diameters of the reactor and regenerator in their upper part, which ensures a dense phase of fluidized catalyst between the distributor and this section with a bulk density of about 0.3 g/cm^3 . The increase of the diameter in the upper part decreases the amount of catalyst which is in this zone and accordingly decreases the rate of the overcracking reactions that lead to the decomposition of the gasoline to gases. Figure 7.11 gives the variation of the bulk density along the reactor height for different operating condition [21].

Another design adopted in the same period was to locate the reactor and the regenerator, coaxially, one above the other. This resulted in metal economy and the decrease of investment costs.

Thus units were built with the reactor overlapping the regenerator as in the UOP “stacked unit” (1947) and the Kellogg Orthoflow A (1951), and wherein the regenerator is overlapped to the reactor: Orthoflow B. The first option corresponds to a higher pressure in the regenerator, which increases the burning rate of the coke and leads to the decrease of the equipment diameter, but in exchange, needs a larger consumption of energy for air compression. The schematic flow sheet of the Orthoflow system A is given in Figure 7.12.

A more detailed description of the catalytic cracking units of the classical type including the sizes and the characteristic operating parameters, the yields, and the quality of the products was presented earlier by Raseev [4] and by other authors, such as Wuithier [22].

7.2.3 Units with Riser Reactors

The reactors of units of the classical type, which are described in the previous section, are characterized by intense backmixing of the catalyst and of the hydrocarbons, the behavior of the reactor being similar to that of a perfectly mixed reactor. On the other hand, the reactor of the “riser” type is in fact a tubular plug-flow reactor.

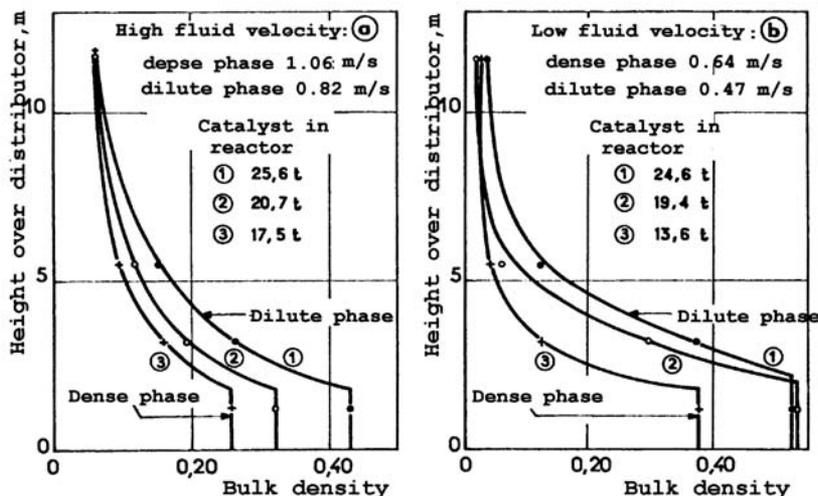


Figure 7.11 Variation of catalyst bulk density in Model IV reactors. (From Ref. 21.)

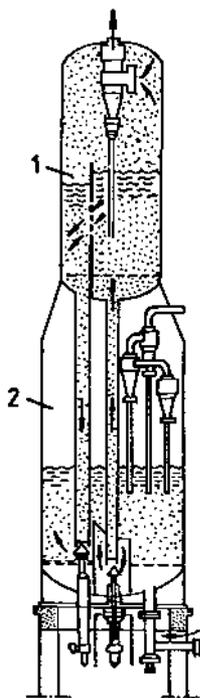


Figure 7.12. Kellogg Orthoflow A catalytic cracking. 1 – reactor, 2 – regenerator.

Since gasoline constitutes the intermediary product of a process made of successive steps, the maximum conversion of the gasoline will be higher in a riser reactor than in one containing a mixed fluidized bed.

In Sections 3.1 and 2.3.5 the equations of the maximum yield of an intermediary product were deduced for the two types of reactors. They are:

$$z_{\max} = \frac{1}{(1 + \sqrt{k_2/k_1})^2} \quad (7.1)$$

for the perfectly mixed reactor and

$$z_{\max} = (k_1/k_2)^{\frac{1}{1-k_1/k_2}} \quad (7.2)$$

for the plug-flow reactor.

Since for the catalytic cracking the ratio of the rate constants for the gasoline formation k_1 and for its decomposition k_2 is of the order 3–10, it results that z_{\max} will have the values (Table 3.1):

		$k_1/k_2 = 3$	$k_1/k_2 = 10$
Perfectly mixed reactor	$z_{\max} =$	0.402	0.577
Plug-flow reactor	$z_{\max} =$	0.577	0.774

Despite the fact that in the reactors with dense phase fluidized beds of the classical units a perfect mixing is not achieved and thus, the maximum of the yield

will have somewhat larger values and the kinetic of the catalytic cracking is more complex than that for two successive reactions, the advantages of the reactor of the “riser” reactors are obvious.

Therefore, after 1960, when the first riser type unit was developed by Kellogg, all new units are provided with a reactor of this type. Moreover, the classical plants in operation were revamped and the reaction system was modified to riser.

7.2.3.1 Revamping of Classical Units

The revamping of classical catalytic cracking units by the incorporation of the “riser” reactor was applied to all plants in operation. The manner in which the revamping was implemented depends on the type of the classical unit.

The following examples refer to plants IA/IM, which are similar to the classical Model II, of the former Soviet Union and to the Model IV, which was revamped at the ESSO Refinery of Port-Jérôme (France) and the revamping of a riser plant in Caltex Refinery in Kurnell (NSW, Australia).

Revamping of the plant of the type IA/IM. A complex program for the modernization of the IA/IM units, with the purpose of bringing them to the performances of the modern plants, was decided in 1985 and comprised of 8 tasks, of which 5 were implemented by the year 1992 [23].

The process scheme of the system reactor–regenerator, as it will appear after all the modifications have been implemented is shown in [Fig. 7.13](#).

The performed modifications refer to: a) use of high efficiency dispersers for achieving a good mixing of the feed with the regenerated catalyst; b) increase of temperature in the catalyst-feed mixing point, which leads to the increase of the temperature in the transport line to the reactor, which fulfils thus the part of a riser; c) improvement of the valves on the transport lines; d) use of promoters for the $\text{CO} \rightarrow \text{CO}_2$ conversion, which increases the temperature in the catalyst-feed mixing point; e) additives for decreasing the emissions of SO_2 and SO_3 . Concomitantly, the catalysts were replaced with others that are more active and more resistant to attrition.

Until the end of 1992, the following modifications were implemented: f) the modification of the devices through which the catalyst-feed mixture enters the reactor; g) the two-step regeneration of the catalyst, the first taking place in a central fluidization chamber, marked by 10 in the figure; h) the completion of the system for the retaining of the catalyst fines by installing a group of external cyclones and the use of existing Cottrell filters, without reintroducing into the system the dust retained therein. The last measures limited the concentration of the catalyst in the flue gases to 0.15 mg/m^3 , compared to 0.6 g/m^3 reported previously.

The results following the revamping are compared in [Table 7.8](#), with the previous situation and the final results obtained after the completion of the revamping.

Revamping of the Model IV unit. The Model IV unit was presented in [Figure 7.10](#) and described, in its classical version, in Section 7.2.2.

The modifications focused on the reactor and they were performed in succession as indicated by a, b, and c in [Figure 7.14](#) [20]. The modifications are justified by the fact that for the zeolitic catalyst used, the maximum gasoline yield corresponds to the composition at the inlet in the vessel marked “reactor”, the transfer pipe fulfilling the part of riser (see [Figure 7.15](#)) [24].

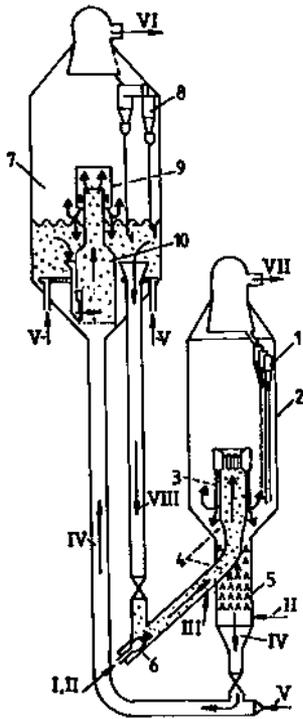


Figure 7.13 Revamped 1A/1M plant. 1,8 – cyclones, 2 – separator, 3,9 – inertial separators, 4 – riser, 5 – stripper, 6 – feed injection, 7 – regenerator, 10 – central fluidization chamber. I – feed, II – steam, III – recycle, IV – catalyst to regeneration, V – air, VI – flue gases to external cyclones, VII – products, VIII – regenerated catalyst.

In these conditions it was correct to reduce to a minimum and then to eliminate completely the cracking in the dense phase of the vessel that was initially the reactor and at the end, will act as catalyst separator and stripper.

The modifications indicated in [Figure 7.14](#) were accompanied by the revamping of the feed dispersion system when coming in contact with the catalyst, in order to ensure a uniform cracking.

Revamping of a riser unit. The revamped unit of type UOP “straight run” ([Figure 16a](#)) at the Caltex Refinery in Kurnell, Australia came on-stream in 1961. The revamping realized in 1998 included a new air distributor, a new spent-catalyst distributor and new stripper internals. In addition, an inertial separator installed during the riser revamp in 1989 was replaced with riser cyclones.

The revamping resulted in a significant improvement in regenerator and stripper performance as well as improved yields and less catalyst deactivation [7].

7.2.3.2 Further Units of the “Riser” Type

The “riser” reactor was invented by Shell in 1956 [19] after extensive studies at pilot and semi-industrial scale. The unit was conceived so that the cracking reactions that take place in the riser are continued inside the reactor in dense phase.

Table 7.8 Results of the Plant 1A/1B Revamping in Romania

Parameters	Before revamping	After partial revamping (1991)	Second revamping (estimation)
Operating conditions			
capacity, % from the project	110	120	133
temperature after cat./feed mixing, °C	490–500	510–520	560
final reaction temperature, °C	460–470	470–480	510
catalyst/feed ratio	4–5	5–6	6–7
feed, h ⁻¹	10	12	14
catalyst residence time in reactor, s	80	60	15
regeneration temperature, °C	535–550	600–615	645–665
residual coke on catalyst, wt %	0.4	0.25	0.1
flue gases: vol %			
CO ₂	7.5	13.5	14.5
CO	5.5	0.05	0.05
O ₂	6.5	4	3
SO ₂	0.08	0.03	0.03
dust in flue gases, g/m ³	0.95	0.6	0.15
catalyst consumption, kg/t feed	1.5	0.9	0.5
Yields (wt %)			
H ₂ S	0.3	0.3	0.4
C ₁ + C ₂	3.0	2.8	3.2
C ₃ + C ₄	3.0	2.9	5.6
C ₃ ' + C ₄ '	2.4	2.7	9.0
gasoline, FBP 195°C	31	38	48
LGO, 195–350°C	26	30	18
HGO, > 350°C	32.2	20.1	11.1
coke, wt %	3.1	3.2	4.5
conversion	41.8	49.9	70.7
gasoline F2 octane	79.6	80.1	81

The advantages of the system were evident and other construction firms adopted this principle and designed units that differed by the relative positions of the reactor and of the regenerator, the position of the lines for the catalyst circulation, etc.

The units from the first period were characterized by the fact that the cracking reactions took place partially in the riser and were continued in a reactor, in dense phase, in conditions of backmixing.

Two units of this type are presented as illustration, in [Figures 7.16a](#) and [b](#). The unit of [Figure 7.16c](#) is provided with two independent risers, one for the cracking of the feed and the other for the cracking of the recycle*. Such a measure is justified by the large difference in the cracking rates of the two flows. This requires quite different reaction times in order to achieve for each of the flows the maximum yield of the

*The system with two risers is used also in the units by Kellogg-Orthoflow and Texaco.

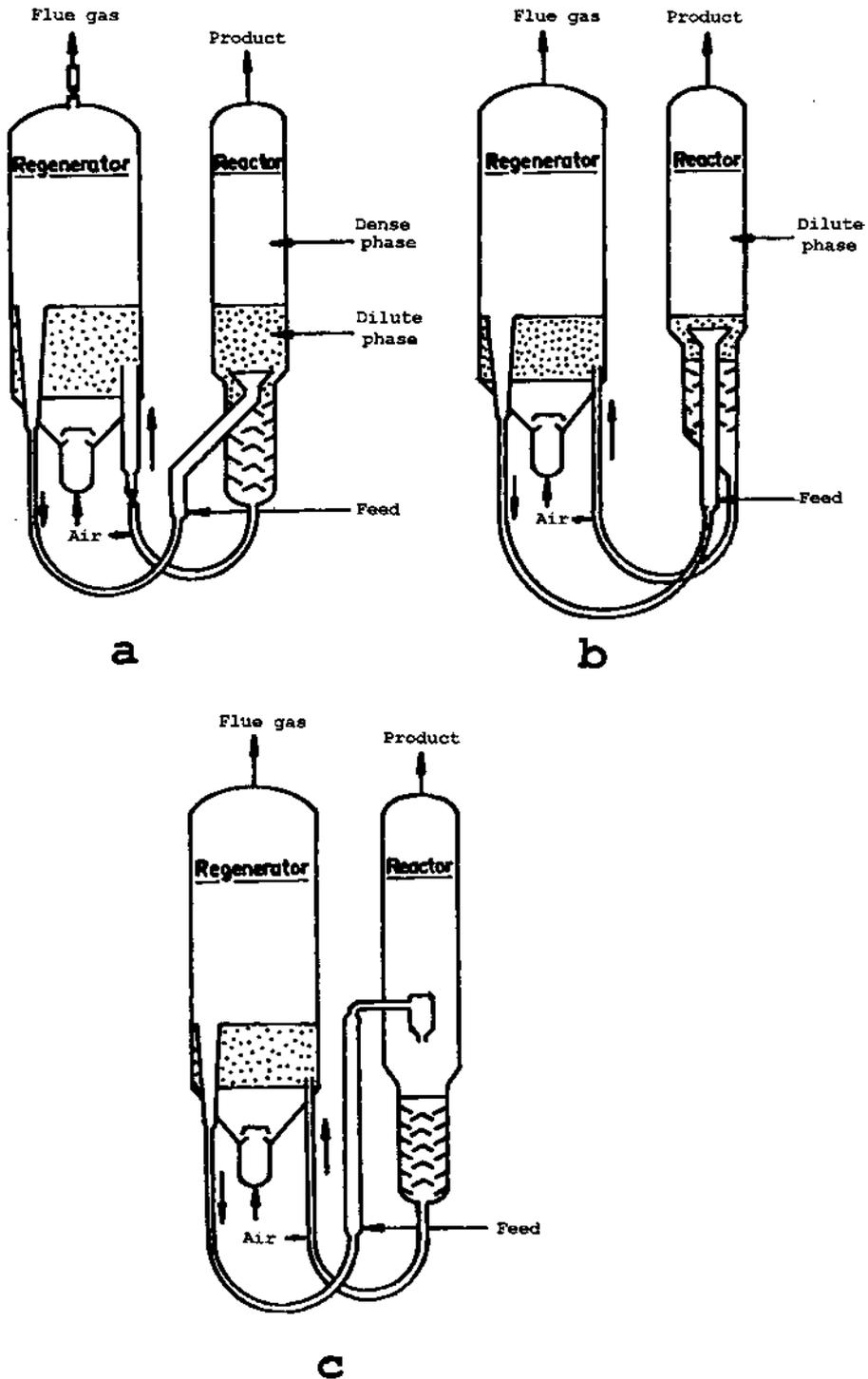


Figure 7.14 Revamping of the Model IV unit at Esso Port-Jérôme refinery (France). (From Ref. 20.)

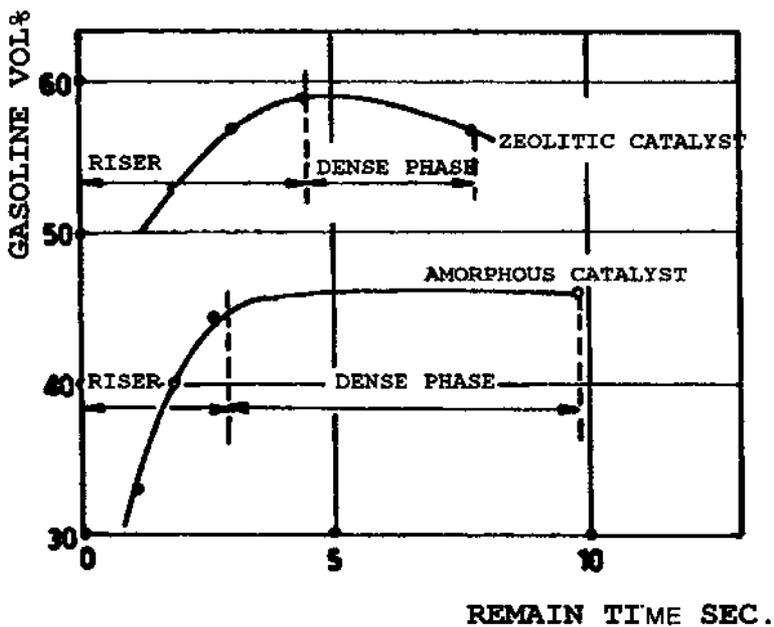
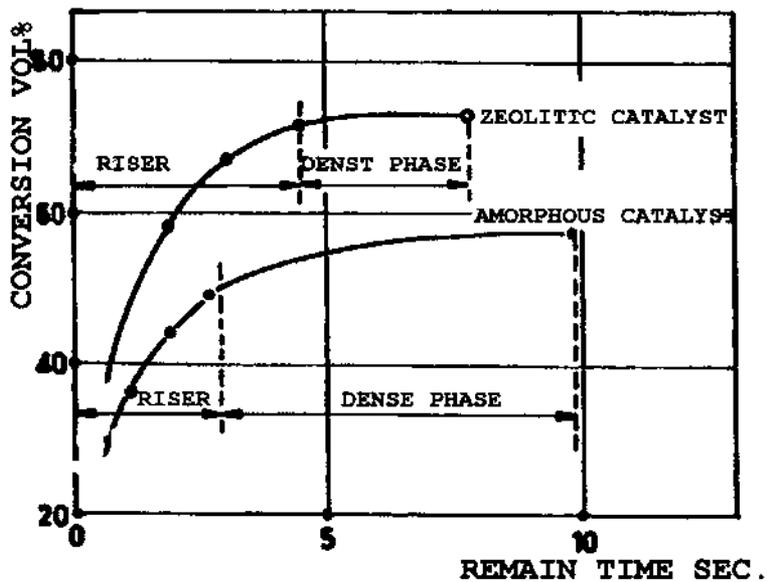


Figure 7.15 Conversion and gasoline yield evolution using amorphous and zeolitic catalysts. (From Ref. 24.)

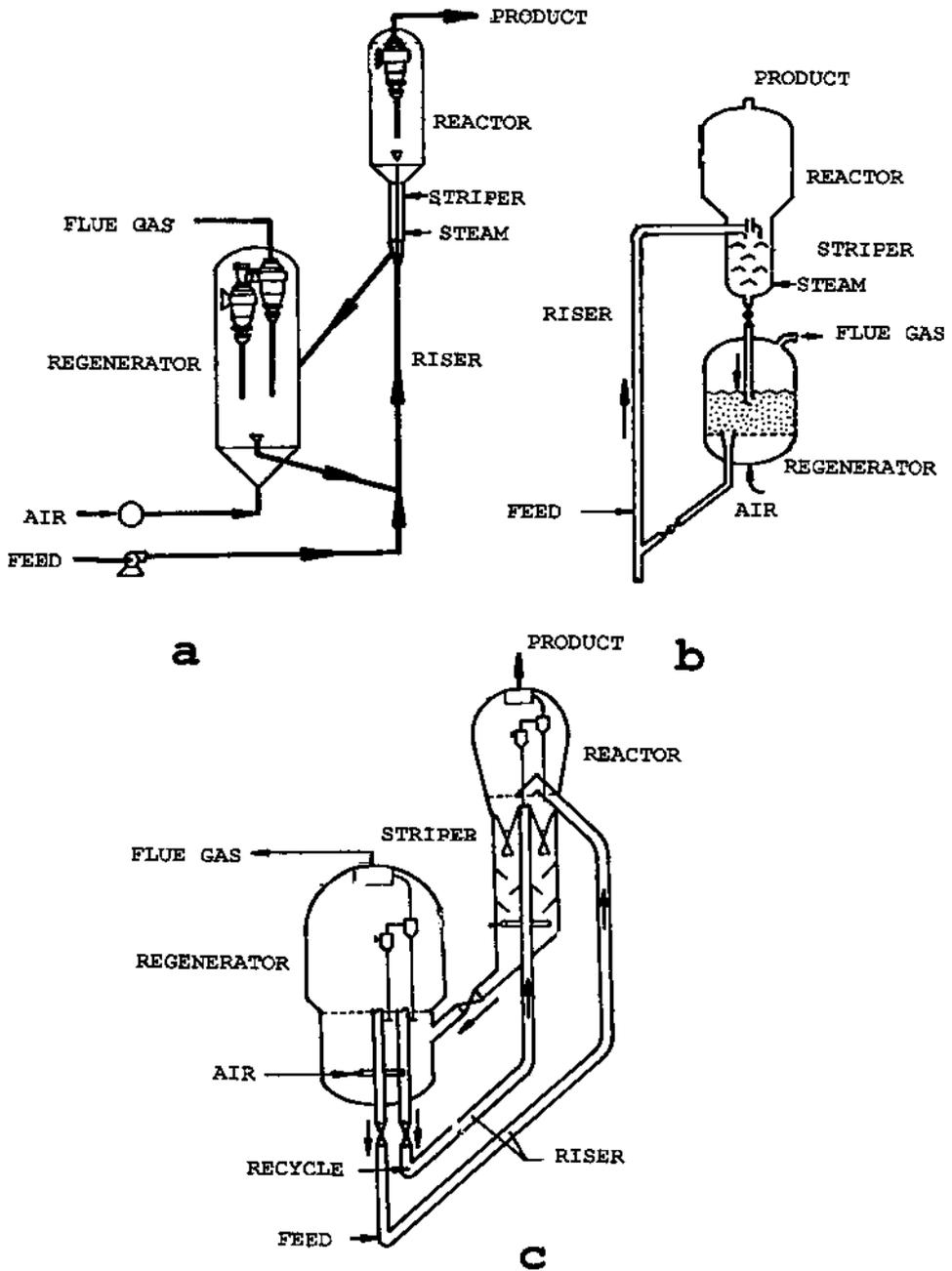


Figure 7.16 First generation catalytic cracking riser units. (a) UOP "Straight riser," (b) Esso Flexicracking, (c) Texaco, two risers system.

intermediary product—gasoline. In subsequent units, this objective was achieved by feeding the two flows into the riser at two different heights.

The fact that the reactions continued in the reactor in dense phase, where the prevailing backmixing led to longer average residence times, led to excessive cracking and to the decrease of the gasoline yield.

In order to remedy this disadvantage, several solutions were suggested: the decrease of the height of the catalyst bed in the reactor, devices that decreased the internal mixing etc., arriving finally at the solution adopted in the modern units: directly connecting the exit from the riser to a cyclone dedicated to this purpose (Figure 7.17) or to the cyclone system of the reactor. In this latter case, the separated reaction products pass directly to the fractionation tower without entering the reac-

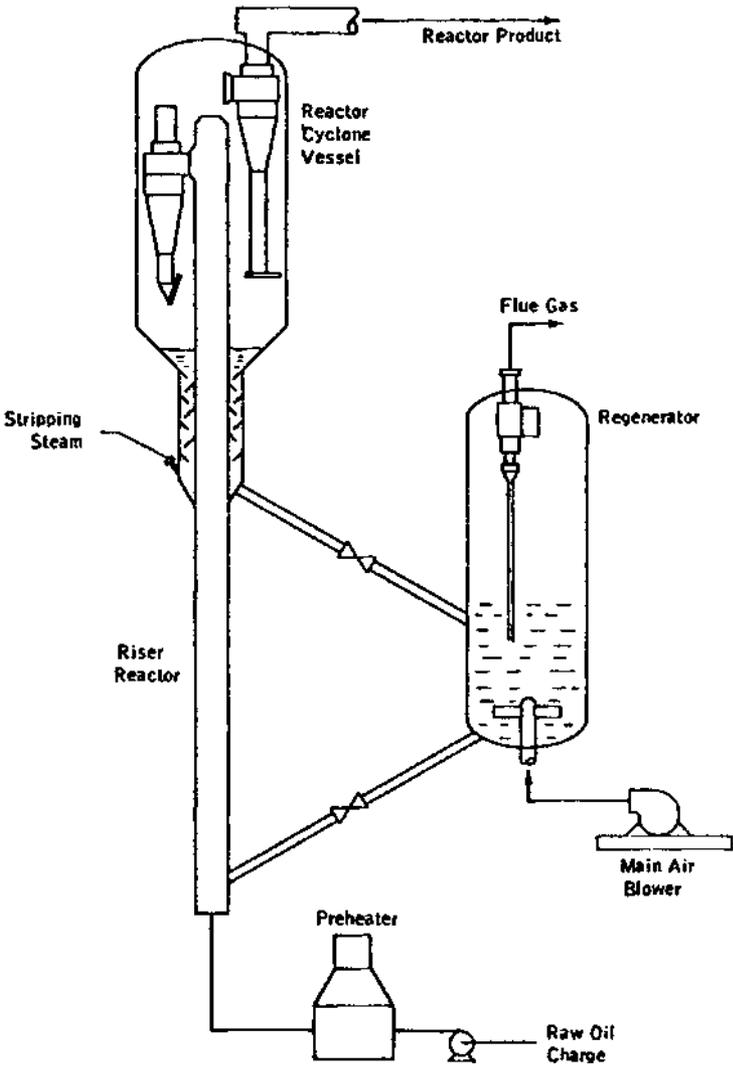


Figure 7.17 UOP unit without dense phase cracking in reactor.

tor, the role of which remains only to ensure the operation of catalyst stripping. These solutions require, of course, substantial improvements of the performance of the cyclone system.

The complete elimination of the dense phase leads to a substantial improvement of process performances. The data of Table 7.9 compares the performance of the UOP unit of Figure 7.17 with that of Figure 7.16a.

Improvements were brought also to the regeneration system by introducing two regeneration zones. The result was a reduction of the residual coke and thus, an increase of the process performances. The Orthoflow, model F units of Kellogg (Figure 7.18), is an example of the application of this concept.

A more advanced solution is the system where the first step of coke calcination is performed in a system type riser and only the second step takes place in dense phase in a classical fluidized bed. Together with these constructive improvements, the process conditions were also optimized: the pressure in the system reactor/regenerator was increased in order to increase the partial pressure of oxygen and accordingly, the burning rate of the coke. Thus, in the UOP unit of Figure 7.19, which applies these concepts, the pressure in the regenerator is of 1.75 bar compared to a maximum of 1.4 bar in the previous units, with the regenerator being located below the level of the reactor. The pressure in the reactor reaches 1.4 bar compared to 0.4 bar in earlier units. Overall, since the regenerators of this type were capable of increasing the amount of burned coke by means of controlling the CO₂/CO ratios in the two zones, they are currently used for the cracking of noncontaminated residues or of distillates with residue addition.

Table 7.9 Effect of Complete Elimination of the Dense Phase Cracking in Reactor

	UOP Fig. 7.16a*	UOP Fig. 7.17	
		Middle severity	High severity
Feeding with Mid-Continent GO			
density	0.876	0.886	0.888
UOP characterization factor	12.14	12.01	12.13
Conradson carbon, wt %	0.20	0.20	0.20
Conversion, vol %	80.2	77.5	89.6
Yields			
C ₃ ^o , wt %	7.7	5.7	10.6
C ₄ , wt %	10.9	10.0	13.3
gasoline (90% at 193°C), vol %	63.0	67.1	70.2
GO (90% at 310°C), vol %	15.0	14.5	6.9
heavy GO and residue, vol %	4.9	8.0	3.5
coke, wt %	4.9	4.5	5.7
Gasoline + alkylate			
yield, vol %	84.4	89.3	103.4
F1 octane number	90.1	89.2	92.5
F2 octane number	82.1	81.9	84.4

*Reactor temperature 505°C with diminished catalyst level.

Source: Ref. 24.

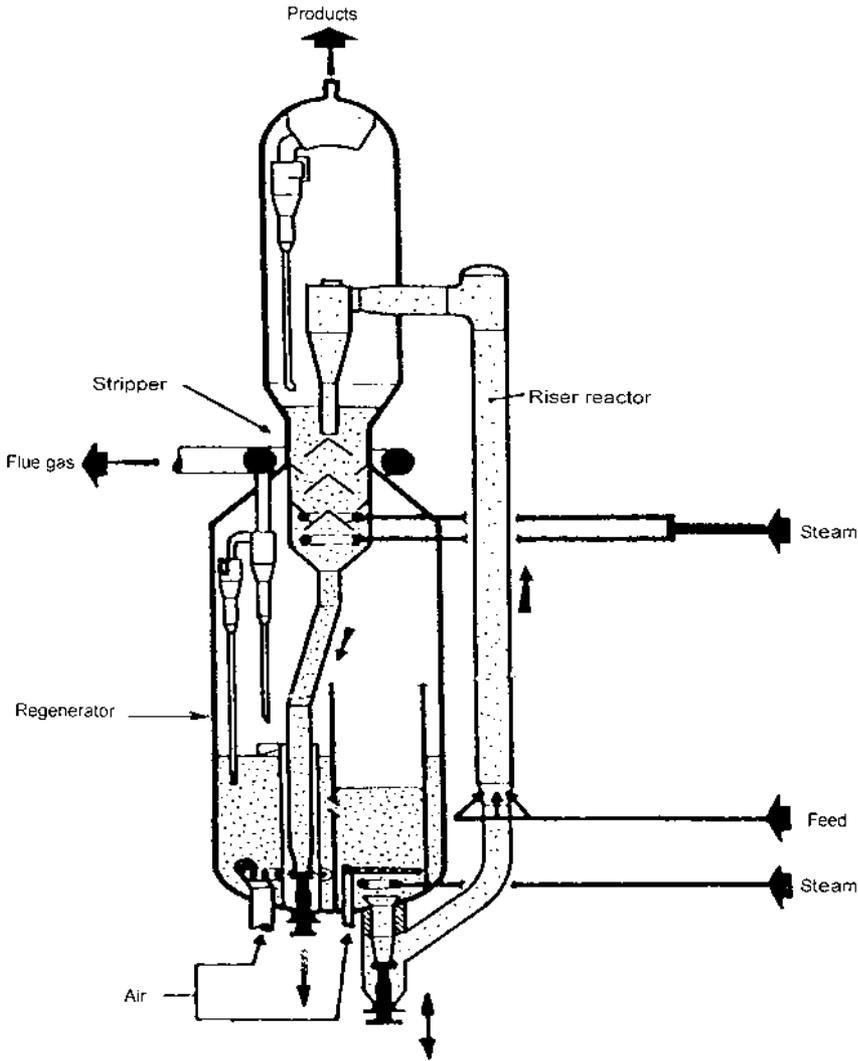


Figure 7.18 Kellogg Orthoflow F unit.

Since the constructive details and the operation conditions are common for all units of this type, they will be covered in Section 7.3.

7.2.4 Units for Residue Cracking

As indicated earlier, the direct catalytic cracking of residues is possible in units specially designed for this purpose when the content of Ni+V does not exceed 30 ppm and the Conradson carbon is below 5–10% by weight. Feedstocks with 150 ppm metals and 20% coke have to be submitted to a preliminary hydrofining. It must be mentioned that the above limits are not rigid, since they depend on the

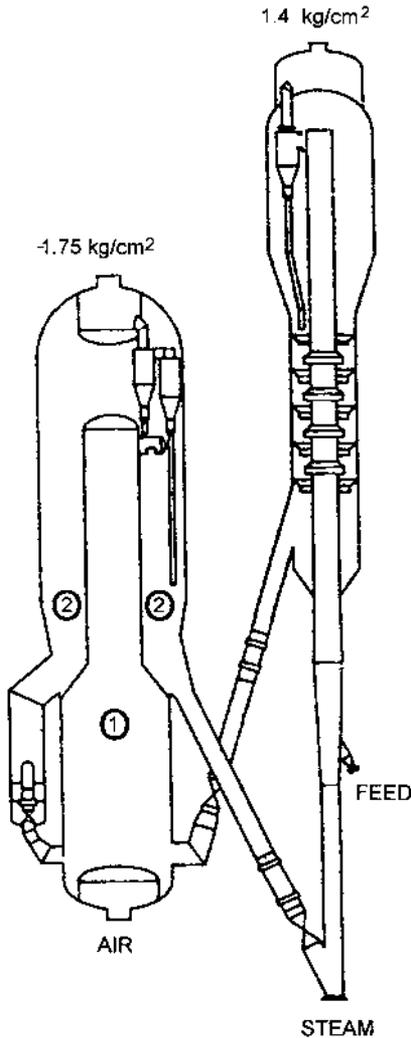


Figure 7.19 UOP unit with two steps regeneration.

type of unit, on the catalyst and on the passivators used for controlling the effect of the metals deposited on the catalyst.

The catalytic cracking of residues raises interest in estimating the content in metals (Ni + V) and Conradson coke in the straight run residues ($> 370^{\circ}\text{C}+$) of the known crude oil reserves. These estimations are depicted in [Figure 7.20](#) [25, 91].

Based on the data from this figure it is estimated [26] that 25% of the world reserves of crude oil allow the direct processing of the straight run residues by catalytic cracking. With a preliminary hydrofining and with the improvements brought to the process, this percentage could reach 50%.

The first residue catalytic cracking unit, with a capacity of $4,700\text{ m}^3/\text{day}$, was built by Kellogg in the Borger, Texas refinery and came on-stream in 1961. 20 years later saw the beginning of the intense building of such units, so that at the end of

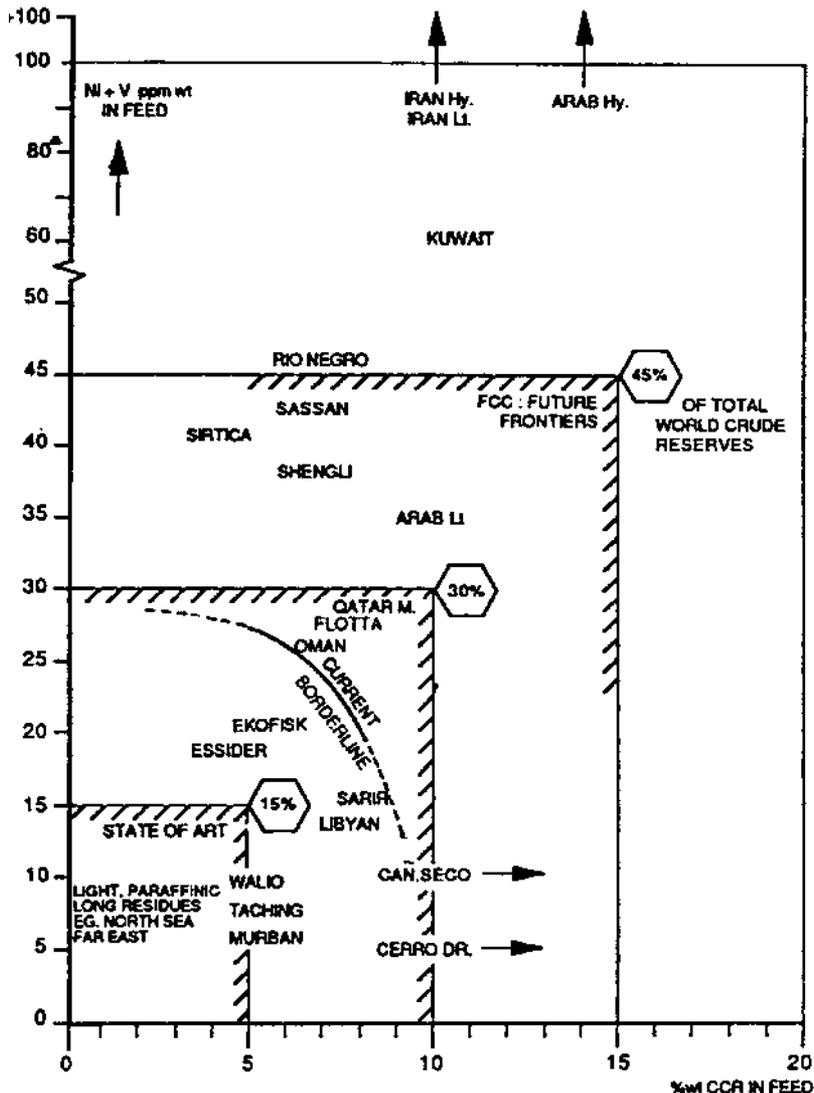


Figure 7.20 Ni+V and Conradson carbon contents in the $>370^{\circ}\text{C}$ fractions of several crude oils. (From Ref. 25.)

1983 processing capacity reached $38,800\text{ m}^3/\text{day}$, at the end of 1989, $81,500\text{ m}^3/\text{day}$, and at the end of 1994, it was $132,400\text{ m}^3/\text{day}$.

Table 7.10 shows the units put on-stream up to 1994 [26].

The successful catalytic cracking of the residues requires the solution of two problems: (1) coping with the noxious effect of the heavy metals, especially Ni and V, contained in larger amounts in residues than in the distilled fractions and (2) the much larger amounts of coke produced in the process, the burning of which generates a much larger amount of heat required for maintaining the thermal balance of the process.

Table 7.10 Residue Catalytic Cracking Plants Put on Stream up to 1994

Refinery, country	Licenser	Capacity (m ³ /day)	Go in stream year
Philips 66 Co., Borger, Texas	Kellogg	4,700	1961
Philips 66 Co., Sweeny, Texas	Kellogg	8,000	1981
Total Petroleum Inc., Arkansas City, Arkansas	Stone & Webster	3,000	1981
Total Petroleum Inc., Ardmore, Okla	Stone & Webster	6,400	1982
Valero Refining Co., Corpus Christi, Texas	Kellogg	10,300	1983
Ashland Petroleum Co., Catlettsburg, Kentucky	UOP-RCC	6,400	1983
Shell Canada Ltd., Montreal, Canada	Stone & Webster	4,000	1987
Petro-Canada Products Inc., Montreal, Canada	Stone & Webster	3,000	1988
Shell U.K. Ltd., Stanlow, Great Britain	Shell	10,200	1988
Idemitsu Kosan CL, Tokyo, Japan	IFP	5,600	1988
BP Australia, Kwinana, Australia	Stone & Webster	4,000	1988
4 plants in China	Stone & Webster	15,900	1989
Chinese Petroleum Corp, Taiwan	Kellogg	4,000	1990
Statoil A/S, Norway	UOP-RCC	6,400	1990
Schell Eastern Petroleum Ltd., Singapore	Schell	4,700	1990
Mitsubishi Oil Cl, Japan	Kellogg	4,000	1992
Schell Refining PL, Geelong, Australia	Schell	4,700	1992
Nippon Petroleum Refining CL, Japan	Stone & Webster	4,700	1992
Suncor Inc., Sarina, Canada	Kellogg	3,200	1994
Pertamina, Indonesia	UOP-RCC	13,200	1994
Caltex Petroleum Corp., Map Ta Phut, Thailand	Stone & Webster	6,000	—
	Total	132,400	

Note: The reconstructed plants are not indicated in this table.

Source: Ref. 26.

The first problem was solved by the development of Zeolite catalysts that are resistant at much larger concentrations of metals in the feed [27]. The use and the improvements brought to the passivators decreased the damaging effect of the metals. Hydrofining of the feed [28] is practiced for reducing the metals and coke concentrations to those tolerated by the catalysts.

The second problem was more difficult to solve. The decrease of the inlet temperature of the feed to the riser could reduce the heat excess only to a small extent. More efficient was to decrease the CO₂/CO ratio in the flue gases leaving the regenerator, decreasing in this way the heat of combustion (see Figure 7.21). This measure was however limited by the increase of residual coke, which strongly decreased the performance of the unit.

The burning of coke in the conditions of reduced CO₂/CO ratio in the flue gases, while holding the residual coke at the same or lower values, was achieved without difficulties in units with two regeneration zones, such as are the Orthoflow F, units of Figure 7.18. In this case, in the first zone the largest fraction of the coke is burned while using a reduced amount of air, at a minimum CO/CO₂ ratio. In the second zone, the remaining coke is burned in excess air until the desired residual coke level is reached. In units of the type shown in Figure 7.18, the flue gases from

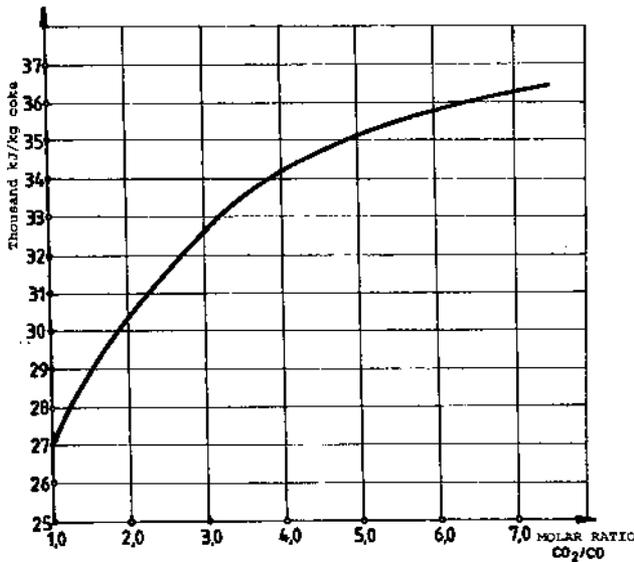


Figure 7.21 Coke (with normal hydrogen content) heat of combustion function of CO_2/CO ratio in flue gases.

the two zones are mixed and pass through a common cyclone system. In such systems, special measures must be taken in order to prevent the burning (in the upper part of the generator, in the cyclones system, or in the transport pipe) of the CO coming from the first zone, with the O_2 left over from the air excess used in the second zone.

The application of these two measures in the existing catalytic cracking units made it possible to include in the feed 10–20% straight run residue having a reduced content of Conradson carbon and metals.

Since the use of two regeneration steps was shown to be an efficient solution, the revamping of older units was accomplished by modifying the existing regenerator, and when this was not possible, by adding a supplementary regenerator. Such a solution applied by UOP is shown in Figure 7.22 [29].

The radical solution, applied to plants especially designed for the processing of residue, is to remove the excess heat directly from the regenerator by an adequate heat exchanger.

To this purpose two main systems are used:

1. Cooling coils are located in the lower part of the regenerator. They remove the heat from the dense phase of the fluidized bed. The boiler feed water which is fed to the coils generates steam as it expands into an external vessel. Such coils are sometimes placed in the regenerator also when the revamping of the units is made by the addition of a supplementary regenerator [9].

2. Tubular heat exchangers (vertical tubes) are located in the regenerator. A portion of the regeneration air is used for ensuring circulation of the catalyst through the tubes.

Details concerning these systems are given in Section 7.3.2.2.

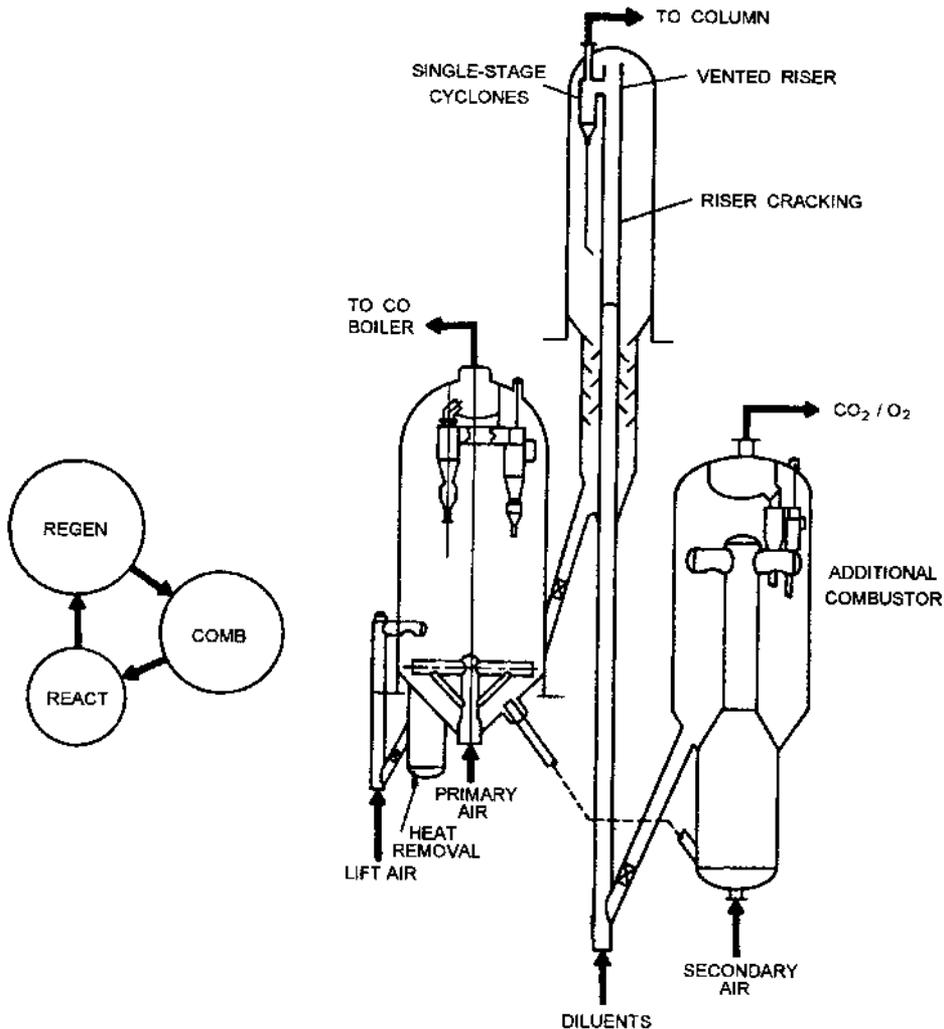


Figure 7.22 UOP unit with supplementary regenerator for residues processing. (From Ref. 29.)

It must be mentioned that both systems for heat removal were used in the first catalytic cracking units Model II and type B-1 respectively [4]. This was being justified by the larger amounts of coke that resulted when the natural or synthetic catalysts containing 12% Al_2O_3 were used.

The system was abandoned as a result of the improvement achieved in the feed pretreatment of the use of more active catalysts.

Various constructors use one or the other of the two systems and sometimes even both of them in order to remove a larger amount of heat or for a higher degree of safety in operation.

Figure 7.23 depicts the Kellogg Heavy Oil Cracker unit, which uses a coil as heat recovery system [30].

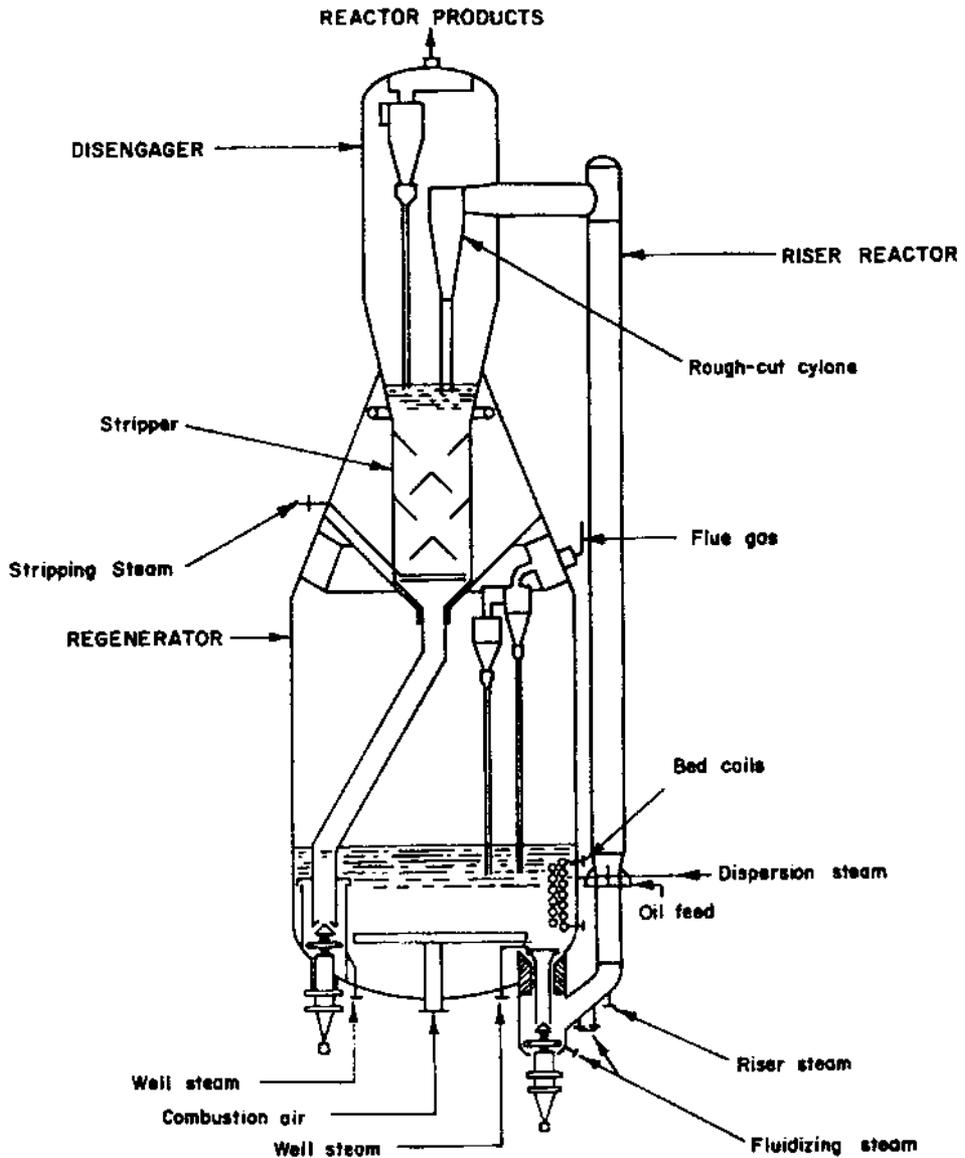


Figure 7.23 Kellogg Heavy Oil Cracker. (From Ref. 30.)

In Figure 7.24 a residue cracking plant is presented, which applies to both systems of heat recovery [30].

A special design is represented by the Total R2R process built by the French Petroleum Institute, where, following the second regeneration step the regenerated catalyst enters a vessel where it is submitted to a last contact with air in dense phase, the vessel serving also as catalyst buffer (see Figure 7.25) [31–34]. A unit of this type is in operation in Japan at the Aichi refinery.

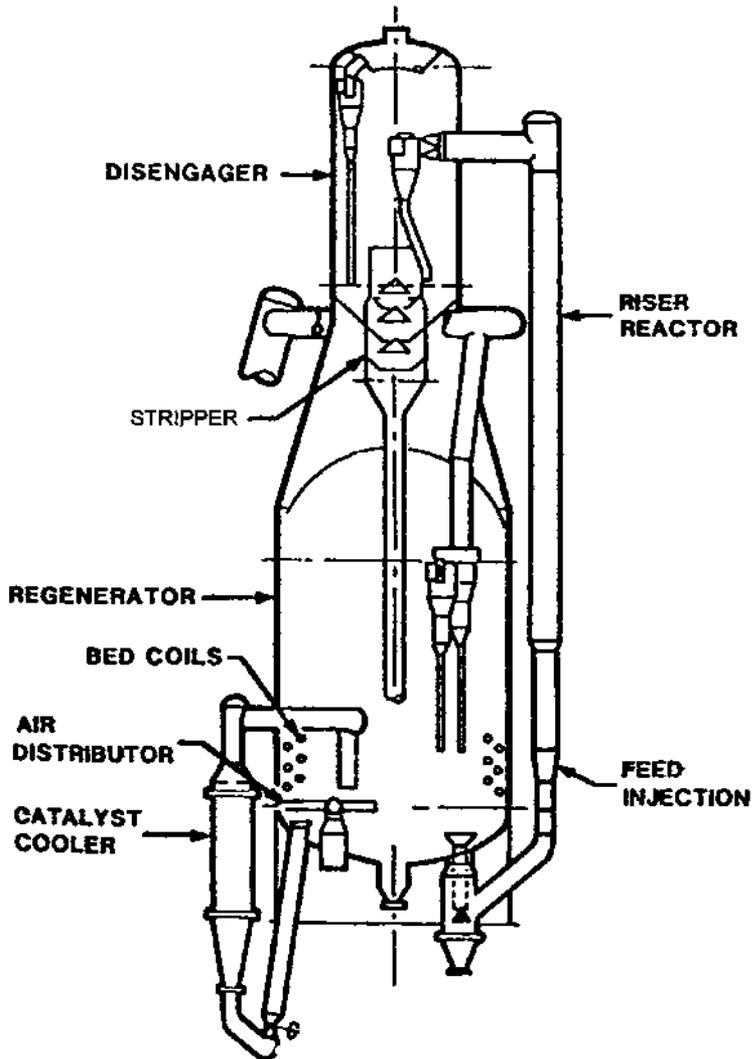


Figure 7.24 Catalytic cracking unit with dual coil and external heat-exchange heat recovery systems from regenerator. (From Ref. 30.)

7.3 CHARACTERISTIC EQUIPMENT

This section examines exclusively the equipment issues that refer to modern units of the riser type, including those for the catalytic cracking of residues.

7.3.1 Reaction and Stripping Equipment

The riser reactors used in modern plants require finding adequate solutions for a number of operating problems, that determine the efficiency of the process. These are: the feed dispersion system; the separation of the product vapors from the catalyst at the top of the riser; the location of the feed flows that enter the riser

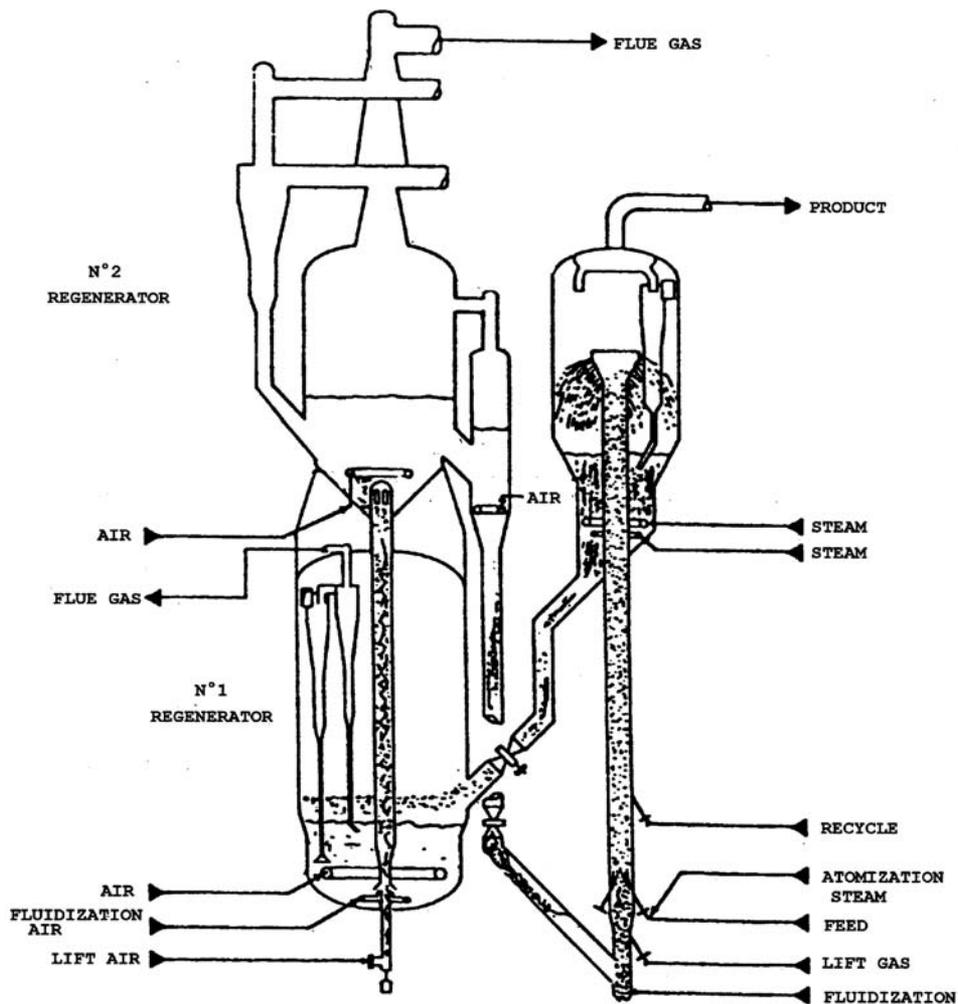


Figure 7.25 Total R2R Residues Catalytic Cracking plant.

and the dynamics of the temperatures and of the velocities along the riser. Issues related to the stripping must be added. An overall picture of the characteristic zones of a riser reactor is given in [Figure 7.26](#).

7.3.1.1 Feed Dispersion

The system that disperses the feed in the ascending flow of catalyst has a direct influence on the final yields. A good dispersion leads to an increase of up to +0.9 wt % in the gasoline yield and to a decrease of the conversion to dry gases and coke [23,35]. A decrease of the latter is more important for feeds with a greater Conradson carbon, such as the residual feeds.

These differences are explained by the fact that a deficient dispersion creates regions with unequal (high and low) catalyst/feed ratios that cause returning

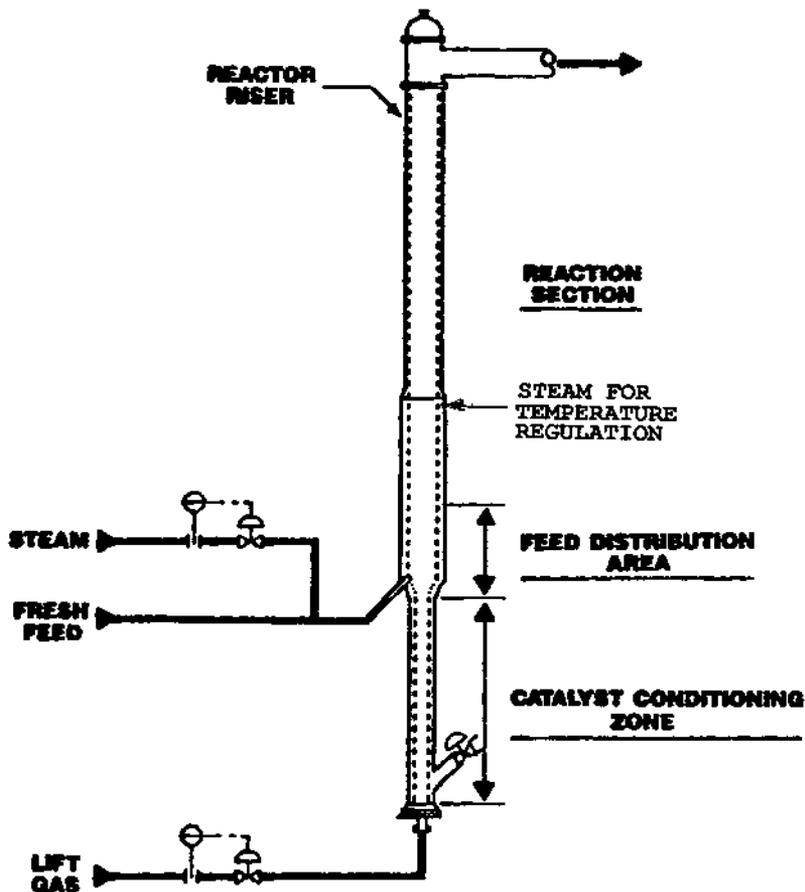


Figure 7.26 Characteristic riser zones. (From Ref. 90.)

streams. The returning streams lead to damaging effects similar to those due to backmixing.

A good injection system must contribute to the creation of as uniform as possible catalyst to feed ratios. Therefore, the distribution of the catalyst over the cross section of the riser before it comes in contact with the feed must be as uniform as possible, and the bulk density must be as high as possible in order to achieve the complete adsorption in the shortest time of the injected feed.

The proper injection system must achieve:

The atomization of the feed in drops as small as possible, having the narrowest possible size distribution

Uniform feed distribution over the cross section of the riser

Drops having sufficient velocity in order to penetrate through the flow of catalyst, without however exceeding the limits that would lead to erosion of the walls of the riser and the catalyst particles

An intimate mixing of the feed with the injection steam

Operation at the lower possible pressure drop

In order to satisfy as much as possible these requirements, several injection devices were developed. They are uniformly distributed on the circumference of the riser (see Figure 7.27) so that the injectors ensure the formation of fine drops of narrow size distribution.

The shape of the injectors has known a remarkable evolution. From the open tube (Figure 7.28a) it was changed to tubes ending with a slit (Figure 7.28b), used by Kellogg in 1980, but both producing a broad size distribution of the drops. The impact system (Figure 7.28c) achieves a good pulverization but requires a high pressure drop. The last system, a Venturi tube (Figure 7.28e), produces drops having diameters comprised between 30–50 μ that vaporize completely at a distance of only 0.5 m from the injection point [16].

Following joint studies carried out in 1990 by Mobil Research & Development Corp. and M. W. Kellogg Co., the system Atomax (U.S. patent 5,305,416) was developed. It was called a “third generation injector” (Figure 7.29) [35].

Comparison of the performances of this type of injector are compared in Table 7.11 to those of the slit injector and that with impact.

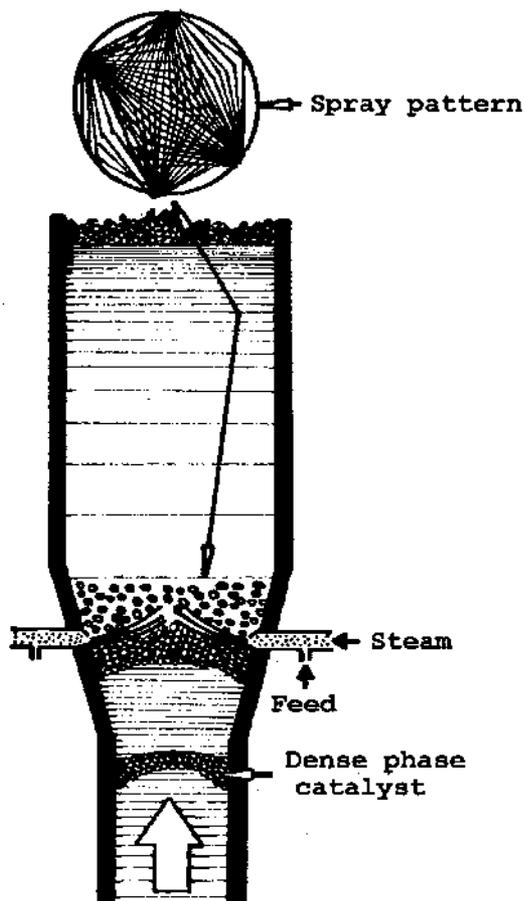


Figure 7.27 Injectors distribution. (From Ref. 36.)

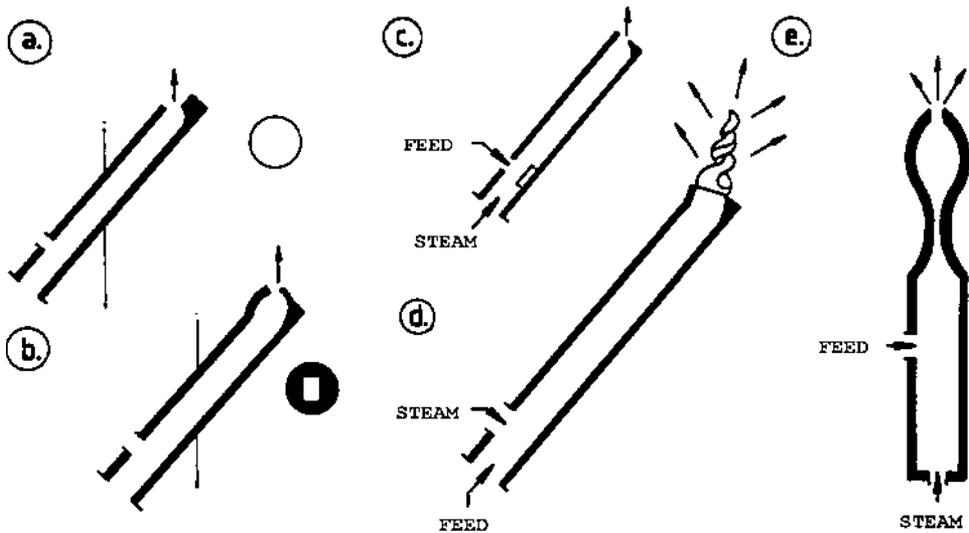


Figure 7.28 Injectors evolution.

The introduction of the Atomax system in a catalytic cracking unit on the Gulf Coast, which was previously provided with the injectors represented in [Figure 7.27e](#), led to the following changes expressed in % by weight:

Dry gases	-0.3
C ₃ -C ₄	-3.3
Gasoline	+5.0
Gas oil	-1.0
Residue and coke	0.0

Details concerning other modern nozzles: Optimax (UOP), Micro-Jet (Lummus), Stone and Webster are given and compared with Atomax nozzle in the excellent monograph of J. W. Wilson: Fluid Catalytic Cracking Technology and Operations [80].

In order to prevent the formation of backflows in the zone of feed introduction the diameter of the riser is narrowed just below this zone ([Figure 7.27](#)) and supplementary steam is injected below this zone (CCS-Catalyst Centering Steam device). Such a measure is provided at the R2R unit of the French Institute of Petroleum [33].

Usually the injectors are orientated upward, so that the feed jet is orientated in the direction of the movement of the catalyst particles. However, the idea of the reversed orientation of the jet was also tested. The results obtained at industrial scale seem to indicate that such a solution is also of interest.

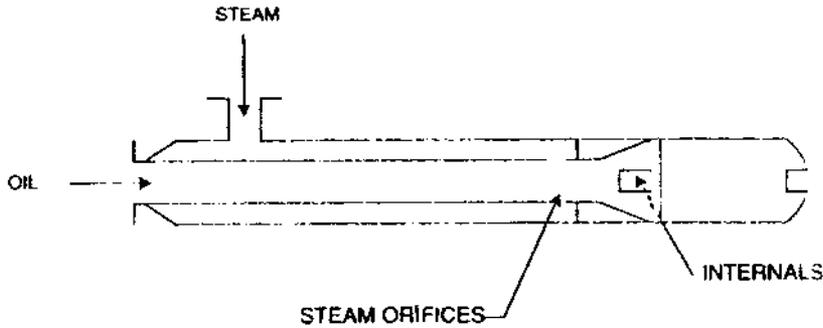


Figure 7.29 M. W. Kellogg Atomax nozzle.

7.3.1.2 Riser Process Conditions

The general temperature regime in the riser depends on the targeted objectives. From this point of view there are three typical regimes, depending on the product whose yield is maximized: medium distillate, gasoline, or lower alkenes [87].

The conditions for the three regimes, the material balance, and the quality of the products are listed in [Table 7.12](#) [29]. The feed in the three cases was the vacuum distillate obtained from a Middle-Eastern crude oil.

Several zones may be identified along the height of the riser ([Figure 7.26](#)).

The first zone situated below the feed introduction point has the role of ensuring uniform repartition of the catalyst over the riser cross section and to provide the particles desired ascending velocity that determines the bulk density in the riser.

Two approaches have been followed for achieving these requirements: the first consists in conferring the catalyst particles a large ascending rate, using steam injectors oriented upwards, located below the section of the riser where the feed is atomized. Such a solution is adopted in the IFP-R2R unit, depicted in [Figure 7.25](#). Thus, the formation of backflow is avoided, the feed rapidly leaves the high temperature zone, and a good penetration and distribution of the feed over the catalyst is easier to obtain. The disadvantage is that since the minimum fluidization velocity is significantly exceeded the formation of bubbles of transport fluid within the catalyst mass will occur and the feed contained in these bubbles be thermally cracked.

Table 7.11 Comparison Between Atomax and Other Injection Systems

	System b	System c	Atomax
Relative mean drops diameter (SMD)	2.35	1.08	1.00
Vol % > 1.6 SMD	81	44	31
Vol % > 8.0 SMD	24	4	0
Relative pressure drop	0.2	7.4	1.0

Systems b and c refer to [Figure 28](#).

Table 7.12 The Three Riser Operation Modes

	Middle distillate mode	Gasoline mode	Light-olefin mode
Operating conditions			
reactor temperature, °C	449–510	527–538	538–560
residence time	< Base	Base	> Base
catalyst/oil ratio	< Base	Base	> Base
recycle, CFR	1.4 (HCO)	optional (HDT LCO)	optional (heavy naphtha)
Catalyst formulation			
zeolite type	ReY	CSDY*	USY
zeolite level, wt %	15	30	40
rare earth, wt %	1–2	0.5–1.5	0
Product yields			
H ₂ S, wt %	0.7	1.0	1.0
C ₂ -, wt %	2.6	3.2	4.7
C ₃ , LV %	6.9	10.7	16.1
C ₄ , LV %	9.8	15.4	20.5
C ₅ +, Gasoline, LV %	43.4	60.0	55.2
LCO, LV %	37.5	13.9	10.1
CO, LV %	7.6	9.2	7.0
Coke, wt %	4.9	5.0	6.4
Product properties, vol/vol			
C ₃ olefin/saturate	3.4	3.2	3.6
C ₄ olefin/saturate	1.6	1.8	2.1
Gasoline			
ASTM 90% Pt., °C	193	193	193
RON clear	90.5	93.2	94.8
MON clear	78.8	80.4	82.1
Light cycle oil			
ASTM 90% Pt., °C	350	316	316
viscosity, cSt (50°C)	3.7	3.1	3.2
sulfur, wt %	2.9	3.4	3.7
cetane index	34.3	24.3	20.6
Clarified oil			
viscosity, cSt (100°C)	10.9	9.0	10.1
sulfur, wt %	5.1	6.0	6.8

*Chemically Stabilized and Dealuminated Y Zeolite.

Source: Ref. 29.

The second system achieves the catalyst flow to the feed injection points in dense phase, eliminating the danger of occurrence of thermal cracking, but making more difficult a good repartition of the feed over the mass of flowing catalyst. Since cracking reactions take place with increased volume, the linear flow velocity increases and the density of the bed decreases as it flows through the feed introduction section. This second system is sketched in [Figure 7.27](#).

Following the feed dispersion and vaporization section is the reaction section ([Figure 7.26](#)). To avoid erosions, the riser must be perfectly vertical, and the flow velocity should not exceed 18 m/s if the inside walls of the riser are not provided with

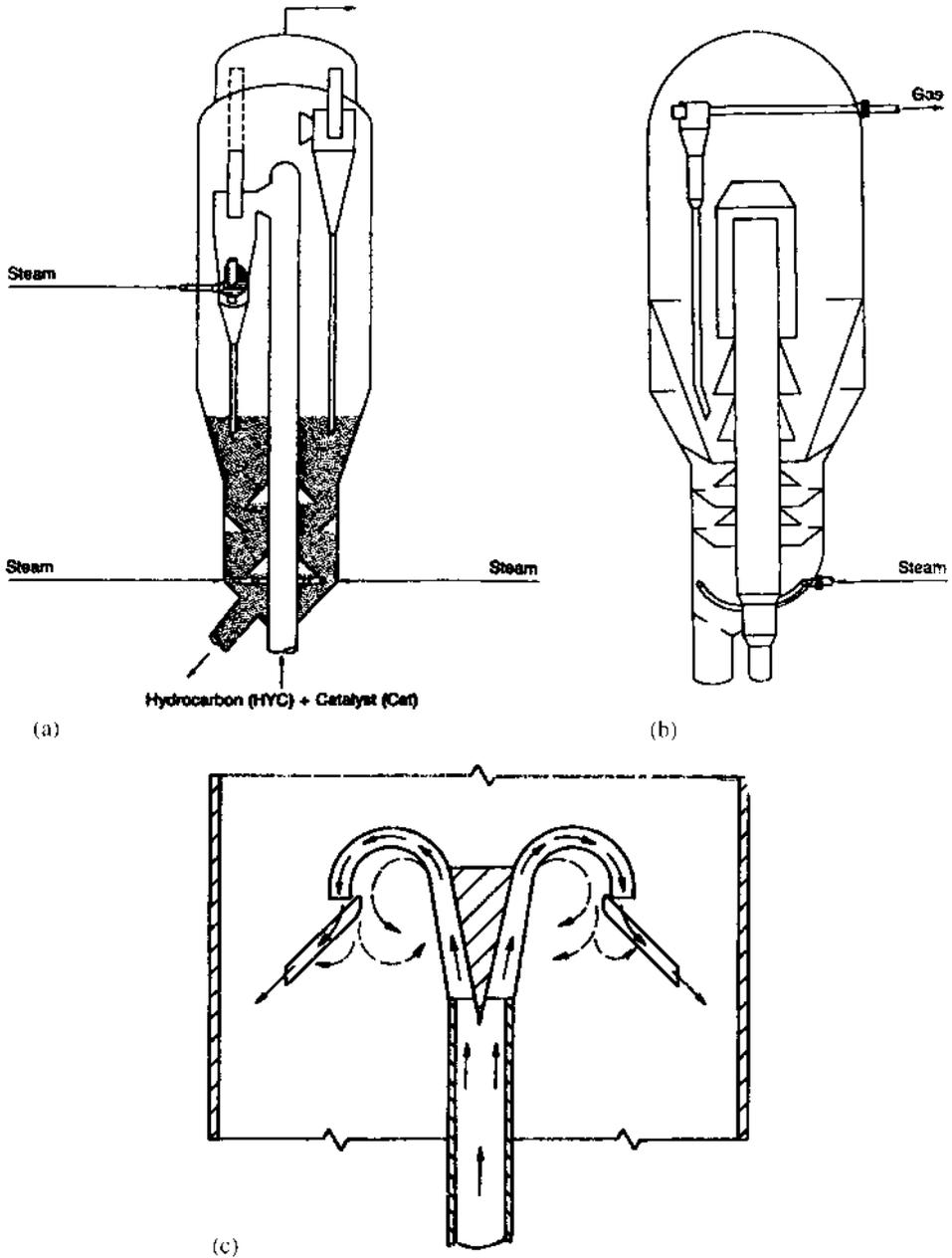


Figure 7.30 Riser top catalyst/products separator systems. (a) Direct connection of the riser with the cyclones system (U.S. Patent 4,043,899), (b) inertial separation (Chevron U.S. Patent 4,721,603–1988), (c) (U.S. Patent 4,664,888).

refractory protection. If the walls are lined with refractory material (usually about 12 cm thick), the linear velocity may be higher.

In order to control the temperature regime in the riser, recycle material is injected at a location above the injection zone of the feed at a distance where the feed is completely vaporized as a result of the contact with the hot catalyst. In this way, without changing the contact ratio or the inlet temperature of the feed, one can control the operation conditions and severity respectively [81].

7.3.1.3 Catalyst-Product Separation

The rapid separation of the catalyst from the reaction products is necessary in order to avoid over cracking and thermal cracking due to the high temperatures used in the modern risers. Thermal cracking would cause also a cooling of the effluent after it separated from the largest portion of the catalyst.

In older systems, the upper part of the riser was of the open type, the mixture of vapors and catalyst being released into an expansion zone, which was connected to the cyclone system. Later on, a system was developed where the products left the riser through a side tube, which made the separation of the catalyst easier. Eventually several improved solutions were developed.

The first improved solution consists in the direct connection of the riser with the cyclone system (Figure 7.30a). The disadvantage is that in this case the whole amount of catalyst passes through the first step cyclones, the size of which has to be significantly increased.

The second solution is that of the inertial separation of the catalyst by imposing a sudden change of direction to the product and catalyst flow (Figure 7.30b,c). Such systems proved to be very efficient, the separation reaching 98% [82] and backmixing currents being completely eliminated.

After the separation, but especially in the case of operation at high temperatures, a cooling liquid is injected in the stream of products immediately after the separation of the catalyst. This measure comes mandatory if the temperature exceeds 535°C [82].

As seen, special attention during the design and operation of the risers is given to the elimination of backmixing, which leads to decrease of the yields.

It was found that backmixing is absent in the descending portion of the inertial separators. This led to the idea to use risers with descending circulation, which will be discussed in Section 7.3.3.

7.3.1.4 Stripping

A rule of thumb is that good stripping must produce a coke containing not more than 6–9 wt % hydrogen in coke. The stripping is very poor when this percentage reaches or exceeds 10 wt % [37].

In the old plants that used less active catalysts and a high catalyst to feed ratio, the residence time of the catalyst in the stripper was short and the usual steam consumption was 6 kg per 100 kg circulating catalyst [36]. As a result of successive improvements, current steam consumption is $\frac{1}{4}$ of that value, whole hydrogen content in coke is only 5–6 wt %.

This spectacular increase of stripping efficiency is the result of several constructive measures:

1. The size of the orifices in the steam distributors was significantly decreased on the basis of accumulated experience with air distributors in the regenerators. In this way, the size of the steam bubbles became much smaller, which favored stripping efficiency.

2. The use of two steam distributors was adopted: one, located near the inlet of the catalyst in the stripper is used to eliminate the product vapors from the space between the catalyst particles; the second, near to the outlet from the stripper, in order to eliminate the vapors from within the catalyst pores or adsorbed on the particles surface.

3. The size of the baffles was decreased to prevent the accumulation of steam, and their location was reduced to the role of preventing the flow of catalyst along the walls.

4. A perfect symmetry of the locations of the catalyst inlet to, and outlet from the stripper was ensured. This measure is needed for efficient stripping by avoiding formation of stagnant spaces, since the dispersion of the catalyst normal to the direction of flow is very limited. Otherwise, a higher stripping zone and a significant increase of the number of baffles would be required.

7.3.2 Equipment for Catalyst Regeneration

The adequate design of the catalyst regeneration equipment provides answers to the following main issues: the design of the injection system for the air and for catalyst distribution; measures for avoiding local superheating within and above the catalyst bed; means for removing the excessive heat developed when residues are incorporated in the feed; systems with two regeneration steps used in the catalytic cracking of straight run residues.

7.3.2.1 Air injection and Catalyst Distribution

In older units the distribution of air and catalyst over the cross section of the regenerator was ensured by gratings with gauged orifices [4]. In large units, the gratings became very heavy and had to be made by assembling several elements together. The main difficulty was ensuring tight seals between the elements and with the wall of the regenerator. The thermal expansion that occurred in operation lead to formation of non-tight spots mostly along the walls, which resulted in preferential flow for the air, bypassing, and flow maldistribution.

For these reasons in the new designs, the injection of air used distribution systems that were formed of tubes provided with injection nozzles (Figure 7.31). The uniform repartition of the catalyst over the cross section of the regenerator is achieved by separate devices. The main problem is that the dispersion of the catalyst particles is very intense along the direction of the gas flow, while it is very small in directions normal to it.

For systems where the spent catalyst is free flowing from the reactor, which is situated at a high level, devices are provided such as that of Figure 7.31. The catalyst is distributed uniformly between several (generally 6) distribution troughs located above the air injection level.

For systems with the reactor and the regenerator placed side by side, the spent catalyst is lifted by using a portion (10–15%) of the regeneration air. In this case, the

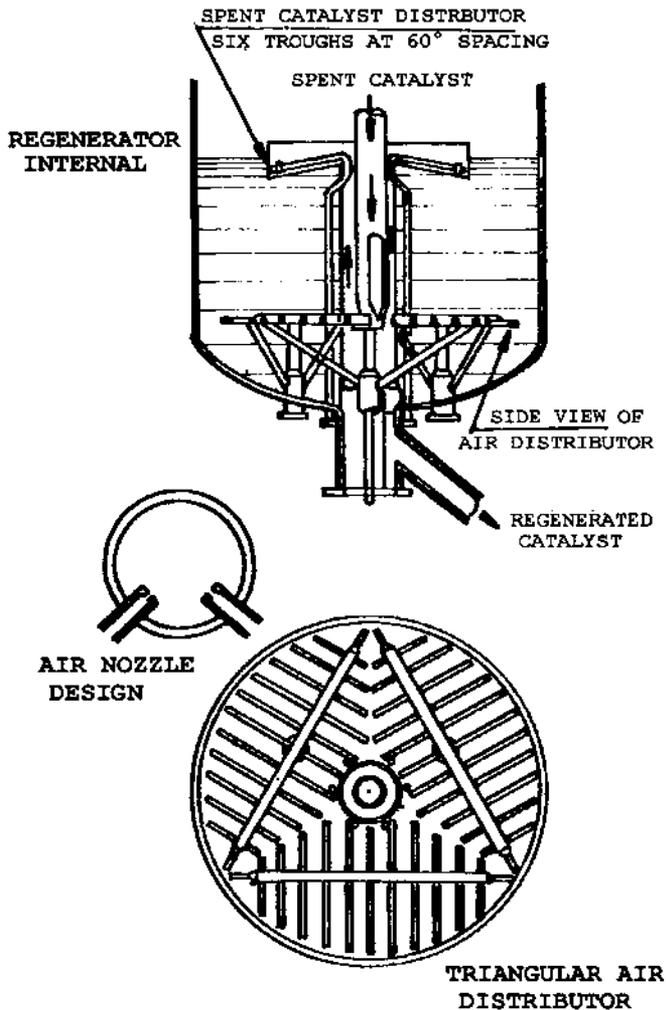


Figure 7.31 Air distributor with nozzles. (From Ref. 36.)

conical shape of the base of the regenerator ensures a good horizontal repartition of the catalyst.

7.3.2.2 Prevention of Overheating

In older units, the excess of oxygen needed for obtaining acceptable values for the residual coke led in many cases to auto-ignitions of CO in the freeboard of the regenerator. In such cases temperatures above those acceptable for the catalyst were produced and catalyst deactivation followed. Such auto-ignitions were catalyzed among others by the nickel deposited on the catalyst.

Several methods were proposed for controlling this phenomenon [4], of which the most efficient proved to be the installation of a bypass valve for the regeneration air, which was activated by the temperature above the bed.

Following the commercial introduction of the zeolite catalysts, which made it possible to increase the regeneration temperatures up to 730°C and even above this temperature, it became possible to completely burn CO to CO₂ by using promoters. This eliminated the danger of uncontrolled overheating above the bed. Despite the fact that the operation is now carried out without any excess of oxygen beyond the amount necessary for converting the CO to CO₂, the residual coke is situated generally below 0.2%.

A special problem is due to local burning that may occur when the total flow of fresh air comes in contact with the spent catalyst, strongly loaded with coke, such as in the processing of residual feeds. In such cases, local combustion may take place that could lead for some catalyst particles to temperature increases of 150–200°C above the one in the bed, leading to their deactivation.

In units with the reactor and regenerator placed side by side, the catalyst is pneumatically lifted to the regenerator by means of air. The air used for lifting represents 10–15% of the total amount necessary for regeneration and the mild combustions that take place in the transport line, removing the danger of local overheating.

In units where the catalyst discharges from the reactor under gravity, designs such as in the Orthoflow units, model F (Figure 7.18), or of an even simpler construction, may be used for achieving a first, mild combustion of the coke with only a portion of the total air.

7.3.2.3 Heat Removal

The possibility of using residue as a component of the feed is dependent on the ability to burn a larger amount of coke in the regenerator. Otherwise, the only possibility would be to decrease the feedrate of the residue containing feed, so as to maintain the amount of coke burned equal to that prior to addition of residue.

The amount of the burnt coke may be limited by the capacity of the blower or by the excess heat produced in the regenerator. In the second case, debottlenecking involves the addition of cooling devices.

Two systems are practiced for the removal of heat from the regenerator: cooling coils which are located inside the bed and tubular heat exchangers, located outside the regenerator.

The actual construction of the cooling coils placed inside the bed of catalyst is shown in Figure 7.32 [39]. It is a simple design that avoids the presence of joints, branchings, or changes in the diameter etc., which are the locations where intense erosions appear first. Their design is based on the lengthy experience of using cooling coils, starting in the years 1942–1948, when the use of the natural catalyst led to deposits of up to 12 wt % coke on the catalyst.

At current practiced densities of the dense phase, of 400–500 kg/m³ and at the low air velocities in the regenerator of 0.6–0.9 m/s, the erosions do not affect the operation life of the coils.

The second solution is the installation of external coolers (Figures 7.33, 7.24).

It is to be observed that the circulation in current coolers is different from that used in the period 1942–1948, when the ascendant mixture air/catalyst circulated through tubes provoking intense erosions. In current coolers the circulation is descendent through the shell side. The catalyst is maintained fluidized by air injection at the lower end of the cooler. This injection may be also used, within some limits, for

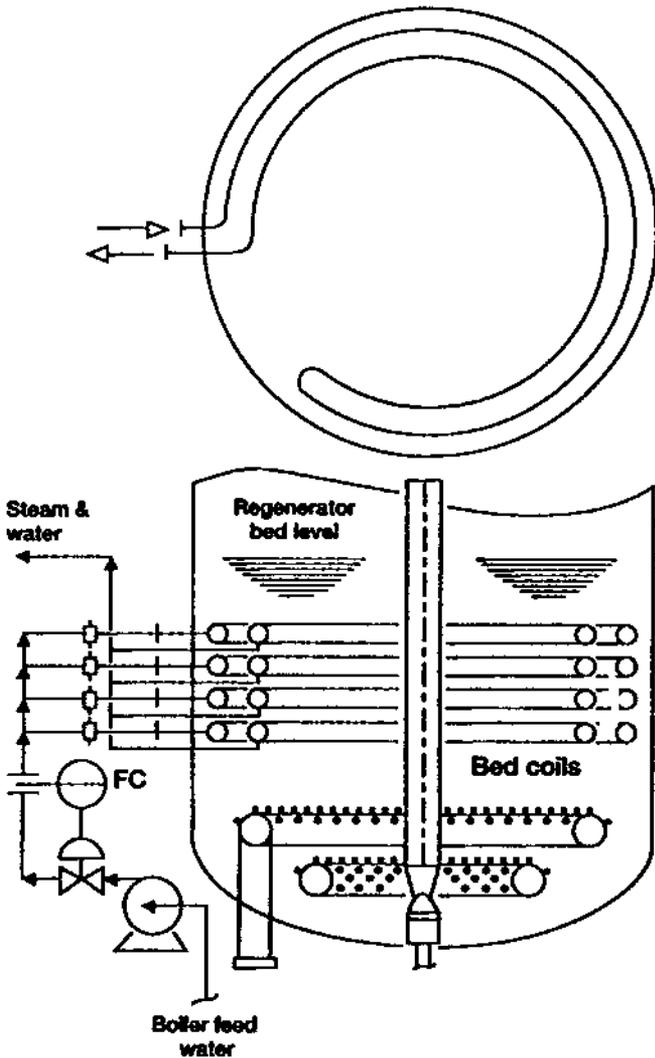


Figure 7.32 Cooling coil inside regenerator. (From Ref. 39.)

the control of the heat transfer. An increase of the air flow decreases the catalyst density but increases the heat transfer.

7.3.2.4 Two-step Regeneration

Catalytic cracking units with two regeneration steps were depicted in [Figures 7.19, 7.22, and 7.25](#).

These systems make it possible to reach residual coke concentrations below 0.05 wt %, even during the cracking of heavy residues that generate a large percentage of coke [33].

The hydrogen present in the coke burns in the first regeneration step. Therefore, in the second step there is no steam present and the temperature can

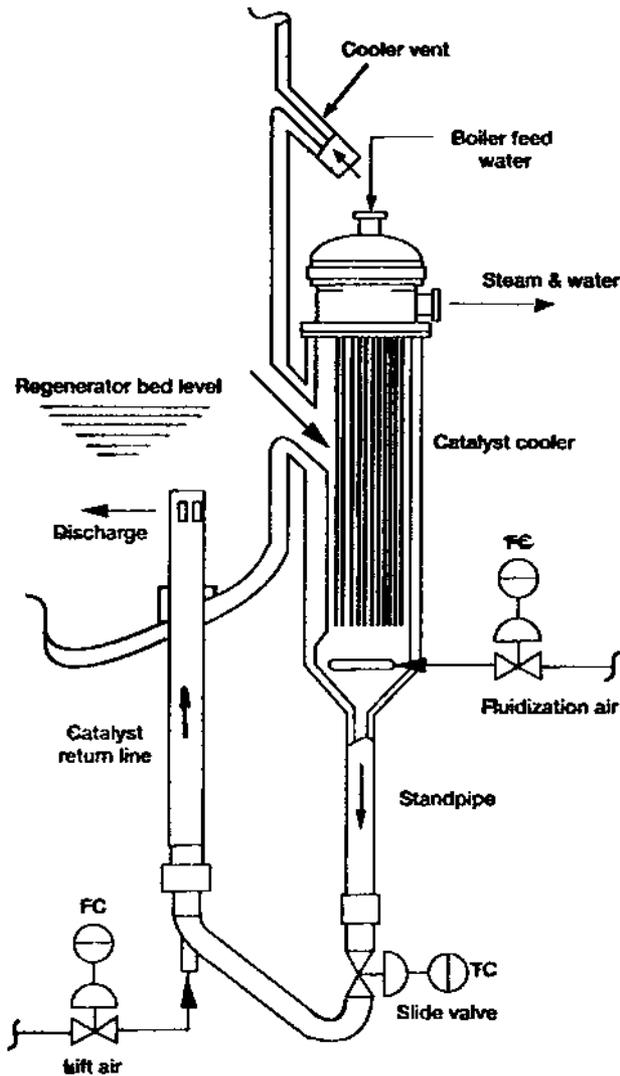


Figure 7.33 Regenerator external cooler. (From Ref. 39.)

reach 850–900°C without danger of destroying the catalyst since, in absence of steam, the main culprit for catalyst deactivation, vanadic acid, is not formed. At these temperatures the reaction rate is increased greatly so that coke burning is complete at short contact times in regenerators of the riser type, where the back-mixing is virtually absent (Figure 7.19).

The pattern of catalyst circulation in the regenerator is of importance. In the first regeneration step, the preferred pattern is one in which the air flows countercurrent to descending catalyst. In this manner, the strongly coked catalyst does not come into contact directly with the fresh air and thus, local uncontrolled combustion and overheating of the catalyst particles are prevented. The influence of the flow pattern on the increase of the temperature of catalyst particles is plotted in Figure 7.34 [40].

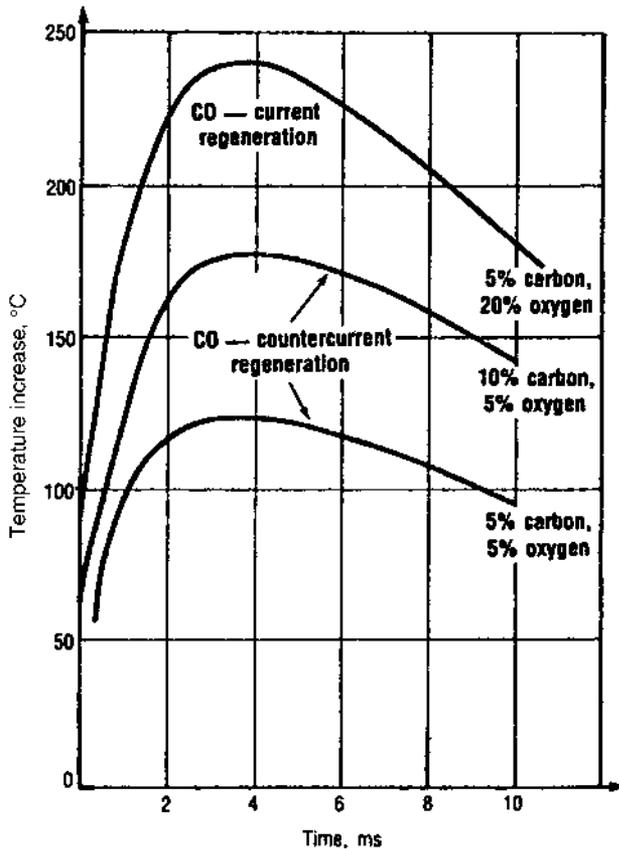


Figure 7.34 Effect of catalyst circulation pattern on the temperature increase of catalyst particles. (From Ref. 40.)

7.3.3 Future Outlook

The information on the reaction/regeneration systems presented above is the basis for ideas on possible directions for the future development of this technology. These ideas are generally accepted by the people involved in the development, design, and operation of catalytic cracking units [36].

Reactors having the overall structure of a riser, but in which the catalyst and feed flow cocurrently downwards, will completely eliminate the back-mixing and stagnation zones. In these conditions, a shorter reaction time can be achieved, since the vapor flowrate can be varied independent of the catalyst flowrate. Since in these conditions the diameter/height ratios become impractically high, it will become beneficial to use a series of parallel “risers” with descending flows, which will be fed with a variety of streams submitted to catalytic cracking.

The concept of using two steam injection points in the stripper will be maintained. The first steam injection immediately downstream of the catalyst entry line,

will displace most of the product vapors between the catalyst particles. The second steam, at the exit of the catalyst from the stripper will remove product adsorbed on the catalyst particles as completely as possible.

The design of the regenerator must ensure the initial combustion of the coke in mild conditions by using only 10–15% of the incoming air. This may occur in the catalyst transport line. It will be followed by as complete combustion of the coke as possible. A regenerator containing a diluted catalyst phase over its whole length is preferred for this duty.

These ideas were concretized by J. R. Murphy [36] in the scheme of Figure 7.35.

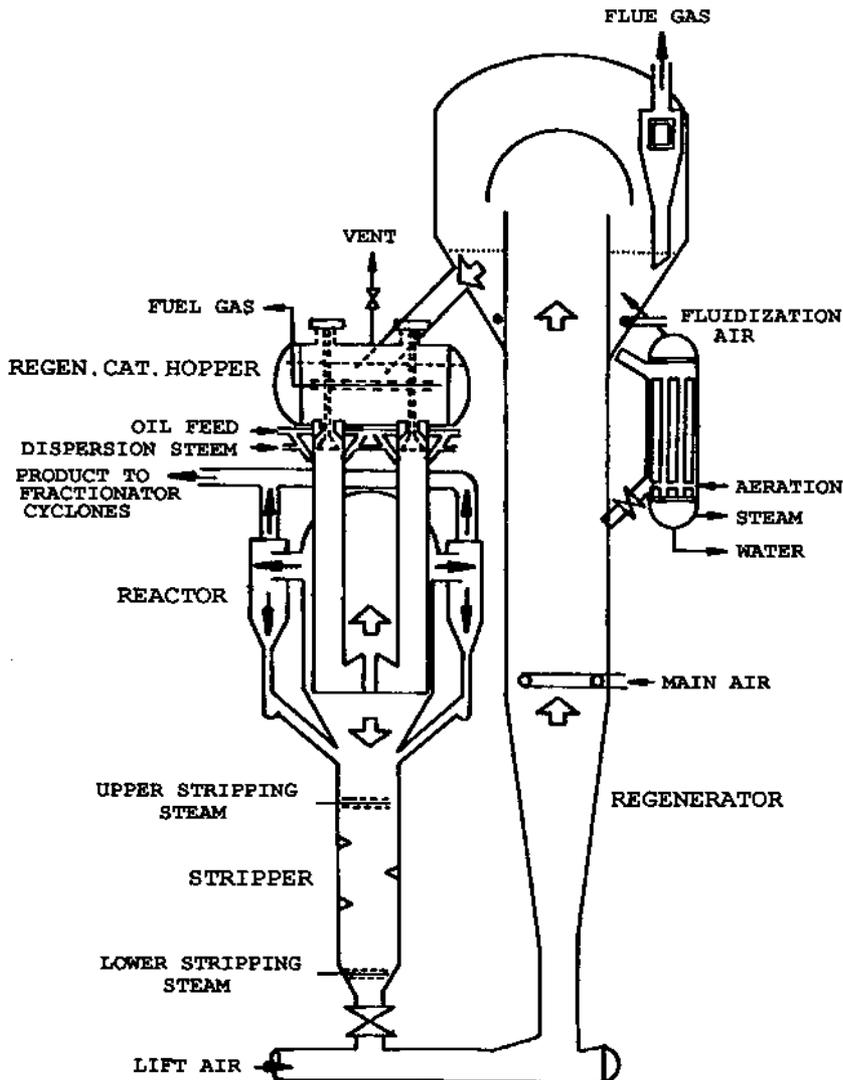


Figure 7.35 D.R. Murphy concept for a future catalytic cracking unit. (From Ref. 36.)

7.3.4 Energy Recovery from Flue Gases and Emissions Control

The energy recovery from flue gases by the means of expansion turbines requires an additional stage for the recovery of traces of catalyst situated after the regenerator (Figure 7.36), called the third separation stage.

Today's popular separator (Figure 7.37) was designed and patented by Shell Oil Co., UOP and M. W. Kellogg Co. The main feature of the separator is the tubes, which cause a sudden change of the direction of flow by 180°, thus producing the inertial separation of the gas from the catalyst particles. The number of tubes varies between 50 and 150 depending on the size of the unit [42].

Another option is the use of classical cyclones with large diameters. The high temperature of the flue gases leads to protecting with refractory material the walls of the cyclones.

The expansion turbine, which serves as a compressor for the air used in the regeneration, is located following the last separation step. Downstream of the turbine are located the heat recovery and the purification of the flue gases prior to their release in the atmosphere.

The operation of the turbine-compressor system are the object of specialized papers [43]. Their discussion exceeds the framework of this book.

The degree of purity of the flue gases is determined by the regulations imposed in each country for the protection of the environment. Some of the limit concentrations are given for several countries in Table 7.13. The table shows that the acceptable concentrations are different in the various countries, but in all the cases the standards become more restrictive with time.

Chevron [44], Exxon [45] and other refiners have published designs for the purification of flue gases resulting from catalytic crackers. The latter [45] gives interesting details concerning contacting systems for the neutralization of acid gases with NaOH and for the elimination of solid particles. The principle is to use venturi contac-

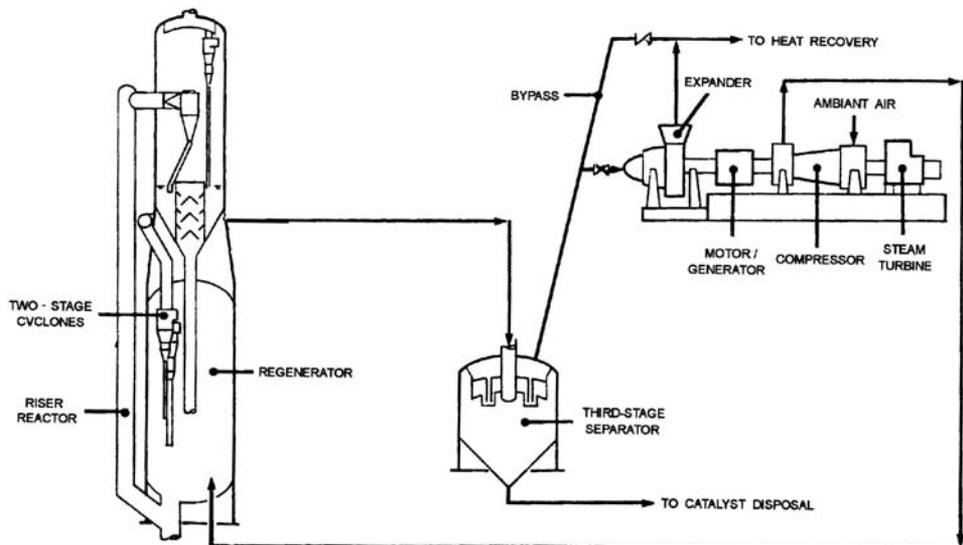


Figure 7.36 Ultra-Orthoflow. Energy recovery from flue gases. (From Ref. 41.)

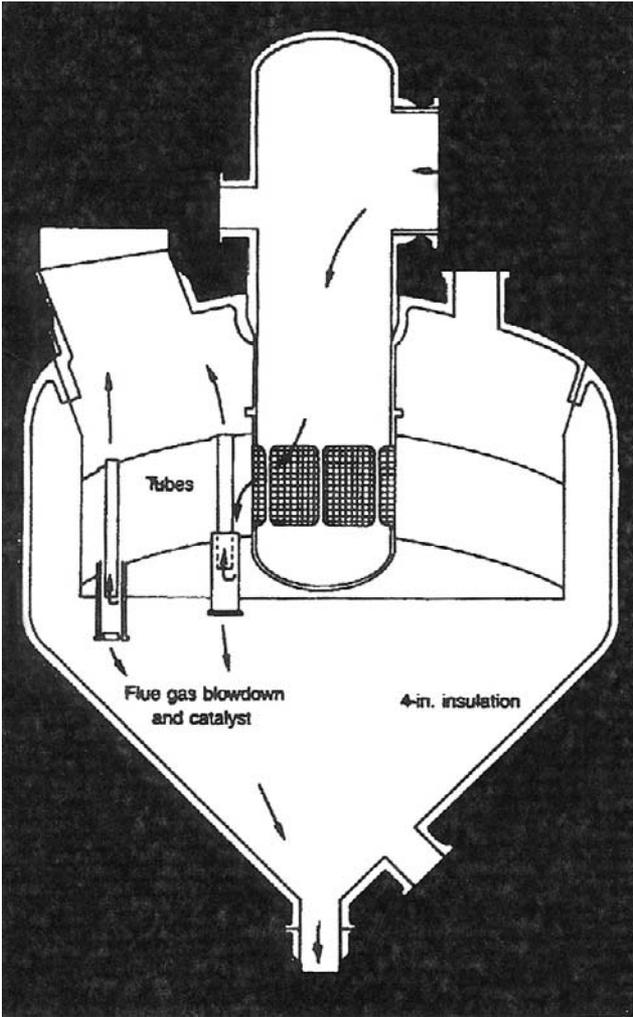


Figure 7.37 External third separation stage. (From Ref. 40.)

tors where the pulverized liquid retains the solid particles and neutralizes the acid gases.

Such a system removes 93–95% of the SO_2 and 85% of the catalyst dust. Excellent efficiency is also achieved in the elimination of nitrogen oxides [83,84] and hydrocarbons.

7.3.5 Products Recovery; Process Control

Product recovery equipment is designed with specific features as a consequence of the high temperature and low pressure (slightly above the atmospheric) at which the effluent leaves the reactor. The temperature in the vaporization zone is lowered by recycling the cooled product recovered at the bottom of the column and means of several interval refluxes, which discharge the thermal load in the upper part of the

Table 7.13 Regenerator Flue Gas Pollution Limits (g/Nm³)

Country	SO _x	NO _x	Dust
U.S. 1970	4.50	0.00	0.150
U.S. 1990	0.90	0.00	0.100
California 1995	0.06	0.06	0.006
Germany 1991	1.70	0.70	0.050
Germany 1995	0.50	0.50	0.050
Japan	0.90	0.50	0.040

fractionating column [46,47]. The heat of the reactor effluent is best utilized if it enters the fractionation column in its lowest section.

The configuration of a typical fractionating column and that which resulted following its thermal optimization are sketched in [Figure 7.38](#) [47].

The separation of gases is performed by adsorption-fractionating using classical methods.

Much attention is given to the control of the fractionating system in order to ensure in all cases the proper processing of all products that leave the reactor [48]. This issue, as well as the control of the compression of the air for the regenerator [43], exceed the scope of this book.

In several studies, the operating parameters of the fluid catalytic cracking units are correlated with the help of computers, in order to achieve optimization of the process [49,50,88]. The problem seems to be extremely complex. Even before a complete solution was found, several ways were identified for improving the operation of existing units [50].

Of special interest is the processing of the product at the bottom of the fractionating column. Normally, it was separated in two layers by settling: the upper layer of free catalyst particles (the decant oil) was used as a component for hearth fuels or as raw material for the production of carbon black. The lower layer was recycled to the reaction system in order to recover the catalyst it contained.

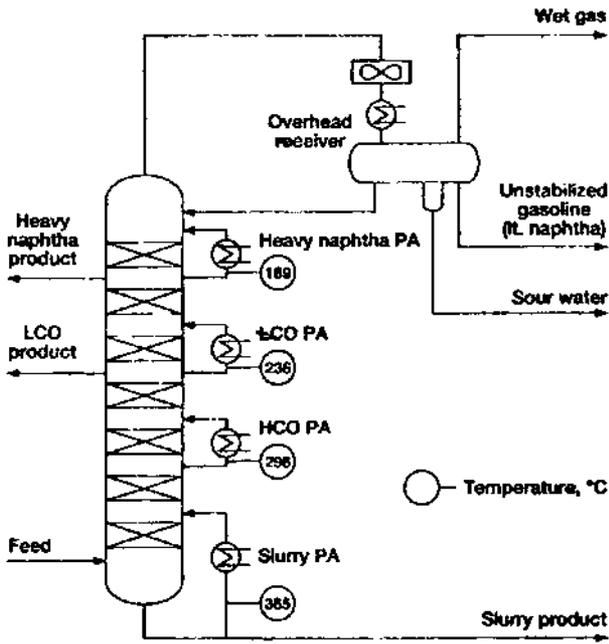
The bottom product has a strong aromatic character and, its recycling decreases gasoline yield. To avoid this disadvantage, starting in 1979 the electrostatic separation of catalyst particles was studied and improved, which eliminated the requirement for recycling [51].

The system is very efficient; two oils with ash contents of 1.22% and 1.89% respectively, after electrostatic separation had ash contents of 46 ppm and 85 ppm respectively.

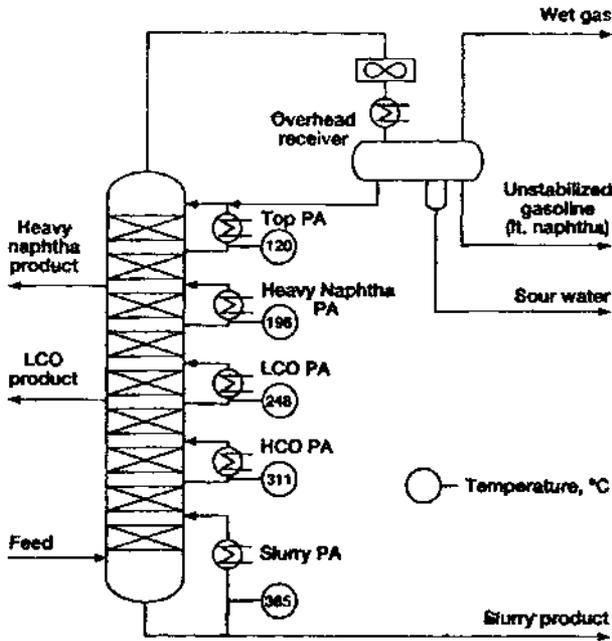
The aromatic character of the recovered oil and the significant amounts recovered by electrostatic separation suggest that recovered oil could be an excellent raw material for needle coke, either by itself or in a mixture with heavy coking gas oil.

7.4 OPERATION ASPECTS

Three specific aspects related to fluidized bed catalytic cracking will be discussed: the maintenance of catalyst properties, equipment erosion, and the quality of fluidization.



(a)



(b)

Figure 7.38 Catalytic cracking fractionation column. (a) before, (b) after revamping.

7.4.1 Maintenance of the Catalyst Properties

The maintenance of adequate activity and physical characteristics of the catalyst inventory is not limited to the control of the general phenomena of aging and poisoning by metals, which are common to all catalytic systems and which were discussed in Section 6.5.5.3. In the fluidized bed systems, maintenance of the size characteristics and of the particle size distribution are necessary for good fluidization and for not exceeding the admissible entraining losses through the cyclones. Besides, in view of the high cost of the catalysts it is important to have catalysts with high resistance to attrition so as to decrease mechanical losses.

The particle size distribution of the microspherical catalysts used presently in fluid catalytic cracking units is characterized by a Gauss curve having a maximum corresponding to diameters between 60 and 80 μm . It is important that the form of this curve should correspond to a minimum content of particles below 40 μm and especially below 20 μm , while the particles with diameters above 140 μm should be completely absent, since they have a negative effect on the quality of the fluidization [52].

A typical distribution of the sizes of the catalysts particles [53,54] corresponds to a content of below 15 wt % for particles below 40 μm , of 30–35% below 60 μm , about 60 wt % below 80 μm and of about 80 wt % below 100 μm .

Over time, the size repartition of the catalyst will change as result of the catalyst losses, which affect especially the particles below 40 μm , and of the shrinkage and attrition suffered by the particles. These losses are compensated by the addition of fresh catalyst, the size of which is selected in order to maintain the size distribution, indicated above as being necessary for a good quality of fluidization.

The shrinkage phenomenon and the attrition were studied [55] by taking into consideration the following size fractions expressed in microns: 0–10, 10–20, 20–40, 40–60, 60–80, > 80.

For any one of these fractions, the equations describing the shrinkage were written assuming that the kinetics of the process is of the 1st order, and the variation of its rate constant with the temperature may be expressed by the Arrhenius equation. The shrinkage was characterized by the fraction of particles which remained unchanged after the shrinkage:

$$F = \frac{W}{W_0} \quad (7.3)$$

where W is the amount of the size fraction remaining after shrinkage, and W_0 the added amount.

The time was expressed by the age of the catalyst, θ , given by the ratio between the inventory of catalyst within the system and the amount of catalyst that is added per day.

Using these notations, the shrinkage equations become:

$$-\frac{dF}{d\theta} = k_T F \quad (7.4)$$

$$F = e^{-k_T \theta} \quad (7.5)$$

$$k_T/k_{T_0} = e^{E(1/T_0 - 1/T)} \quad (7.6)$$

where k_{T_0} has the value of 0.00693 at $T_0 = 992 \text{ K}$, k_T is measured at temperature T and $E = 5,944$. The temperature is expressed in K.

For erosion the calculation may be carried out only for the fractions above 40 μm .

The attrition is described by an expression identical to (7.3) but where W_0 expresses the weight of the 40 μm fraction of the added catalyst W is the weight of the 40 μm fraction remaining after attrition.

The erosion process being of the 1.5 order it will be expressed by the equations:

$$-\frac{dF}{d\theta} = kF^{1.5} \quad (7.7)$$

$$F = \left(\frac{2}{2 + k\theta} \right)^2 \quad (7.8)$$

The rate constant k is independent of the temperature and has the value $k = 0.00828$.

On basis of equations (7.3–7.8) the graph of Figure 7.39 was plotted.

Equations (7.3)–(7.8) are expected to be valid also for other catalysts than those studied in 1981 [55]. The two rate constants k_{T_0} and k have to be determined for each individual catalyst.

7.4.2 Equipment Erosion

The equipment erosion caused by the catalyst particles depends on their velocity, diameter, and density. Depending on these parameters, the erosion may be correlated by the empirical equation:

$$\text{Erosion} = C \cdot \gamma_a^2 \cdot d^3 \cdot v^3 \quad (7.9)$$

where:

C = constant

γ_a = density of the particles in g/cm^3

d = their mean diameter in μm

v = velocity in m/s .

As a result of the correlation of the experimental data, Eq. (7.9) was written as [54]:

$$\text{Erosion} = C \cdot D^3 \cdot \gamma_v^2 \cdot v^3 (E/D^2)^{0.36} \quad (7.10)$$

where:

D = mean weighed diameter of the fractions with diameters above 40 μm ,
or corresponding to 50% of these fractions, in μm

γ_v = bulk density of the catalyst

E = erosion of a standard catalyst of a refractory standard material in
wt %, determined according to the Engelhard method

v = velocity in m/s .

Without knowing the values of the constant that intervene in Eqs. (7.9) and (7.10), or the values that are not available such as E , they may be used with success for determining the effect modifying some parameters on the erosion of the equipment. Thus, if the bulk density of the equilibrium catalyst increases from 0.82 to 0.92, and the mean diameter of the particles from 0.70 to 0.76, the rest of the parameters remaining the same, the erosion will increase by 52%.

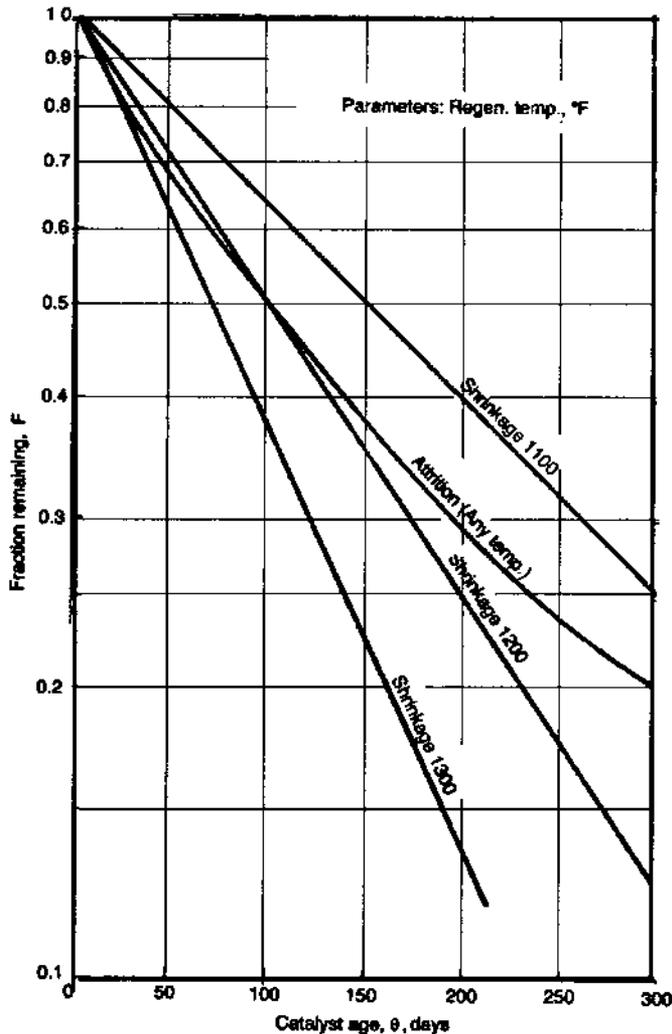


Figure 7.39 Shrinkage and erosion of catalyst particles above 40 μm . (From Ref. 89.)

The shape of the particles has a large influence on the erosion. Particles with a wholly irregular form, as those which result from the crushing operation cause in identical conditions, erosions about 10 times larger than those of spherical shape. Even the degree to which the surface of the spheres is or not smooth influences the erosion. Thus, the equilibrium catalyst which has a rougher surface on the balls, provokes stronger erosions than the fresh catalyst.

These influences are manifested in the value of the constant C in Eqs. (7.9) and (7.10), but do not affect the form of the equations.

The regions strongest affected by erosion are the outlet from the riser and the inlets to the first cyclone of the reactor and of the regenerator [85]. In the regenerator itself, the erosions are very reduced, because the linear velocities are below 1.5 m/s.

In order to avoid erosion, it is recommended [37] that the velocities in the two steps of the reactor cyclones should not exceed 18 m/s, 18.5 m/s in the first cyclone step of the regenerator while in the second step, 23 m/s. Similar values are recommended in other publications [54]. But also recommendations exist [56] to use higher velocities, of up to 28 m/s in the inlet of the cyclones if modern refractory materials of high resistance are used. While such velocities lead to a more efficient operation of the cyclones, the erosions become stronger.

Also, other parts of the equipment of the unit are submitted to erosion, which imposes the prescription of maximum pressure drops, in those locations where exceeding them may lead to abnormal erosions. Such prescriptions are:

The control valves for the catalyst flow	41 kPa
The valves for pressure control	103 kPa
The nozzles of the regenerator distributor grate through which also the catalyst flows	7 kPa
The nozzles of the regenerator distributor grate, when through them only the air passes	21 kPa
The nozzles of the reactor grill	14 kPa

The pressure drops shown for the grill nozzles do not eliminate the erosion of the catalyst particles.

In the case of feeds containing above 0.5% sulfur, the erosion effects are combined with those of the corrosion, which requires the use of alloyed steels with 12% Cr at reduced sulfur content and 18/8 Cr-Ni at higher contents.

The use of the alloyed steels is recommended in the areas where the temperature exceeds 480°C in order to decrease the wear. The austenitic stainless steels, strongly alloyed, become compulsory in the areas where the temperature (in the regenerator) exceeds 650°C.

Details concerning the design of the equipment, the maintenance, and the periodic revisions are given in the paper of Luckenbach et al. [37].

7.4.3 Quality of Fluidization

A good fluidization is very important for obtaining optimal performances. Four states may be distinguished as air or vapors pass upwards through a layer of small catalyst particles: moving dense bed, fluidized bed, bubbling fluidized bed, transported diluted bed.

All these four states are used in the catalytic cracking. It is important to avoid operating in the intermediary domain between two states, because such a situation could lead to unstable operation of the unit. Thus, in the descendent pipes an excessive flow rate of the aeration fluid may produce bubbles which, in their ascending motion, could prevent the descent circulation with the necessary flowrate of the catalyst and eventually could block up the normal operation of the unit. Such blocking could be provoked also by an insufficient flowrate of the fluid in the ascending pipes.

It is desirable that in the ascending and descending pipes the catalyst particles should be in a fluidized state. However, if the aeration is not correct, the pressure drop in the descending pipes could lead to states close to settling in the lower portion and to the formation of bubbles in the upper portion of the pipe.

The key values that determine the selection of the working parameters are given by the following ratios and values, expressed by empirical equations [54]:

$$\frac{v_b}{v_i} = \frac{6.9}{(V_{80} - V_{40})^{0.2} \cdot [D + 0.5 \cdot V_{80}/100]^{3.6}} \quad (7.11)$$

$$\tau_B = \frac{38}{[(D + 0.5 \cdot V_{80})/100]^{6.8}} \quad (7.12)$$

where:

V_i and V_b are the fluid velocities in m/s at which the fluidization and the bubbling begins respectively,

V_{80} and V_{40} = volume % of catalyst particles with sizes below 80 μm and 40 μm respectively

D = mean weighed diameter of the fractions with diameters above 40 μm , or corresponding to 50% of these fractions in μm

τ_B = blocking time by settling from a rate of the fluid through the bed of 10 cm/s in s/m of bed (the reverse phenomenon to aeration)

The values given by the Eqs. (7.11) and (7.12) may be directly measured in the laboratory using samples of equilibrium catalyst from the unit.

Equation (7.11) shows that the ratio v_b/v_i will increase and thus the fluidization will be better as the fraction of catalyst particles with diameters below 80 μm will be larger. This confirms the observation that the larger particles worsen the quality of fluidization. By increasing the v_b/v_i ratio, the situation is reached that in the conditions of the dense phase process, no large fluid bubbles are formed or only small bubbles are formed, which ensure good conditions for the process of chemical transformation.

According to Eq. (7.12), the increase of the fraction of particles with diameters below 80 μm decreases the duration for blocking by settling of the particles, which is a disadvantage for the transport pipes.

One should note that the density of the particles is not present in Eqs. (7.11) and (7.12), which means that it does not influence the quality of fluidization.

7.5 CATALYST DEMETALLATION

The demetallation of the spent catalyst may be performed continuously in a separate unit, attached to the catalytic cracking unit. The result is the decrease of the metal content of the equilibrium catalyst, the decrease of the amounts of fresh catalyst addition, and the improvement of the unit yields. Its performance become similar with those obtained with hydrofined feed.

The demetallation processes, which address especially the nickel and the vanadium, are based on a large number of studies that proposed a number of possible routes: extraction of the previously oxidized metals by means of organic acids; various acid–basic treatments; chlorination, which allowed the partial extraction of nickel; treatment with CO etc. In the same time studies were carried out on the removal of sodium from the catalyst [57].

As a result of these studies the processes MET-X [58–60] and DEMET [51–63] were developed.

The emergence of passivators, which are a solution much easier to implement and did not require any supplementary investments, caused a substantial reduction in the interest in demetallation units and even opinions were expressed that demetallation technologies had been surpassed [64].

However, they reappear under an improved form in 1989–1990 [65–69], a period where the construction of two industrial units was announced [69], of which the second one, for 20 t/day (Wichita, Kansas, U.S.) was directly coupled to a fluid catalytic cracking unit. The investment cost for this unit was \$7.4 million and the exploitation costs of \$130 per ton of treated catalyst.

The process flowsheet is shown in Figure 7.40 [69].

The efficiency of the demetallation is about 75% for nickel and of 46% for vanadium. At the same metal content in the catalyst, no differences are observed in the yields in products between the approaches of maintaining of a constant metal content by demetallation, versus the addition of fresh catalyst.

However, the order and use of the demetallation processes are of concern especially for the following reasons:

There is no data on the possible influence of demetallation on the metals used as promoters.

Technology for catalyst production and its characteristics advance very quickly and there is no insurance that the new catalysts will resist the treatments of demetallation or that they will be efficient.

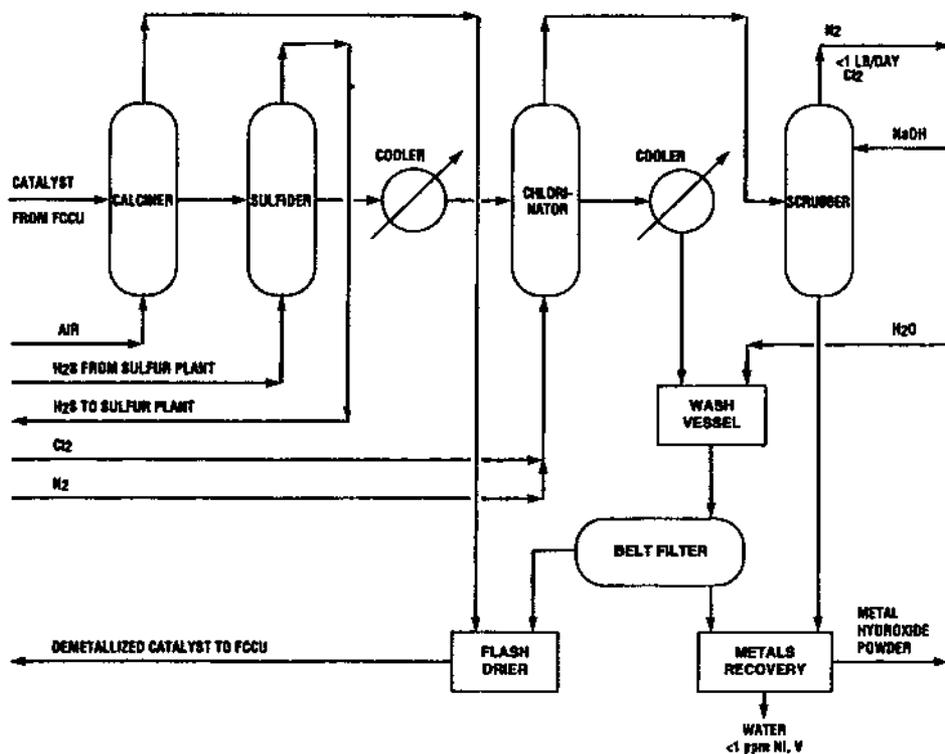


Figure 7.40 Catalyst demetallization plant. (From Ref. 69.)

The experience of industrial use of the process is too short for the formulation of reliable conclusions concerning the duration in exploitation and efficiency of the catalyst.

7.6 YIELD ESTIMATION

Methods for the estimation of yields from processes with moving bed of catalyst and for classical processes of fluid catalytic cracking on alumo-silica catalysts are given in a study by Raseev [4]. Also, other graphs for quick calculations of a more specialized interest were published [70].

For modern units using zeolite catalysts and distilled feeds, the graphs for the estimation of the yields and of the product qualities are given in Figures 7.40–46 [71]*.

On the basis of feed density and K_{UOP} , the UOP characterization factor indicated on the curves of the graphs and of the selected conversion, the estimation of the yields is effected in the following way:

1. From Figures 7.41 and 7.42 the wt % coke and fuel gases are obtained.
2. From Figures 7.43 and 7.44 the C_3 and C_4 components in vol % are obtained. The total LPG must be adjusted, as shown by Figure 7.45 using the feed K_{UOP} characterization factor.

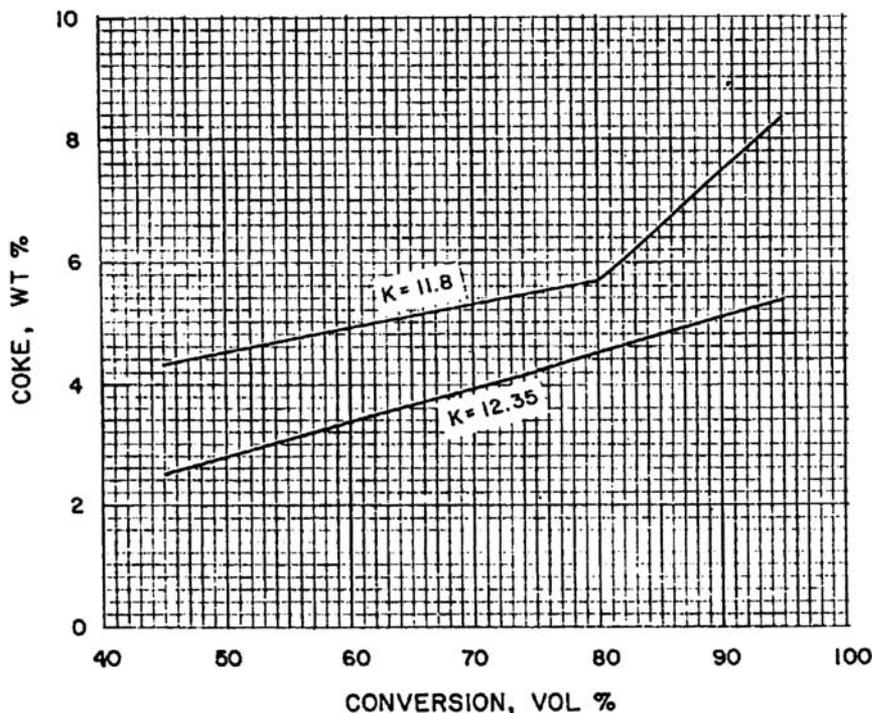


Figure 7.41 Coke yields on zeolite catalyst. (From Ref. 71.)

*The graphs for amorphous catalysts given in the same work [71] are not reproduced here.

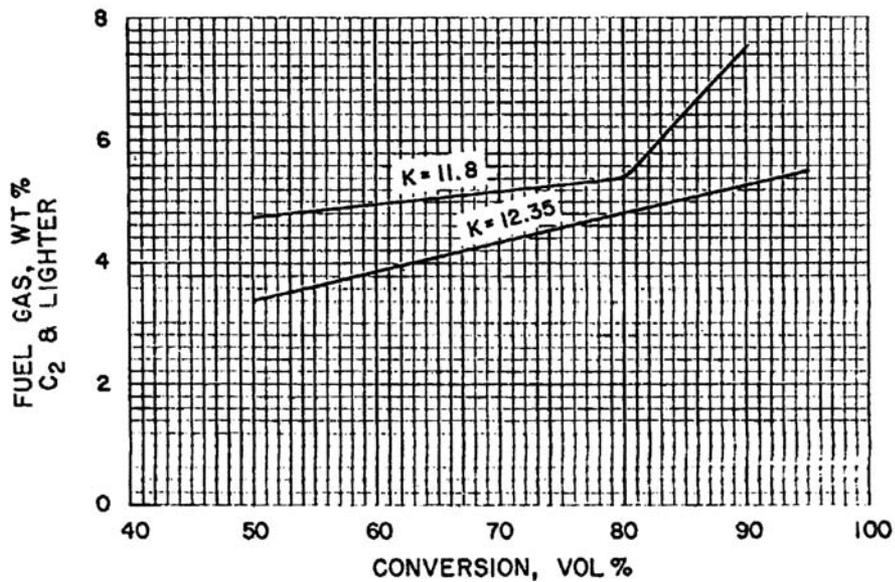


Figure 7.42 Fuel gas yield on zeolite catalyst. (From Ref. 71.)

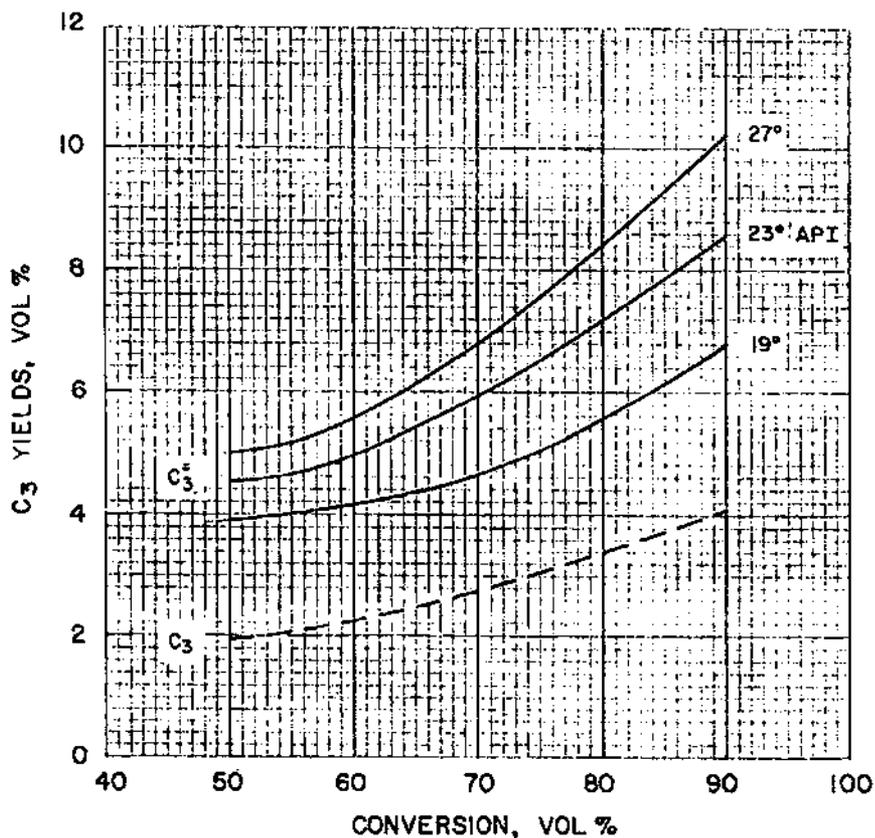


Figure 7.43 Propane and propene yields on zeolite catalyst. (From Ref. 71.)

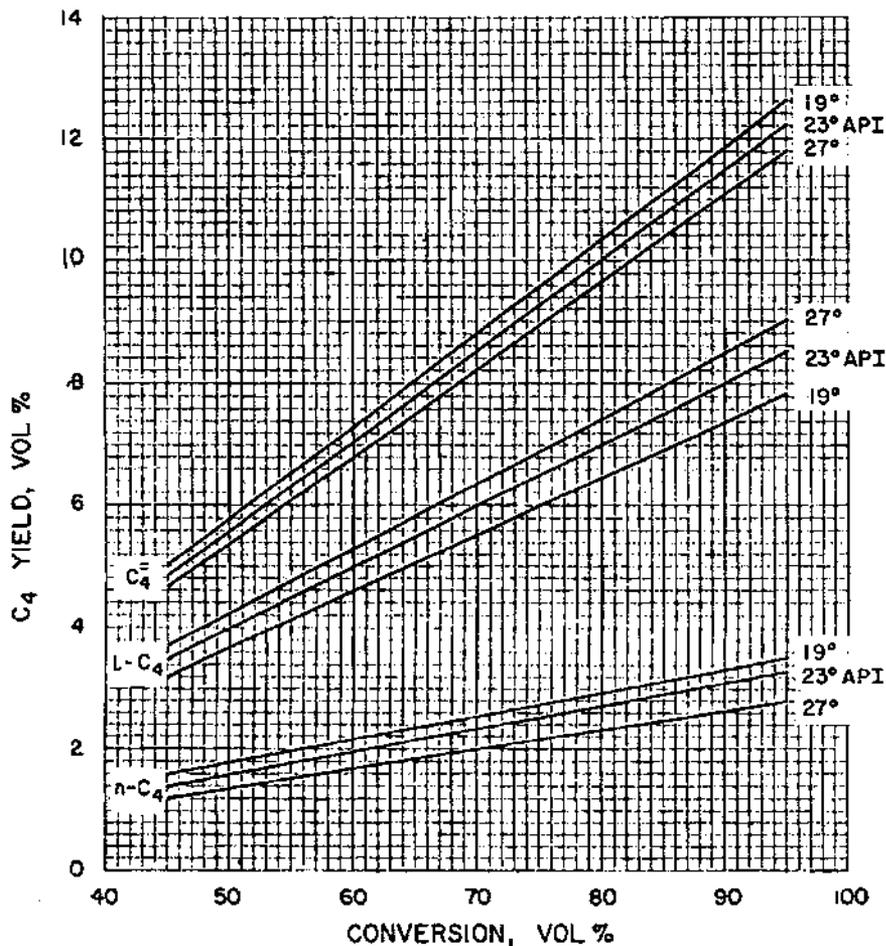


Figure 7.44 Butane, *i*-butane and butenes yields on zeolite catalyst. (From Ref. 71.)

3. From Figure 7.46, C_5^+ gasoline yield in vol % is obtained.
4. Figures 7.47 and 7.48 give all products repartition in vol % and give the yields of light and heavy gas oil.
5. Figure 7.49 gives the sulfur distribution in the products. Figure 7.50 gives the gasoline and the gas oil densities for vol %, wt % calculations.

Software allowed estimation of yields, so that a larger number of parameters may be taken into account than in a graphical calculation [72–74]. But it must be mentioned that works [37] that developed these methods of calculation recommend using graphic methods from Figures 7.41–7.50 for a first approximation.

7.7 ECONOMIC DATA

The investments in a fluidized bed catalytic cracking unit of 1,150,000 m³/year, processing a feed that gives 5.5% coke, was estimated at year-end 1983 to be [75]:

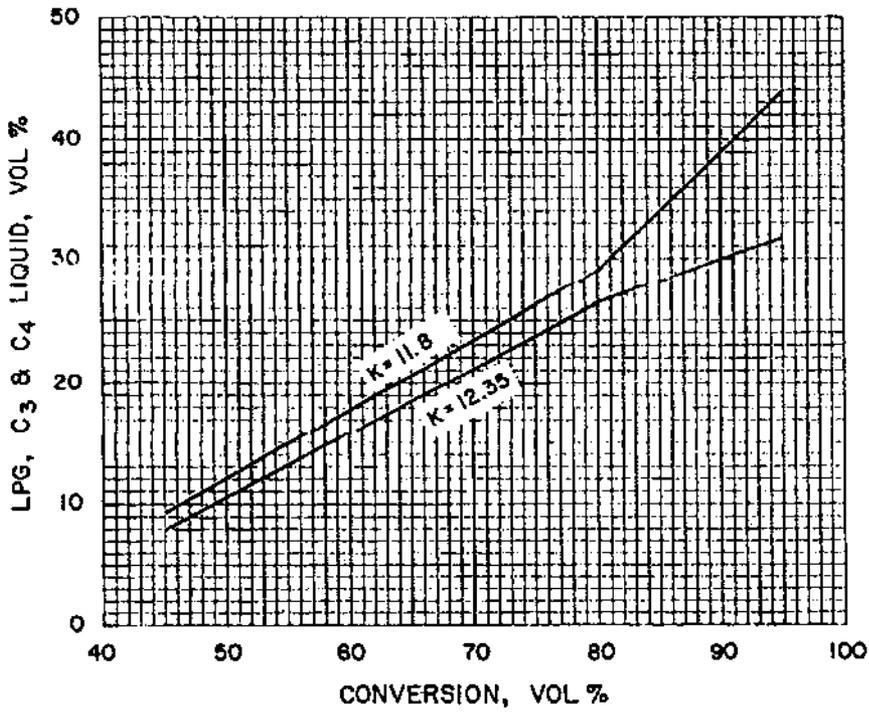


Figure 7.45 Total LPG yield on zeolite catalyst. (From Ref. 71.)

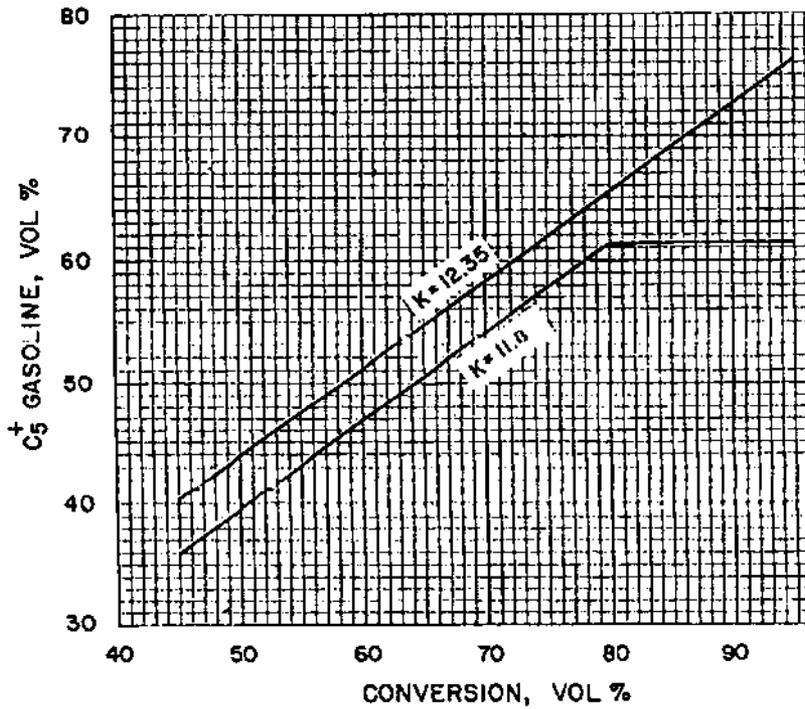


Figure 7.46 Gasoline yield on zeolite catalyst. (From Ref. 71.)

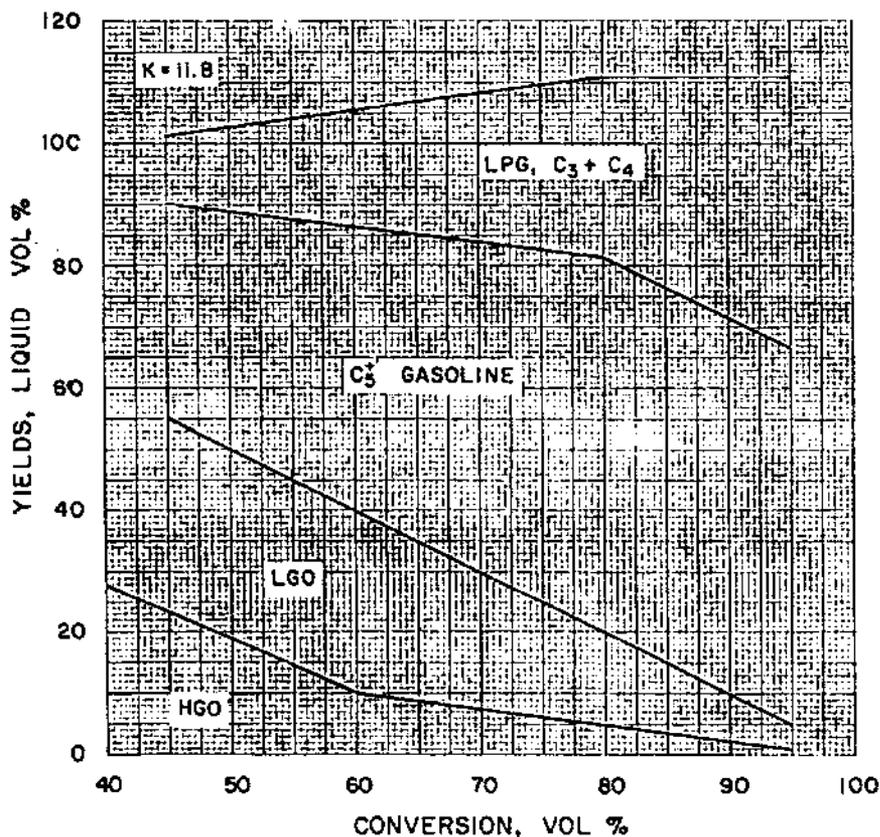


Figure 7.47 Products distribution on zeolite catalyst. Feed $K_{UOP} = 11.8$. (From Ref. 71.)

Catalytic cracking + gas concentration	31.0 million \$
Catalytic cracking + concentration of gases and gases recovery	37.5 million \$
Catalytic cracking, gas concentration, energy recovery, and electrostatic precipitation	38.5 million \$

The authors estimate that depending on stable conditions the investment could vary within $\pm 30\%$.

Other authors supplied concurring data in 1992 [71] giving the investments depending on the capacity of the plant (Figure 7.51). The investments from the graph contain, besides the system reactor-regenerator, also the fractionating of the products: the compression of the gases with the recovery of 95% C₄ and 80% C₃, the heat exchange and the cooling of the products to the surrounding temperature, and the central control system.

The utilities consumption in two alternatives with and without energy recovery is given in the Table 7.14 [75].

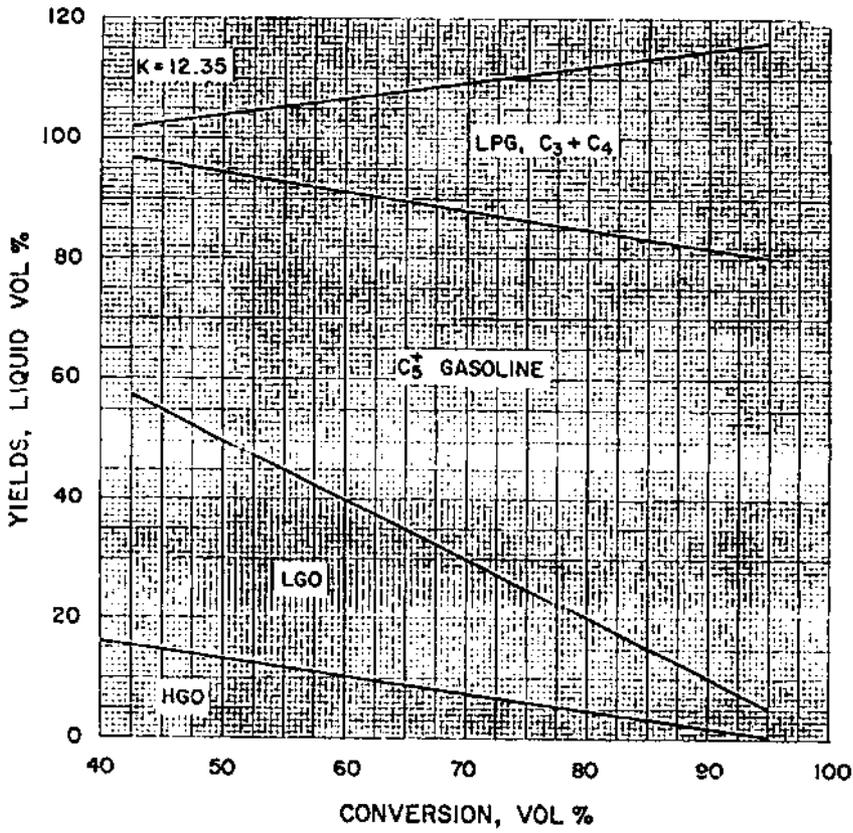


Figure 7.48 Products distribution on zeolite catalyst. Feed $K_{UOP} = 12.35$. (From Ref. 71.)

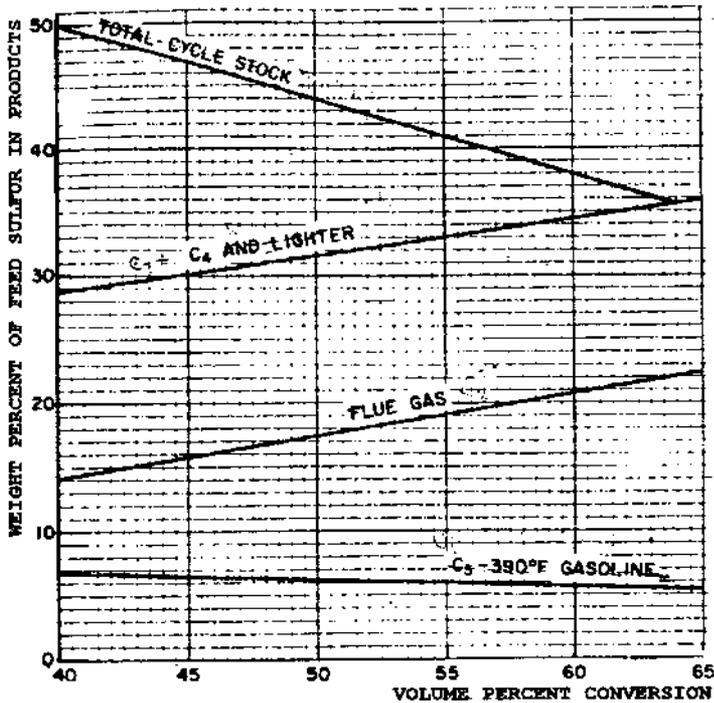


Figure 7.49 Sulfur distribution in products. (From Ref. 86.)

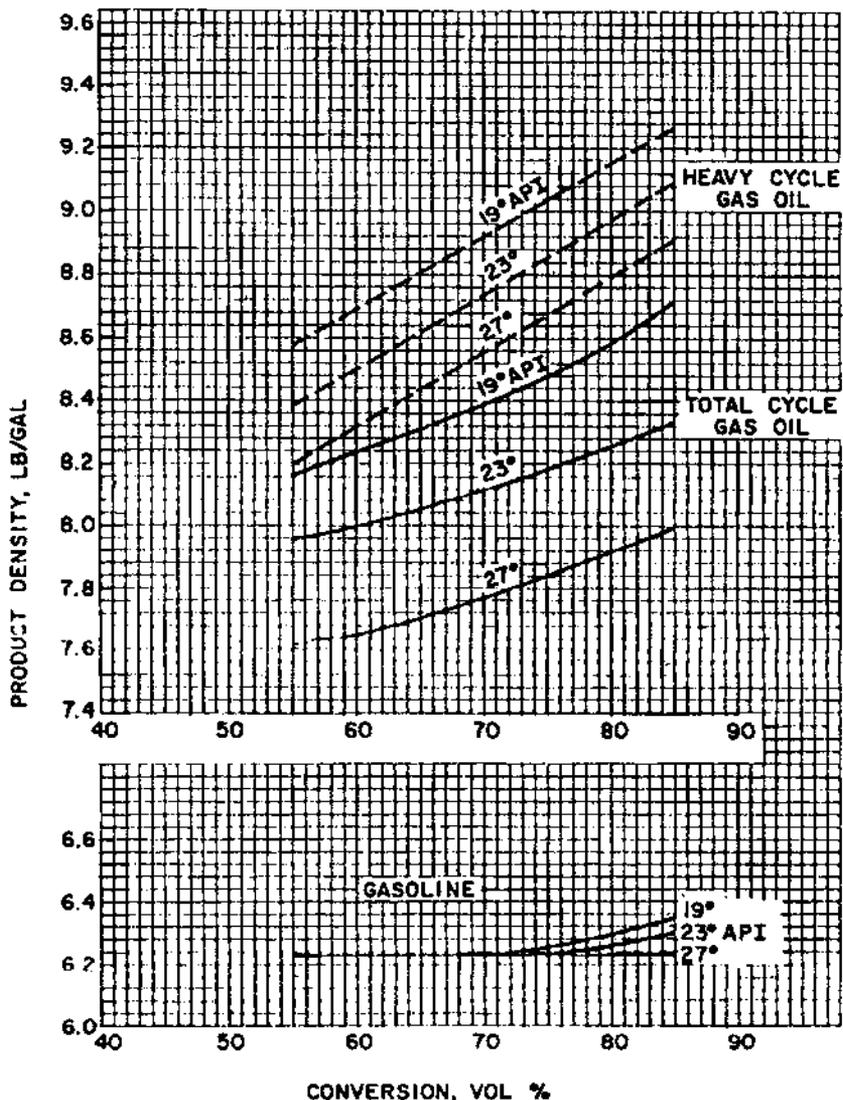


Figure 7.50 Densities of catalytic cracking gas oil and gasoline. (From Ref. 71.)

Taking into account more severe measures taken during recent history for the protection of the environment, investment and operating costs corresponding to the various measures that could be considered were studied [76]. Since these costs depend on regulations from the respective country, they are not presented here.

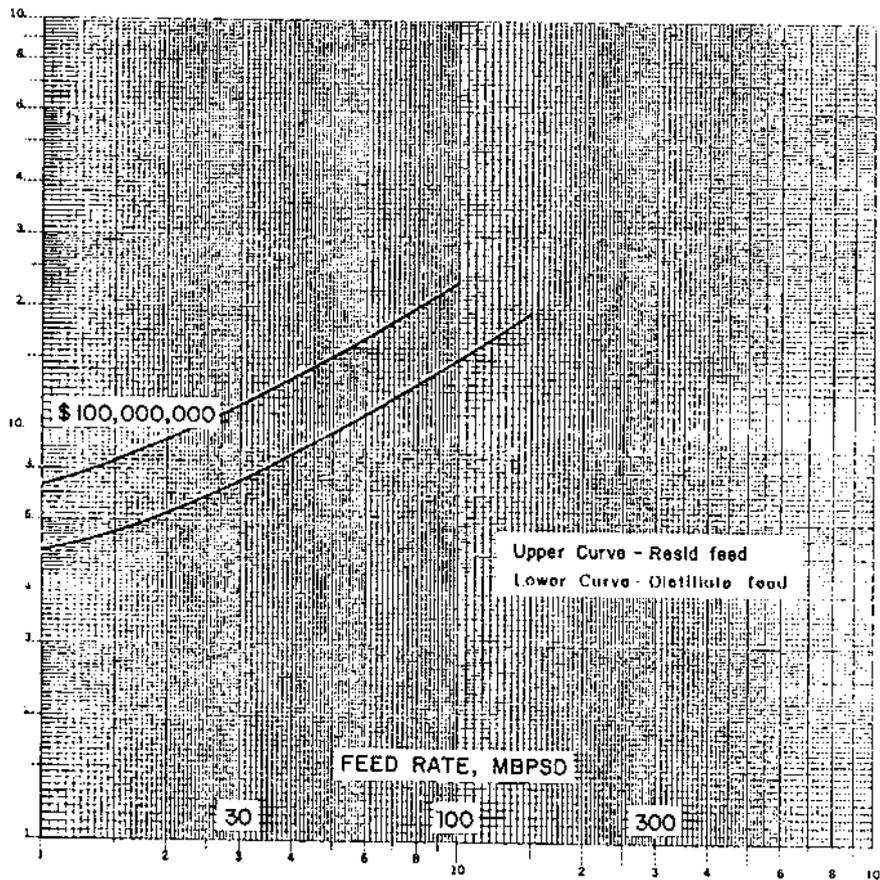


Figure 7.51 Investment cost for fluid catalytic cracking unit, 1992 U.S. Gulf Coast.

Table 7.14 Utilities Consumption

Utilities	m ³ feed	With energy recovery*	Without energy recovery*
electricity	kWh/1000	-1900	7550
steam 42 bar	t/1000	34.30	91.40
steam 10.5 bar	t/1000	-40.00	-40.00
steam 3.5 bar	t/1000	6.60	6.60
demineralized water	t/1000	97.10	97.10
cooling water	t/1000	4.80	4.80
Catalyst consumption	kg	0.46	0.46

*Minus for energy production.

Source: Ref. 75.

REFERENCES

1. SV Golden, GR Martin. *Hydrocarbon Processing* 70: 69–74, Nov. 1991.
2. KV Krikorian, JC Brice. *Hydrocarbon Processing* 66: 63, Sept. 1987.
3. EC Herthel, EH Reynolds, JH Roe. *Oil and Gas J* 58: 86, 1960.
4. S Raseev. *Procese distructive de prelucrare a titeiului*, Editura Tehnica Bucuresti, 1964.
5. JF Le Page, SG Chatila, M Davidson. *Raffinage et conversion des produits lourds du petrole*, Technip Paris, 1990.
6. MJ Hunbach, DM Cepla, BW Hedrick, CL Hemler, HJ Niclaes. *UOP-Residue Conversion*. 1990.
7. JR Murphy. *Katalistiks*, Third Annual Fluid Catalytic Cracking Sym., Amsterdam, 1982.
8. GH Dale. *Heavy Oil Cracking*. In: *Proceedings of the 11th World Petroleum Congress*, vol. 4, 83. New York: John Wiley and Sons.
9. GE Weismantel. *Heavy Oil Cracking*. In: JJ McKetta, ed. *Petroleum Processing Handbook*. New York: Marcel Dekker, Inc. 1992.
10. DB Bartholic, RP Haseltine. *Development in Catalytic Cracking and Hydrocracking*. *Oil and Gas J*: 80, 10–13, 1982.
11. S Raseev, V Tescan, D Ivanescu. *Bull Inst Petrol, Gaze si Geologie* 18, 25, 1971.
12. BE Reynolds, EC Brown, MA Silverman. *Hydrocarbon Processing* 71: 43, 1992.
13. T Nguyen, M Skripek. *Hydrocarbon Technology International*. P Harrison, ed. London: Sterling Publ. Ltd 1993 p. 33–43.
14. GD Hobson. *Modern Petroleum Technology*. 4th ed. New York: John Wiley & Sons 1973, pp. 288–309.
15. SC Eastwood, CJ Plank, P Weisz. *Proceedings of the eighth World Petroleum Congress*, vol. 4. London: Applied Science Publishers, 1971.
16. AA Avidan, E Michael, H Owen. *Oil and Gas J* 88: 33, 8 Jan. 1990.
17. AD Reichle. *Oil and Gas J* 90: 41, 18 Mai 1992.
18. AA Murcia. *Oil and Gas J* 90: 68, 18 Mai 1992.
19. AA Avidan, R Shinnar. *Ind Eng Chem* 29: 931, 1990.
20. D Decroocq, R Bulle, S Chatila, JP Franck, Y Jacquir. *Le craquage catalytique des coupes lourdes*. Technip, Paris 1978.
21. AL Saxton, AC Worley. *Oil and Gas J* 68: 82, 18 Mai 1970.
22. P Wuithier. *Le Pétrole-Raffinage et Genie chimique*. Technip, Paris 1965.
23. AF Babicov, BZ Soliar, LS Glazov, JM Liberson, RV Basov, TH Melik-Ahnazarov, AV Elsin, VM Zarubin. *Himia Tehnol Toplivi Masel* 38: 9, 1993.
24. CW Strother, WL Vermilion, AJ Connes. *Oil and Gas J*. 70: 102, 15 May 1972.
25. FHH Khaw, GV Tonks, KW Szetch, ACC Van Els, A Van Hatten. *The Shell Residue Fluid Catalytic Cracking Process*. Akzo Catalysis Symposium, Scheveningen, Netherlands, May 1991.
26. AA Avidan. *Oil and Gas J* 90: 59, 18 May 1992.
27. CR Santner. *Hydrocarbon Processing* 69: 75, Dec. 1990.
28. FM Hibbs, O Genis, DA Kauff. *Hydrocarbon Technology International 1994*, P Harrison, ed. London: Sterling Publ. Ltd., 1994.
29. DA Lomas, CA Cabrera, DM Cepla, CL Hemler, LL Upson. *Controlled Catalytic Cracking*, UOP, 1990.
30. JR Murphy, EL Whittingen. *Development of Reduced Crude Catalytic Cracking Technology*. In: *Proceedings of the 11th World Petroleum Congress*, vol. 4. New York: John Wiley & Sons, 1990.
31. L Upson. *Hydrocarbon Technology International 1987*. P Harrison, ed. London: Gibbons Sterling Publ. Ltd., p. 53.
32. L Upson. *Hydrocarbon Processing* 66: 67, Sept. 1987.

33. JL Mauléon, G Heinrich. *Revue de l'Institut Français du Pétrole* 49: 509, 1994.
34. K Inai. *Revue de l'Institut Français du Pétrole* 49: 521, 1994.
35. DL Johnson, AA Avidan, PH Schepper, RB Miller, TE Johnson. *Oil and Gas J* 92: 80, 24 Oct. 1994.
36. JR Murphy. *Oil and Gas J* 90: 49, 18 May 1992.
37. EC Luckenbach, AC Worley, AD Reichle, EM Gladrow. *Cracking Catalytic*. In: *Petroleum Processing Handbook*, JJ McKetta, ed. New York: Marcel Dekker, Inc., 1992.
38. KE Londer, L Kulapaditharom, EJ Juno. *Hydrocarbon Processing* 64: 80, Sept. 1985.
39. TE Johnson. *Hydrocarbon Processing* 70: 55, Nov. 1991.
40. JL Mauleon, JB Sigaud. *Oil and Gas J* 85: 52, 23 Feb. 1987.
41. AD Scheiman. *Development in Catalytic Cracking and Hydrocracking*. *Oil and Gas* 53, 60–64, 1982.
42. HL Franzel. *Hydrocarbon Processing* 64: 51, Jan. 1985.
43. MCMC Campos, PSB Rodrigues. *Oil and Gas J* 91: 29, Jan. 11, 1985.
44. WA Blanton. *Development in Catalytic Cracking and Hydrocracking*. *Oil and Gas J* 53, 1982.
45. JD Cunic, R Diener, GE Ellis. *Hydrocarbon Technology International*. P Harrison, ed. London: Sterling Publ. Co., 1994, p. 49.
46. SW Golden, AW Stoley, PB Fleming, S Costanzo. *Hydrocarbon Technology International* 1994. P Harrison, ed. 1994, pp. 73–79.
47. SW Golden, AW Stoley, PB Fleming. *Hydrocarbon Processing* 72: 43, 1993.
48. G Rowlands, A Knouk, F Kleinschrod. *Oil and Gas Journal* 89: 64, Nov. 25, 1991.
49. H Dhulesia. *Refining and Petrochemical Technology Yearbook 1987*. Tulsa, Oklahoma: Penn Wellbooks, 1987, p. 241.
50. SS Elshishini, SSEH Elnashaie. *Chemical Engineering Science* 45: 553, 1990.
51. GR Fritsche, AF Stegelman. *Development of Catalytic Cracking and Hydrocracking*. *Oil and Gas Journal* 53, 1982.
52. J Scherzer. *Octane Enhancing Zeolitic FCC Catalysts*. New York: Marcel Dekker, Inc., 1990.
53. LL Upson. *Hydrocarbon Processing* 60: 253, 1981.
54. MA Murphy. *Oil and Gas Journal* 92: 54, Feb. 21, 1994.
55. RB Ewell, G Gadmer, WJ Turk. *Hydrocarbon Processing* 60: 103, 1981.
56. JL Mauleon. *Revamping of FCC Units*. Seminar on Fluid Catalytic Cracking, organized by Engelhard on Sept. 1989 at Brugge.
57. JE Boevink, CE Foster, SR Kumar. *Hydrocarbon Processing* 60: 123, Sept. 1981.
58. RJ Dilliplane, GP Middlebrooks, RC Hicks, EP Bradley. *Oil and Gas Journal* 61: 119, Aug. 5, 1963.
59. PT Atterding, J Hunible. *Hydrocarbon Processing and Petroleum Refining* 42: 167, Apr. 1963.
60. DH Stormont. *Oil and Gas Journal* 61: 89, Jan. 14, 1963.
61. RA Sanford, H Erickson, EH Burk, EC Gossett, SC Van Petter. *Hydrocarbon Processing* 41: 103, July 1962.
62. NR Adams, MJ Sterba. *Hydrocarbon Processing* 42: 175, May 1963.
63. NR Edison, JO Somessen, GP Masoligites. *Hydrocarbon Processing* 55: 133, May 1976.
64. C Marcilly. *Revue de l'Institut Français du Pétrole* 42(4): 481, 1987.
65. FJ Elvin. *Oil and Gas Journal* 85: 42, March 2, 1987.
66. FJ Elvin. *Hydrocarbon Processing* 68: 71, Oct. 1989.
67. FJ Elvin, SK Pavel. *Oil and Gas Journal* 89: 94, July 22, 1991.
68. FJ Elvin, O Pallotta. *Hydrocarbon Technology International* 1992, vol 51. P Harrison, ed. London: Sterling Publ. Int., 1992.

69. FJ Elvin, SK Pavel. 1993 NPRA Annual Meeting, Sept. 21–23, 1993. Convention Center, San Antonio, Texas.
70. BP Castiglioni. *Hydrocarbon Processing* 62: 35, Feb. 1983.
71. JH Gary, GE Handwerk. *Petroleum Refining Technology and Economics*, 3rd ed. New York: Marcel Dekker, Inc., 1994.
72. WL Pierce, et al. *Hydrocarbon Processing* 51: 92, May 1972.
73. EG Wollaston, et al. *Oil and Gas Journal* 73: 87, Sept. 22, 1975.
74. GWG McDonald. *Oil and Gas Journal* 87: 80, July 31, 1989.
75. DG Tajb. UOP Fluid Catalytic Cracking Process, published in *Handbook of Petroleum Refining Process*, RA Meyers, ed. New York: McGraw-Hill, 1986.
76. MJ Humbarch, DM Cepla, BW Hedrick, CL Hemler, HJ Niclaes. *Residue Conversion*, edited by UOP, 1990.
77. CW Stanger, R Fletcher, Jr., C Johnson, TA Reid. *Hydroprocessing/FCC Synergy*. *Hydrocarbon Processing* 75: 89–96, Aug. 1996.
78. SW Shorey, DA Lomas, WH Keesom. Use FCC Feed Pretreating Methods to Remove Sulfur. *Hydrocarbon Processing* 78: 43–51, Nov. 1999.
79. JW Wilson. FCC Revamp Improves Operations at Australian Refinery. *Oil and Gas Journal* 97: 63–67, Oct. 1999.
80. JW Wilson. *Fluid Catalytic Cracking Technology and Operations*. Penn Well Books, 1997, pp. 97–100.
81. G de la Puente, G Chiovetta, U Sedran. FCC Operation with Split Feed Injection. *Ind Eng Chem* 38: 2, 1999, pp. 368–372.
82. B Jazayeri. Optimize FCC Riser Design. *Hydrocarbon Processing* 70, May 1991, pp. 93–94.
83. X Zhao, AW Peters, GW Weatherber. Nitrogen Chemistry and NO₂ Control in Fluid Catalytic Cracking Regenerator. *Ind Eng Chem* 36(11): 4535–4542, 1997.
84. KL Dishman, PK Doolin, LD Tullock. NO₂ Emissions in Fluid Catalytic Cracking Catalyst Regenerator. *Ind Eng Chem* 37(12): 4631–4636, 1998.
85. JB McLean. Fluid Catalyst Properties can affect cyclone erosion. *Oil and Gas Journal* 98: 33–36, Jan 3, 2000.
86. MJ Fowle, RD Bent. *Petroleum Refiner* 26(11): 719–727, 1947.
87. MJ Fowle, RD Bent. *Hydrocarbon Processing* 78: 124, March 1999.
88. G Xu, B Chan, X He. *Hydrocarbon Processing* 80: 81, April 2001.
89. MB Ewell, G Gardmer, WJ Turk. *Hydrocarbon Processing* 60: 103–112, Sept. 1981.
90. CA Cabrera, D Knepper. *Hydrocarbon Technology International 1990/91*. P Harrison, ed. London: Sterling Publ. Int.
91. JE Naber, M Akabar. Shell's residue fluid catalytical cracking process. *Hydrocarbon Technology International 1989/90*. P Harrison, ed. London: Sterling Publ. International, pp. 37–43.