1

NOVEL FLUID CATALYTIC CRACKING PROCESSES

Jinsen Gao, Chunming Xu, Chunxi Lu, Chaohe Yang, Gang Wang, Xingying Lan and Yongmin Zhang

College of Chemical Engineering, China University of Petroleum, Beijing, PR China

Petroleum resources are subjected to a trend toward heavy and low quality in recent years. Then the heavy oil became the main feedstock all over the world. On the basis of the official Manual of First World Heavy Oil Conference in 2006, the recoverable reserve of conventional crude oil is only 1450×10^8 ton, while that of heavy crude oil and oil sand bitumen will reach to 8500×10^8 ton. Furthermore, the highest consumption of crude oil will reach up to $40–45 \times 10^8$ ton/annum, among which the heavy oil fractions will take up more than 30×10^8 ton/annum. It has been reported that the proportion of heavy crude oil increased to 17% in 2010 from 11% in 1995 within the petroleum resource supply worldwide. Further, the heavy fraction takes up to more than 50%. As we well knew, the heavy oil fractions cannot be utilized directly. They have to be converted into light transportation fuels, such as gasoline, jet fuel, and diesel, or petrochemical feedstocks, such as ethylene, propylene, benzene, and toluene, which featured with high values. Therefore, the heavy oil upgrading is the key issue to the best utilization of petroleum resources.

The fluid catalytic cracking (FCC) process is one of the most important technologies all over the world among the heavy oil upgrading processes in petroleum refining industries. It was reported that the global refinery capacity was 44.48×10^8 ton/annum up to the end of 2012, while the FCC capacity reached to 7.30×10^8 ton/annum, which took up 16.4% of the total refining capacity worldwide [1], about 45% of all gasoline comes from FCC and ancillary units, such as the alkylation unit. FCC continues to play a predominant role in China as the primary conversion process as well. For many refiners, the FCC unit is the key to profitability in that the successful operation of the unit determines whether or not the refiner can remain competitive in today's market. Up to the end of 2013, China's FCC process capacity reached to 1.5×10^8 ton/annum, making up 30.8% of total refining capacity in China. It provides approximately 30% of the diesel pool and almost 80% of the gasoline pool as a whole to supply the Chinese fuel market.

1.1 FCC PROCESS DESCRIPTION

The FCC process employs a catalyst in the form of very fine particles (average particle size about 60 μm (microns)), which behave as a fluid when aerated with a vapor. The fluidized catalyst is circulated continuously between the reaction zone and the regeneration zone and acts as a vehicle to transfer heat from the regenerator to the oil feed and reactor. Two basic types of FCC units in use today are the "side-by-side" type, where the reactor and regenerator are separate vessels adjacent to each other, and the Orthoflow, or stacked type, where the reactor is mounted on top of the regenerator. Typical FCC unit configurations are shown in Figures 1.1 and 1.2. Although the mechanical configuration of individual FCC units may differ, their common objective is to upgrade low-value feedstock to more valuable products. The main purpose of the unit is to convert high-boiling petroleum fractions called *gas oil* to high value, high-octane gasoline, and heating oil. Gas oil is the portion of crude oil that commonly boils in the 650+ to 1050+°F (330–550°C) range.

The gas oil feed for the conventional FCC units comes primarily from the atmospheric column, the vacuum tower,

Multiphase Reactor Engineering for Clean and Low-Carbon Energy Applications, First Edition. Edited by Yi Cheng, Fei Wei, and Yong Jin.

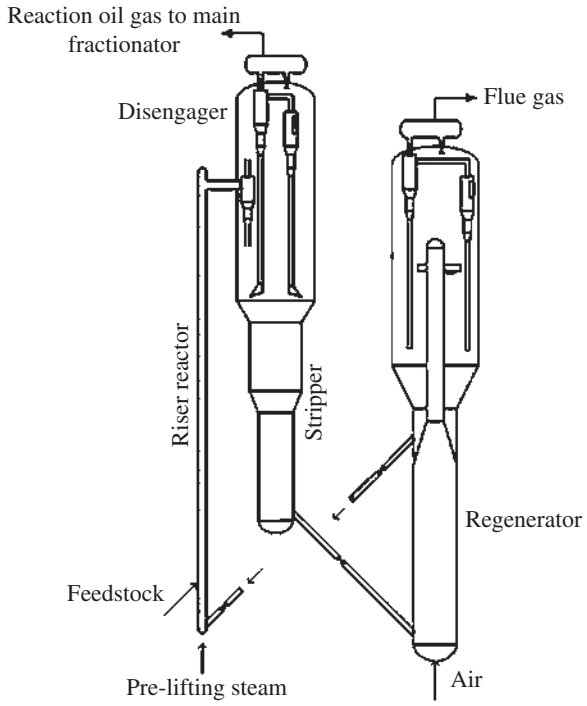

FIGURE 1.1 The basic "side-by-side" type FCC unit configurations.

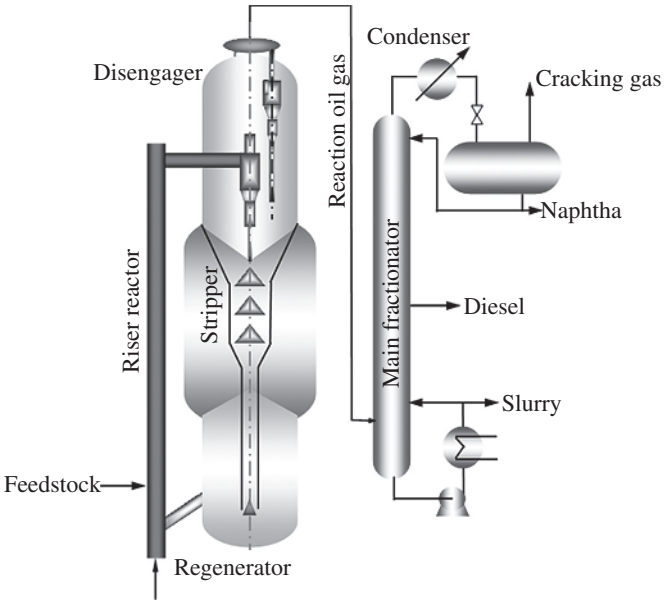

FIGURE 1.2 The basic Orthoflow or stacked-type FCC unit configurations.

and the delayed coker. In addition, a number of refiners blend some atmospheric residue (AR) or vacuum residue (VR) into the feedstocks to be processed in the FCC unit. Table 1.1 presents the typical FCC process product yields on various feedstocks.

The fresh feed and recycle streams are preheated by heat exchangers or a furnace and enter the unit at the base of the feed riser where they are mixed with the hot regenerated catalyst. The heat from the catalyst vaporizes the feed and brings it up to the desired reaction temperature. Average riser reactor temperatures are in the range 900–1000°F (480–540°C), with oil feed temperatures from 500 to 800°F (260–425°C) and regenerator exit temperatures for catalyst from 1200 to 1500°F (650–815°C). The mixture of catalyst and hydrocarbon vapor travels up through the riser reactors. The cracking reactions start when the feed contacts the hot catalyst in the riser inlet and continues until the oil vapors are separated from the catalyst in the riser exit. The hydrocarbon vapors are sent to the main fractionator for separation into liquid and gaseous products.

TABLE 1.1 The Typical FCC Process Product Yields on Various Feedstocks

Components	Daqing VGO, wt%	Daqing Atmospheric Residue, wt%	Shengli VGO, wt%
Fresh feed	100	100	100
Dry gas	1.7	2.4	1.8
LPG	10.0	10.9	9.9
C_5+gasoline	52.6	50.1	52.9
Light cycle oil	27.1	26.7	30.8
Decant oil	4.5	—	—
Coke	4.1	9.9	4.6
Total	100	100	100

The catalyst leaving the reactor is called "spent catalyst" and contains hydrocarbons adsorbed on its internal and external surfaces as well as the coke deposited by the cracking. Some of the adsorbed hydrocarbons are removed by steam stripping before the catalyst enters the regenerator. In the regenerator, coke is burned from the catalyst with air. The regenerator temperature and coke burnoff are controlled by varying the air flow rate. The heat of combustion raises the catalyst temperature from 1150 to 1550°F (620–845°C), and most of this heat is transferred by the catalyst to the oil feed in the feed riser. The regenerated catalyst contains 0.01 to 0.4 wt% residual coke depending upon the type of combustion (burning to CO or CO_2) in the regenerator.

Since the startup of the first commercial FCC unit in 1942, many improvements have been made in respect to the catalyst, processes, engineering or facilities, and so on. These improvements have enhanced the unit's mechanical reliability and its ability to crack heavier, lower value feedstocks. The FCC has a remarkable history of adapting to continual changes in market demands. In recent years, FCC process including catalysts shows rapid development for the light fuel yield increase, clean transportation fuel production, maximum production of light olefins, and so on. There are some targeted novel processes that appeared actually, such as reaction process regulation for the heavy oil FCC, advanced riser termination devices for the FCC processes, a multi-zone coordinated-controlled (MZCC) FCC process,

the two-stage riser FCC process, and FCC gasoline upgrading by reducing olefin content using subsidiary riser FCC (SRFCC) process. All these novel processes have made substantial contributions to China's petroleum refining industry for the improvement of light fuel yield, clean fuel production, and maximum production of light olefin.

1.2 REACTION PROCESS REGULATION FOR THE HEAVY OIL FCC

1.2.1 Technology Background

FCC is one of the core technologies to process the heavy oil efficiently. It could convert the heavy oil into valuable and light oil products and meet the demand for light oil in the market and had the best economic benefit.

In recent years, with the increasing of processing methods in resid–blend and the increasing of the resid–blend ratio, FCC would apply much severe operation conditions (higher temperature, shorter residence time, and larger catalyst-to-oil (C/O) ratio) in order to give thermal shock to the colloid and asphaltene in the residuum oil, and further to crack the residuum oil sufficiently. Universally, this will lead to the overcracking (to some extent) of the raw oil in the FCC riser, which will affect the yield and selectivity of gasoline and diesel. In other words, the highest yields of gasoline and diesel are not in the exit of the FCC riser but in some places of the middle or upper parts of the riser.

One of the efficient measures to deal with this is to terminate the reaction when the yield of gasoline and diesel reaches to the highest value, or to inject reaction-terminating medium into the riser from the point that gasoline and diesel have the highest yield. The application of the reaction-terminating medium could improve the temperature distribution in the FCC riser, control the extent of the catalytic cracking reaction, and optimize the operation condition of the FCC riser reactor, which aims to increase the yield of the target products and to improve the products' distribution.

1.2.2 Principle of the Technology

From the viewpoint of chemical reactions, the catalytic cracking is a typical parallel–sequential reaction system, where the heavy oil could simultaneously experience several catalytic cracking reactions and the primary products could continue to react (Figure 1.3). The extent of the catalytic cracking reaction will exert critical effects on the product distribution.

With the increasing of both the reaction time and conversion (Figure 1.4), the yields of the final gas and coke will increase continually. The yield of gasoline will increase at the beginning and then decrease from the highest yield, which could be due to the higher cracking rate of gasoline

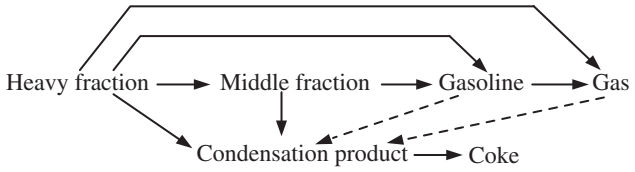

FIGURE 1.3 Catalytic cracking reaction mechanisms for hydrocarbons in petroleum.

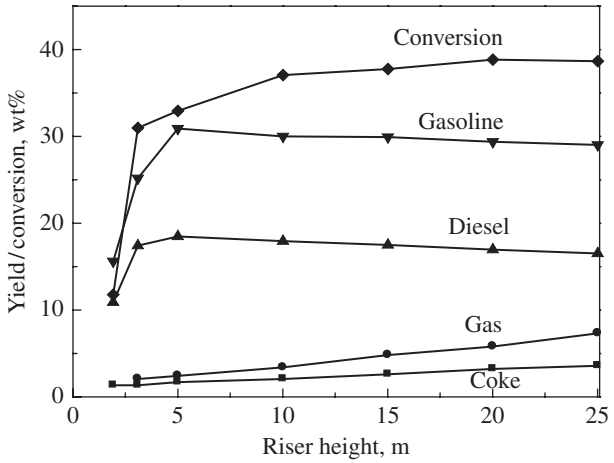

FIGURE 1.4 Product yield along the riser.

into gas compared with the rate of producing gasoline when the reaction proceeds to some extent. Similar to gasoline, the yield of diesel also has a highest value along the riser. However, the highest yield of diesel happens when the conversion of raw oil is still lower. In order to improve the yield of the light oil products in the FCC process, the unbeneficial and secondary reactions (i.e., the overcracking of various hydrocarbons, the dehydrogenation reaction, and the condensation reaction) should be inhibited, which will increase the production of middle products(i.e., gasoline and diesel) and will decrease the yield of gas and coke [2–5].

From the viewpoint of chemical reaction engineering, the catalytic cracking reactions take place in the riser reactor, where complex gas–solid two-phase turbulent flow, heat transfer, and mass transfer take place, showing highly coupling among these reactions and transport phenomena. The regenerated catalyst with high temperature contacts with raw oil in the liquid phase in the FCC riser, which will vaporize the raw oil suddenly. The vaporized oil gas will obtain high velocity due to its suddenly increased volume, which will further accelerate the catalyst particle and raise the turbulence of the particle's flow. Due to the interactions between the oil gas and the catalyst particle, the turbulent flow of the gas phase will be changed by the particle phase, which also exhibits complex turbulent flow. Besides, the oil gas will react on the surface of the catalyst, which means mass transfer between the reactants and the products. There also exists heat transfer between the oil gas and the catalyst

particle due to the vaporization of the raw oil in liquid phase and the heat effect along with the catalytic reactions. The flow behavior will affect the heat and mass transfer, which will further influence the catalytic reaction. The results of the catalytic reaction will also exert effects on the flow behavior and on the heat and mass transfer. Therefore, the highly coupled gas–solid two-phase flow, the heat and mass transfer, and the cracking reaction will continuously take place in the riser reactor from the "feeding zone" to the "reaction zone" and then to the "exit zone," showing coupling and interactions between each other and experiencing continuity temporally and spatially.

Therefore, in order to promote the middle products like gasoline and diesel, to reduce the yield of gas and coke, and to improve the yield of the light oil products, the complex coupling among the flow, the transport phenomena, and the catalytic reactions in the riser reactor should be carefully investigated and revealed. Regarding the different flow–reaction–transport behaviors in different zones and the sequence among these processes and their interactions, the efficient coupling among these processes could be achieved with the knowledge of reaction engineering and fluid flow, which will finally intensify the reaction environment in various zones, on the one hand, and promote the reactions in different zones, on the other hand. This will optimize the catalytic cracking reaction and improve the yield of the light oil products in FCC.

1.2.3 Key Fundamental Research

As known to all, the core part of the FCC is the riser reactor. The research on the FCC process mainly focused on the contact between the oil gas and the catalyst, the reaction, the flow, and the heat and mass transfer process in the riser reactor. The flow–reaction model for the residual FCC (RFCC) riser reactor could be established based on the gas–solid two-phase turbulent flow model and the lump kinetic model for the RFCC. This flow–reaction model could be applied numerically to study the industrial cases of RFCC, which will help us to decide whether the reaction-terminating medium should be injected, and (if the reaction-terminating medium is used) to optimize the injection position of the reaction-terminating medium, the number of the injection points, the type of the reaction-terminating medium, and the injection method. Besides, the industrial test should be performed in order to verify this model. Generally, this is the basic method to deal with such kind of problems involved in RFCC.

In the RFCC riser, there exist complex and interactive processes, including the contact of the raw liquid oil with the catalyst; the vaporization of the raw oil; the transfer of momentum, heat, turbulent energy, and mass between the gas phase and the solid phase; and the cracking reactions of the gas phase. Any changes in one of these coupled processes will affect the whole process. The complete three-dimensional (3D) two-phase flow–reaction model for the numerical simulation of the RFCC riser could be achieved by combining the 13-lump reaction kinetics with the gas–solid turbulent flow and heat transfer (the k–ε–k_p model). This numerical simulation has taken the property of the raw oil, the operation condition, and the characteristics of the catalyst into consideration. Besides, other factors, such as geometries of the riser reactor and the nozzle, behaviors of the flow and the heat transfer, and so on, have also been included in the numerical simulation. The numerical results could be used to describe any operation parameters in any points of the riser. These parameters were, but not limited to, the reaction temperature and pressure, the composition of reactants and products, and the velocity distribution of the gas phase and the solid phase in the axial/radial/tangential directions of the riser. These parameters could be applied to reveal the complex chemical engineering details in the riser, including the fields of velocity, temperature, and concentration; the back-mixing and back-flow behaviors of the gas phase and the solid phase; and the reaction extent (Figure 1.5) [2–6].

This 3D numerical simulation of the riser reactor was different from the conventional methods, which involved the change of lump kinetics and the further modification of the model parameters. The current 3D numerical simulation could

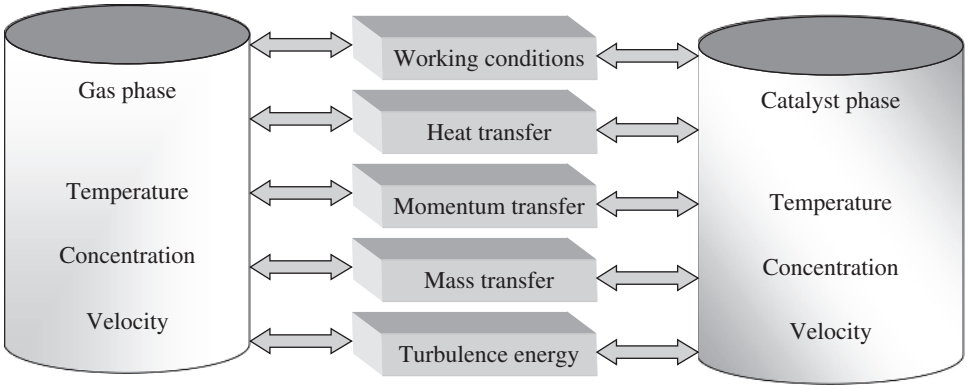

FIGURE 1.5 Gas–solid flow and reaction model in FCC riser.

describe factors of the riser geometry and the inlet conditions. Besides, the interactions like the flow, the heat and mass transfer, the cracking reaction, and the turbulent kinetics were also included into this combined mathematical model in describing the internal flow, the heat transfer, and the cracking reaction pathway in the riser. This model is a system of 3D steady partial differential equations, which could be expressed in the cylindrical coordinate as follows [7–9]:

$$\frac{\partial}{\partial x}\left(\varepsilon_i \rho_i u_i \varphi_i\right) + \frac{\partial}{r\partial r}\left(r\varepsilon_i \rho_i v_i \varphi_i\right) + \frac{\partial}{r\partial \theta}\left(\varepsilon_i \rho_i w_i \varphi_i\right) = \frac{\partial}{\partial x}\left(\Gamma_{\varphi_i} \frac{\partial \varphi_i}{\partial x}\right) + \frac{\partial}{r\partial r}\left(r\Gamma_{\varphi_i} \frac{\partial \varphi_i}{\partial r}\right) + \frac{\partial}{r^2\partial \theta}\left(\Gamma_{\varphi_i} \frac{\partial \varphi_i}{\partial \theta}\right) + S_{\varphi_i} \tag{1.1}$$

where x, r, and q represent the axial direction, the radial direction, and the tangential direction, respectively. u, v, and w are the velocity in the axial, radial, and tangential direction, respectively. ρ is the density. These detailed parameters include: (i) the velocity of the gas and the solid phase in the axial, radial, and tangential direction—u_i, v_i, w_i; (ii) the volume fraction of the gas phase and the concentration of the particle phase; and (iii) the component concentration or mass fraction in the gas phase. By solving this model, the flow, the heat transfer, and the cracking reaction pathway in the riser reactor could be quantitatively obtained. This quantitative information could be used to reveal the complex chemical engineering details in the riser reactor and further to provide theoretical foundations for the development of the new integrated technique of the catalytic cracking system in sequentially regulating the reactions in different reacting zones. The diagram for simulation calculation is shown in Figure 1.6.

The in-house numerical software was developed by adopting the idea and method given earlier. The RFCC riser reactor in the Petrochemical Factory of Shengli Oilfield Company Ltd was studied with this software based on the industrial case of the gasoline production, and results have been obtained as follows [6, 8, 10–14]:

1. The turbulent flow of the gas phase and the solid phase Figures 1.7 and 1.8: The process parameters that could affect the results of the cracking reaction have been

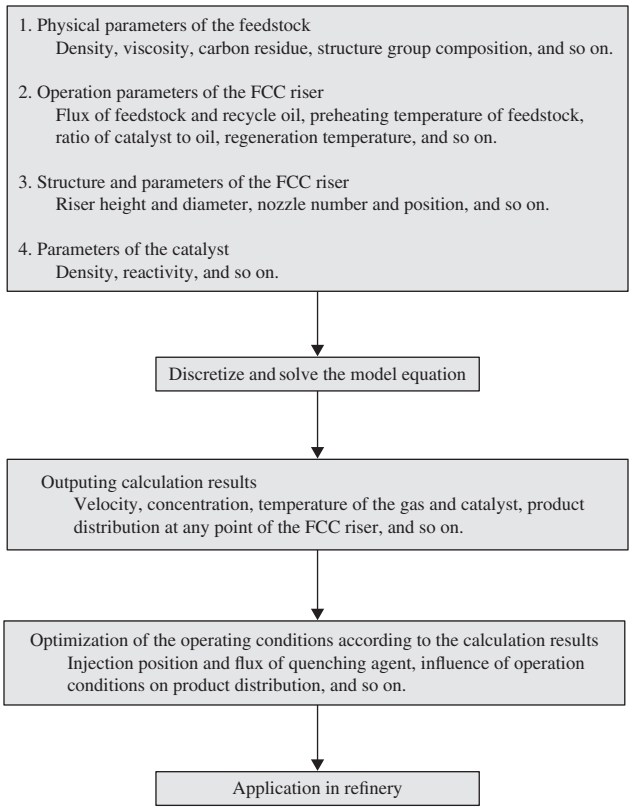

FIGURE 1.6 Overview diagram for simulation calculation.

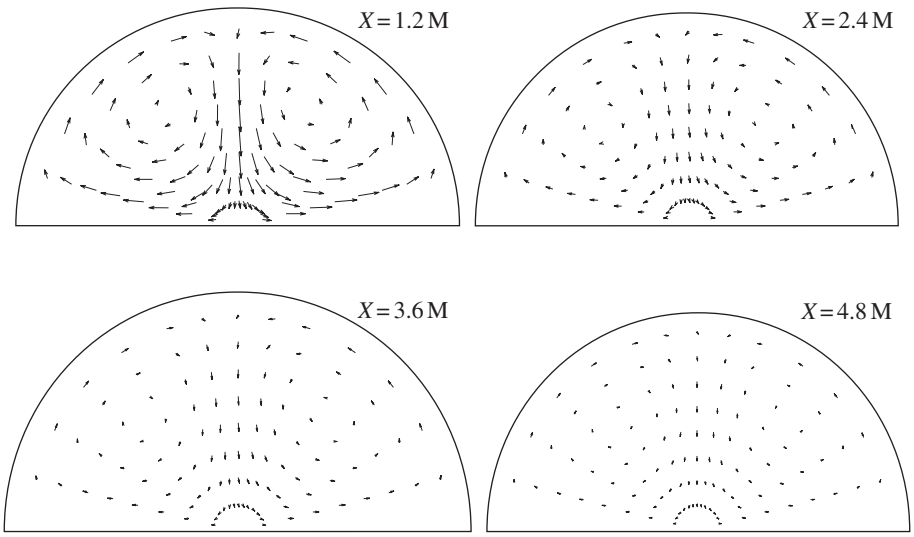

FIGURE 1.7 The gas-phase flow diagrams for different sections in FCC riser.

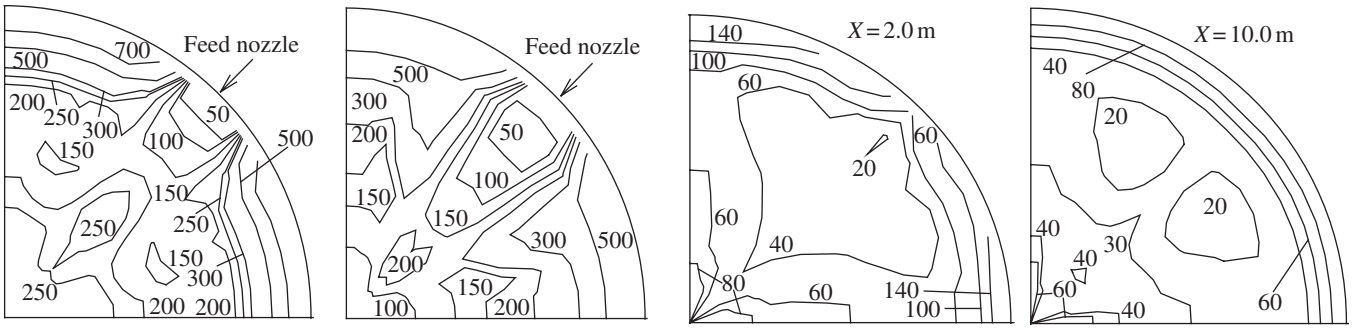

FIGURE 1.8 Catalyst concentration contour plots for different sections in FCC riser (kg/m^3).

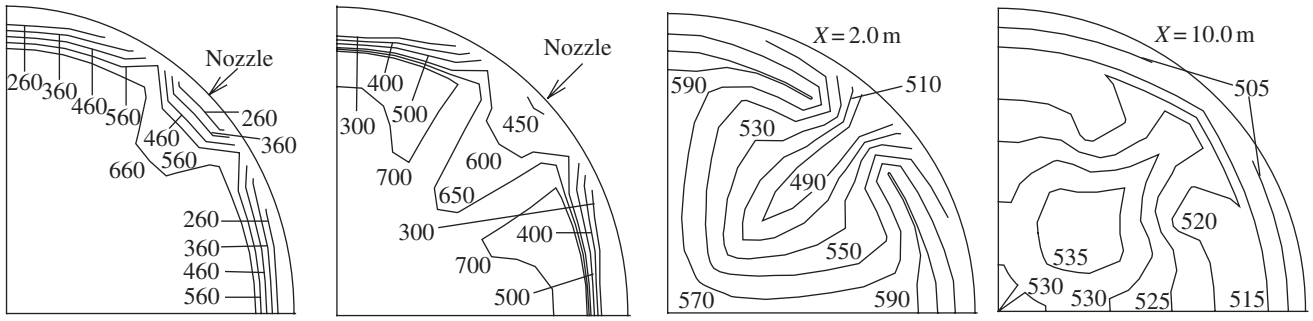

FIGURE 1.9 The gas-phase temperature contour plots for different sections in FCC riser (°C).

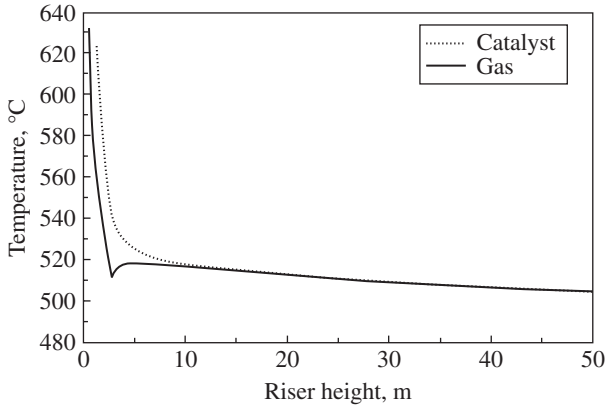

FIGURE 1.10 The gas and catalyst temperature along FCC riser.

calculated, which included the distributions of the velocity, the turbulent kinetic energy, and the pressure for both the gas phase and the solid phase in three coordinates, and also included the slip velocity between the gas phase and the solid phase and the distributions of the catalyst concentration.

2. The temperature distribution of the gas phase and solid phase (Figures 1.9 and 1.10: This temperature distribution could be used to reveal the heat transfer during the vaporization of the raw liquid oil and the heat transfer between the reacting oil gas and the catalyst. The temperature distribution could significantly influence the cracking reactions. However, the temperature distribution is rather complicated due to the complex flow behaviors of the gas phase and the solid phase. The numerical results could give detailed information, such as the temperature distribution of the gas phase and the solid phase in three coordinates and the distribution of the temperature difference between the gas phase and the solid phase. The numerical results could also describe the change of the average gas or solid temperature (in various cross sections of the riser reactor) along the riser height.
3. Distribution of the component concentration in the gas phase: The cracking results could be obtained by analyzing the distribution of component concentration of the gas phase in the riser reactor. Since this computational software adopted the lump kinetics in simulating the cracking reaction of the gas phase, the detailed kinetics could provide quantitative information on the distribution of various cracking products in the riser reactor. The numerical results could include concentration distributions of various components, such as diesel, gasoline, cracking gas, coke, and steam, in the axial/radial/tangential directions of the riser reactor. The numerical simulation could also provide the distribution of average yield and conversion for various products in different cross sections along the riser height (Figure 1.11), which

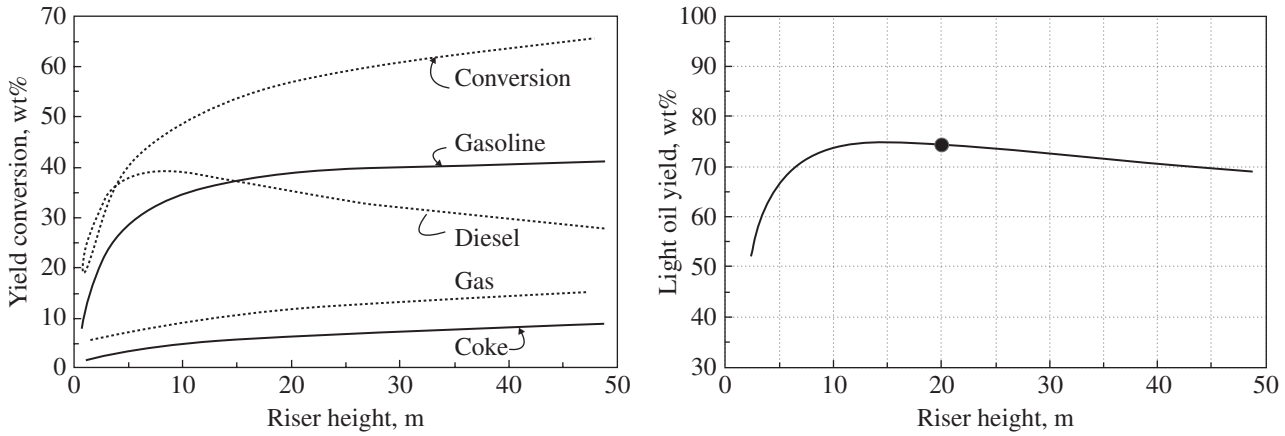

FIGURE 1.11 Product yield, conversion, and the light oil yield along FCC riser.

TABLE 1.2 Product Yield and Reaction Temperature at the Outlet of FCC Riser

Case	Ratio of Quench Medium, %	Gas	Gasoline	Diesel	Slurry Oil	Coke	Reaction Temperature, °C
Original	0.0	15.33	41.29	27.95	6.41	9.02	505.0
Case I	3.0	14.55	41.69	28.52	6.65	8.59	497.3
Case II	4.0	14.37	41.76	28.66	6.7	8.51	495.0
Case III	5.0	14.24	41.78	28.79	6.75	8.44	492.9

could be further applied to accurately understand the cracking reaction pathway in the riser reactor.

The catalytic cracking reaction pathway along the riser height could be obtained by analyzing the distribution of products in the riser as indicated in Figure 1.11, which provided preliminary theoretical foundation for the development and application of the "Reaction-terminating medium technique" [15, 16]. This technique could be used to optimize the temperature distribution, the cracking reaction, the unit operation, and the product distributions. The numerical results showed that diesel could experience some extent of overcracking when it was aimed to produce gasoline from the RFCC riser reactor. The overcracking of diesel means that the highest yield of diesel is not in the exit of the riser reactor but in some point near the middle or upper part of the riser. Therefore, it was required to apply the terminating technique in this riser reactor. Generally, this numerical simulation has provided theoretical foundation in the application of this terminating technique, which could be used to determine the optimal injection point.

4. On this numerical software, numerical experiments could be performed in order to improve and optimize the riser reactor's operation, to apply new techniques, and finally to understand the key factors affecting the accurate application of the terminating technique.

According to the distributions of products and temperature in the numerical results, the injecting point for the reaction-terminating medium could be determined on the riser reactor [17]. As can be seen from Figure 1.11, the yield of gasoline did not reach the highest value even on the exit of the riser reactor. However, Figure 1.11 shows that the light oil obtained the highest yield on the height of about 20.0 m and then decreased by 5.0% when reaching the riser exit. The purpose of this riser reactor with terminating technique was to improve the yield of the light oil products and to reduce the yield of the cracking gas and the coke. Therefore, the injecting point for the reaction-terminating medium should be at the height of about 20.0 m. Since there was a layer of nozzle for the slurry oil at the height of 23.5 m, this height could be specified as the relatively ideal injecting point for the reaction-terminating medium.

When water was selected as the reaction-terminating medium (Table 1.2), the numerical simulation showed that the increase in the amount of water from 3.0 to 5.0% had led to the temperature decrease by 7.7–12.1°C, the yield of gasoline increase by 0.40–0.49%, the yield of diesel increase by 0.57–0.84%, the yield of the light oil products increase by 0.97–1.33%, the yield of the cracking gas decrease by 0.78–1.09%, and the yield of the coke decrease by 0.43–0.58%. These results indicated that the reaction-terminating medium of water had got relatively positive effects.

1.2.4 Industrial Validation

Based on the numerical analysis of the flow–reaction model for the riser reactor, the industrial experiment has been

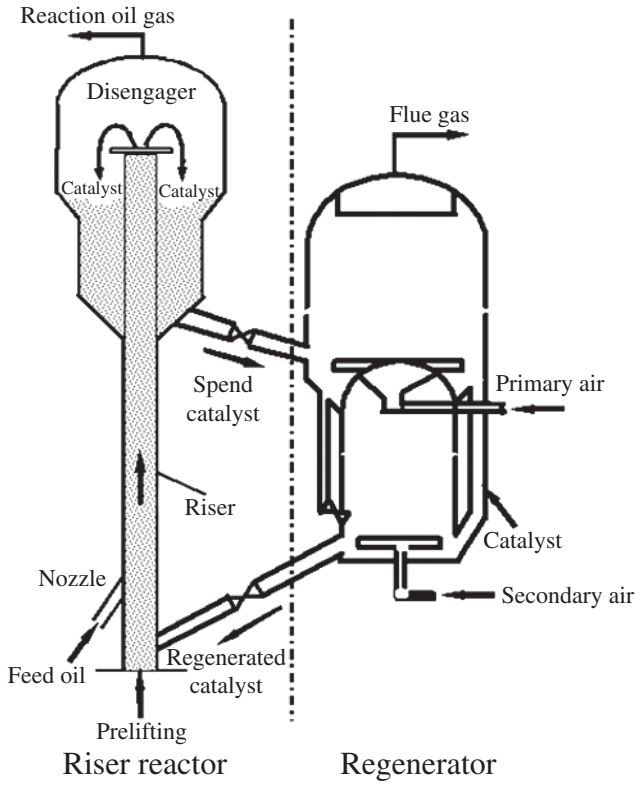

FIGURE 1.12 The schematic diagram for reaction regeneration system in FCCU in Petrochemical Factory of Shengli Oilfield Company Ltd.

conducted on the RFCC riser reactor of Petrochemical Factory of Shengli Oilfield Company Ltd (0.6 Mton/year in capacity) in order to apply the terminating technique to regulate the extent of cracking reactions in the industrial riser reactor. The RFCC system includes six parts: the reaction–regeneration, the fraction, the adsorption–stabilization, the energy recovery, the rich gas compressor, and the boiler for the carbon monoxide. The reactor and the regenerator are of the same height with two-stage regeneration, which can be seen from Figure 1.12.

Based on the practical situation of the Petrochemical Factory of Shengli Oilfield Company Ltd, the light sump oil and the direct distillation gasoline were selected as reaction-terminating mediums. The operation condition was also regulated in order to fit the terminating technique. The result of the terminating technique on the RFCC riser with a capacity of 0.6 Mton/year in Petrochemical Factory of Shengli Oilfield Company Ltd can be seen from the main operation parameters [18] in Table 1.3. With almost constant temperature on the riser exit, the terminating technique has improved the catalyst circulating load, the C/O ratio, and the mixing temperature in the zone where the catalyst meets with the oil gas. With the terminating technique, for example, when the temperature on the exit of the riser reactor was kept between 504.5 and 505°C, the C/O ratio has increased from 5.81 to 6.34 or 6.45. Besides, the temperature of the catalyst/oil mixing zone in the lower part of the riser reactor (at the height of 1.8 m from the bottom where the bottom nozzle

TABLE 1.3 Prevailing Operation Conditions Before and After Quenching Agent Injection

Items	Before Injection	Light-Effluent Oil Injection	Distilled Gasoline Injection
Reaction temperature, °C	504.7	504.5	504.9
Temperature of regenerated catalyst, °C	653.1	652.5	656.5
Reaction temperature (1.8 m above nozzle at the bottom of the riser), °C	572.0	582.0	579.0
Reaction temperature (1.5 m above nozzle at the middle of the riser), °C	509.0	515.0	514.0
Reaction temperature (5.5 m above nozzle at the middle of the riser), °C	504.3	509.2	509.0
Temperature in the dense region of the first stage of regenerator, °C	692.0	676.0	664.0
Temperature in the dilute region of the first stage of regenerator, °C	667.0	661.0	655.0
Temperature in the dense region of the second stage of regenerator, °C	716.0	701.0	702.0
Temperature in the dilute region of the second stage of regenerator, °C	748.0	745.0	752.0
Temperature after the regeneration slide valves, °C	720.0	693.0	690.0
Pressure on the top of disengage, kPa	111.0	121.0	126.0
Temperature of recycle oil, °C	329.0	328.0	327.0
Temperature of atomizing steam, °C	254.0	277.0	258.0
Flux of atomizing steam, kg/h	4900.0	9100.0	8900.0
Flux of preliminary lifting steam, kg/h	481.0	517.0	526.0
Preheating temperature of feedstock, °C	180.0	155.0	154.0
Catalyst-to-oil (C) ratio	5.81	6.45	6.34
Flux of recycle oil, ton/h	18.8	19.9	19.9
Flux of feedstock, ton/h	68.9	75.0	79.0
Flux of quenching agent, kg/h	0.0	4500.0	3500.0

TABLE 1.4 Product Distribution Before and After Quenching Agent Injection

Items	Before Injection	Light-Effluent Oil Injection	Distilled Gasoline Injection
Dry gas, wt%	5.61	5.28	4.99
LPG, wt%	8.93	9.37	9.96
Gasoline, wt%	40.25	70.72	41.19
Diesel, wt%	29.17		29.18
Sully oil, wt%	6.10	5.07	5.13
Coke, wt%	8.93	8.57	8.55
Loss, wt%	1.01	0.99	1.00
Light oil, wt%	69.42	70.72	70.37

was placed) has increased from 572 to 579°C or 582°C, and the temperature at the height of 1.5 m (where the middle nozzle was placed) has increased from 509 to 514°C or 515°C. Though the temperature of the regenerated catalyst behind the regeneration slide valve decreased from 716 to 702°C, the temperature of the regenerated catalyst under the nozzle was almost constant around 653°C.

The material balance before and after injecting the reaction-terminating medium (Table 1.4) indicated that the industrial test of the terminating technique had obtained positive results, and that the extent of the cracking reaction had been controlled based on the detailed understanding and quantitative mastering of the cracking reaction pathway. In detail, before injecting the reaction-terminating medium, the yield of the cracking gas was 5.61%; the injecting of the light sump oil as reaction-terminating medium had reduced this yield to 5.28%, and the reaction-terminating medium of the direct distillation gasoline further reduced the yield of cracking gas to 4.99%. The yield of the liquefied gas had been improved from 8.92% (before using the reaction-terminating medium) to 9.37% (light sump oil as the reaction-terminating medium) or 9.96% (direct distillation gasoline as the reaction-terminating medium). The yield of the coke had been reduced from 8.93% (before using the reaction-terminating medium) to 8.57% (light sump oil as the reaction-terminating medium) or 8.55% (direct distillation gasoline as the reaction-terminating medium). The yield of the light oil products changed clearly from 69.42 to 70.72% (light sump oil as the reaction-terminating medium) or 70.37% (direct distillation gasoline as the reaction-terminating medium). Overall, the terminating technique had obtained quite positive results.

Based on the earlier industrial test, the desalt water was further tested on this industrial RFCC, and more positive results were obtained. These results confirmed the conclusion from the numerical simulation on the terminating technique, and the conclusion was that water as the reaction-terminating medium could receive more ideal results. Table 1.5 lists the main operating condition when injecting the reaction-terminating medium, and Table 1.6 shows the product distribution when injecting water as the reaction-terminating medium.

TABLE 1.5 Prevailing Operation Conditions with Different Quenching Agent Injection

Items	Distilled Gasoline Injection	Desalted Water Injection
Process capability, ton/h	79.00	79.83
Flux of quenching agent, ton/h	4.00	4.00
Reaction temperature, °C	506.0	506.0
Reaction temperature above nozzle at the middle of the riser, °C	531.0	529.0
Reaction temperature at the bottom of riser, °C	560.0	565.0
Preheating temperature of feedstock, °C	188.0	188.0
Temperature difference between the dilute and dense region in the first stage of regenerator, °C	−15.4	−15.2
Temperature difference between the dilute and dense region in the second stage of regenerator, °C	−11.1	−58.0

TABLE 1.6 Product Distribution with Different Quenching Agent Injection

Components	Distilled Gasoline Injection	Desalted Water Injection	Difference Between Desalted Water and Distilled Gasoline Injection
LPG, wt%	7.70	8.65	0.95
Gasoline, wt%	41.51	42.00	0.49
Diesel, wt%	25.02	24.82	−0.20
Surry oil, wt%	10.16	9.04	−1.12
Coke, wt%	8.63	8.58	−0.05
Dry gas, wt%	6.98	6.91	−0.07
Light oil yield, wt%	66.53	66.82	0.29
Liquid yield, wt%	74.23	75.47	1.24

The given data showed that the main operation conditions for the reaction-terminating medium of direct distillation gasoline and the de-salt water were almost the same. However, the actual results with these two different reaction-terminating mediums were quite different. Compared with the reaction-terminating medium of direct distillation gasoline, when the desalt water was injected into the riser reactor, the yield of the slurry oil was decreased by 1.12%, that of both coke and cracking gas were decreased, and that of liquefied gas and gasoline were increased by 0.95% and 0.49%, respectively. The desalt water as the reaction-terminating medium could dramatically improve the desired products and reduced the undesired products compared with the absence of the reaction-terminating medium. Unfortunately, the reaction-terminating medium of the desalt water had reduced the yield of diesel by 0.2% compared with using the direct distillation gasoline. However, the total yield of the

light oil products and the total yield of the liquid products had been largely improved by 0.29% and 1.24%, respectively, when applying the desalt water compared with using the direct distillation gasoline. These results were quite positive.

Overall, the terminating technique for the RFCC riser reactor has obtained satisfying results: the yield of the light oil products has increased by 1–2%, that of the coke and cracking gas has decreased by around 0.7%, and that of the liquefied gas has increased by 0.5%. These results were obtained based on the detailed understanding and mastering of the cracking reaction pathway in the riser reactor and on the efficient control of the extent of the cracking reaction. The key points to success, when the reaction temperature on the exit of the riser was almost stable, included improving the mixing temperature of the catalyst and the oil gas at the bottom of the riser reactor, improving the C/O ratio, and further improving the cracking intensity in this bottom of the riser, which gave thermal shock to the heavy fraction and had achieved the short residence time with high temperature. Based on the study of the cracking reaction pathway in the riser reactor, the performance of the industrial riser reactor could be improved, the temperature distribution could be optimized, and the extent of the cracking reaction could be controlled, which would provide tremendous economical and social benefits for the RFCC unit and even for the whole oil refinery.

1.3 ADVANCED RISER TERMINATION DEVICES FOR THE FCC PROCESSES

1.3.1 Introduction

In modern petroleum refineries, FCC is a ubiquitous process for producing high-value transportation fuels from low-value heavy gas oils and residues. Current FCC units widely choose a vertical pipe called riser as their reactor, which provides an approximately 2 s reacting time for oil gas. After leaving the riser reactor, oil gas flows with deactivated catalyst into the reactor vessel, that is, the disengager, and then enters into the fractionator after catalyst particles are separated by cyclone separators. The reactor vessel is usually huge enough to allow a greater than 20 s residence time for oil gas. The long postriser residence time of oil gas leads to significant increase in dry gas and coke yields [19]. Moreover, the long exposure of oil gas often results in serious coking on the surfaces of reactor and internals. As more refineries chose to process cheaper residue feedstock in their FCC units since the 1980s, serious coking in reactor vessel became a severe threat to unit operation. A lot of unscheduled unit shutdowns were reported due to reactor coking, resulting in serious economic loss [20, 21].

In order to overcome these problems, advanced riser termination devices (RTDs) began to be developed and commissioned since the 1980s [22–24]. By now, there have already been a series of proprietary RTD technologies that have appeared and are applied in commercial units. These RTDs often connect with the riser outlet directly and have higher particle recovery efficiency, which help quickly separate oil gas and catalyst and terminate the catalytic cracking reactions. Moreover, most of these RTDs have their oil gas outlet tube directly connected with the inlets of the downstream cyclones. This shortens postriser residence time and restrains undesirable thermal cracking reactions greatly. The serious coking problems in RFCC units can also be alleviated. Some more advanced RTDs have the spent catalyst stripper and their dust outlet coupled together or add prestripping sections above their dust outlets, which further minimizes the postriser oil gas residence time.

Before the 1980s, the importance of advanced RTDs were not so recognized because oil was very cheap at that time and most FCC units processed lighter vacuum gas oil (VGO). The employed RTDs were usually simple downturn arms, rough-cut cyclones, or other specialized inertial separators. In order to maintain high-efficiency catalyst recovery, two-stage cyclones have to be usually employed in an FCC reactor. The first category of such RTD technologies is the close-coupled cyclone system, represented by Shell's internal close-coupled cyclone system shown in Figure 1.13a [23] and KBR's closed cyclone shown in Figure 1.13b [24]. These RTDs evolve from the direct-coupled cyclone (DCC) system commissioned by Mobil and UOP in 1988. Although with significant improvements in product selectivity, these close-coupled cyclone systems are usually sensitive to pressure upset, especially during unit startup periods, and prone to large amount of catalyst loss, which requires the operators with very high operating levels and is not very welcome in refineries.

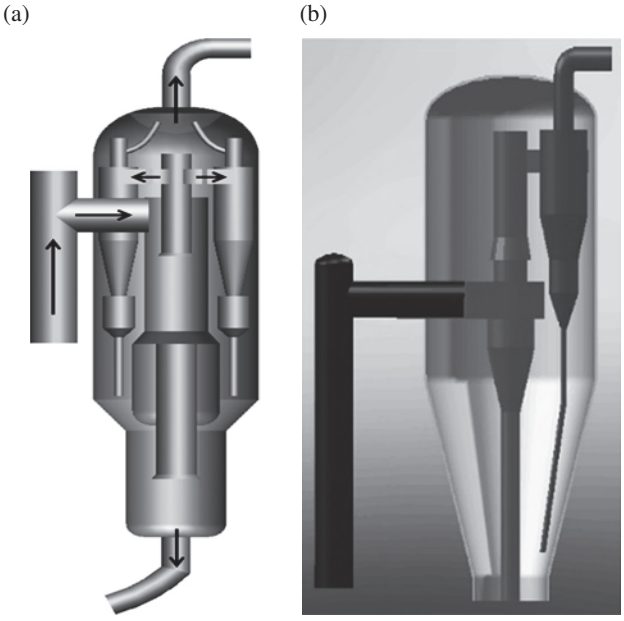

FIGURE 1.13 Close-coupled cyclone systems: (a) Shell's internal close-coupled cyclone system and (b) KBR's closed cyclone.

In 1990s, UOP developed two new RTD systems, namely, the vortex disengager stripper (VDS) system for external-riser FCC units (e.g., KBR's Orthoflow FCC unit) and the vortex separation system (VSS) for internal-riser FCC units (e.g., UOP's straight-riser FCC unit), as shown in Figures 1.14 a and b, respectively [25]. The VDS and VSS employed centrifugal separation to achieve high particle recovery efficiencies. Otherwise, the two RTD systems have close-coupled structures with the bottom spent catalyst stripper containment. Finally, the VDS and VSS were more reliable than the DCC system. For these advantages, 5 VDSs (after 1991) and nearly 30 VSSs (after 1995) have already been commissioned by 2007.

IFP together with Stone and Webster also developed an RTD system, that is, LD2 (Linear Disengaging Device) as shown in Figure 1.15 [24, 26]. The LD2 can be double half-turn design (Figure 1.15a) or single half-turn (Figure 1.15b) design as that reported by Andreux et al. [27]. A unique geometry feature is its lateral gas outlet tube. As shown in Figure 1.15, gas–solid mixture tangentially enters the laterally placed columns, forming centrifugal separation. Separated solids leave the separation chambers from two tangential outlets, while separated gas leaves into the two outlet tubes from the opening slots connected with the separation chambers. The advantage of LD2 lies in its very short residence time for product vapor in itself. However, this makes it difficult to couple a catalyst prestripping structure and keep high oil gas containment. Some oil gas can still be able to leave into the reactor vessel.

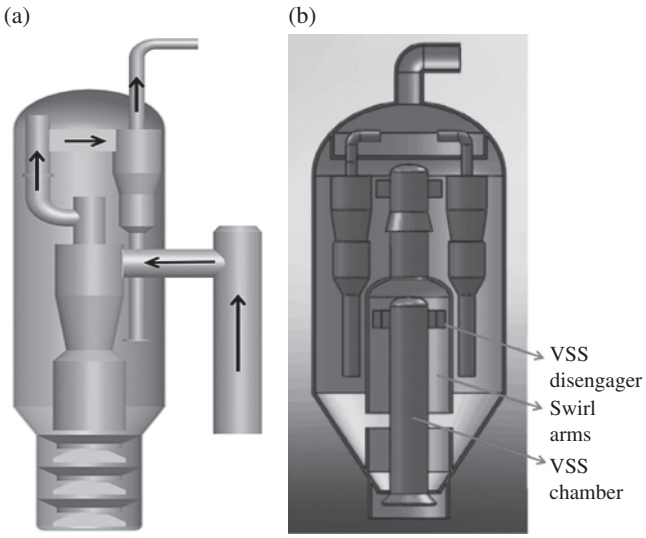

FIGURE 1.14 UOP's (a) VDS and (b) VSS.

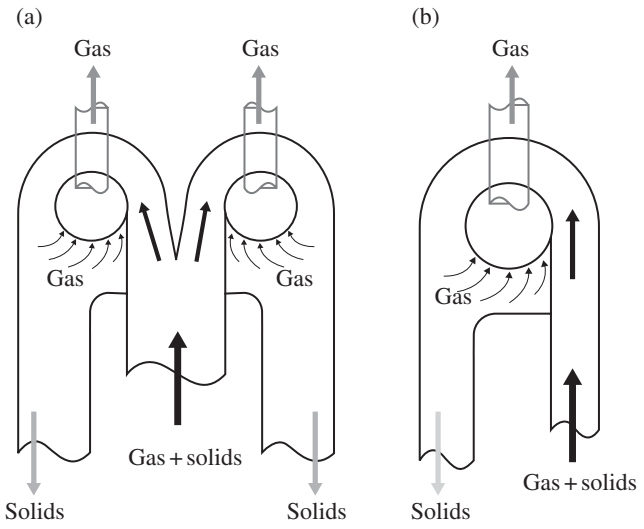

FIGURE 1.15 (a) RS^2 and (b) LD2.

In a long period, FCC has always been the dominant conversion process for producing transportation fuel in most refineries in China. According to a recent survey [28], the total processing capacity of FCC units in China was 146 Mton/annum in 2009. About 80% gasoline and approximately 30% diesel oil blends were produced by FCC process. In the early 1990s, many Chinese FCC units began to process increasing amount of residue feedstock. However, one of the most bothersome problems in most RFCC units was the frequent unscheduled shutdowns due to serious coking in reactor vessels. Sometimes, the dropped-off coke blocked the slide value in the spent catalyst circulation standpipe, resulting in the stoppage of catalyst circulation. In more serious cases, the whole stripper cross section was blocked by the dropped-off coke. Since 1992, a joint research and development (R&D) program was initialized by China University of Petroleum, Beijing (CUPB) and interested oil companies to develop advanced RTD technologies to improve FCC product yields and overcome the coking problems in RFCC units. To date, there have been four RTDs developed and commercialized successfully for both internal-riser and external-riser FCC units, with nearly 50 applications in industrial FCC units. The aim of this chapter is to introduce the R&D history of the advanced RTD program, including its background, the general development idea, the four developed and commercialized RTD systems and their mechanisms, geometrical and operational features, and commercial performance.

1.3.2 General Idea of the Advanced RTD System

For an efficient RTD system, five requirements should be satisfied: (i) high particle recovery efficiency, (ii) high oil gas containment, (iii) quick gas–solid separation, (iv) quick prestripping of spent catalyst, and (v) quick withdrawal of oil gas to the downstream cyclones. This is the two-"high"s and three-"quick"s requirement that we summarized for an efficient FCC RTD system. When RTD's particle recovery efficiency exceeds 90–95%, a single-stage cyclone is enough to guarantee a greater than 99.99% particle recovery efficiency in the reactor system. Otherwise, two-stage cyclones must be installed, but that is often limited by reactor volume. On the

other hand, quick gas–solid separation and high particle recovery efficiency will terminate the postriser catalytic cracking reactions more effectively. This is important to control an accurate reaction time in the riser and achieve high product selectivity. Quick prestripping of spent catalyst and quick withdrawal of oil gas to the downstream cyclones are to achieve a shorter postriser residence time for the product vapor to minimize yields of dry gas and coke and secure high product selectivity. Moreover, an RTD system should also have minimized leakage of oil gas into the huge reactor space, that is, high oil gas containment in the RTD systems. For RFCC units, long staying of product vapors in reactor freeboard can result in not only increased dry gas and coke but also serious coking on the walls of reactor vessel and other internals. The breakup of coke can often block the standpipe slide valve, resulting in frequent unscheduled unit shutdowns. Except for the aforementioned two-"high"s and three-"quick"s requirement, an RTD must be very reliable even during unstable operations, such as during unit startups and some pressure upsets.

To satisfy these requirements simultaneously, our RTD designs follow a similar feature, that is, a centrifugal separation zone and a prestripping zone well coupled as two indispensable parts, as depicted in Figure 1.16. The centrifugal separation zone is to achieve high particle recovery efficiency, while the prestripping zone is to achieve high containment of product vapor by decreasing the amount of oil gas entrained by the downward catalyst flow from RTD's diplegs.

In addition, a specialized design of the connection geometry between RTD's gas outlet and the inlets of its downstream cyclones is also common feature of our RTD systems. This is also to minimize the postriser oil gas residence time and to maintain high containment of the product vapors. Our RTD systems have different geometrical features from UOP's design in VDS and VSS systems shown in Figure 1.14. VDS and VSS systems have their particle separation zone coupled with the bottom spent catalyst stripper to achieve high oil gas containment. However, our RTD systems employ coupled gas–solid separation zone and prestripping zones to realize this objective.

The key to our RTD systems is to couple the two function zones without disadvantageous mutual impacts. However, the two zones have very different inner hydrodynamic features and requirements. The centrifugal separation zone is a dispersed gas–solid flow system highlighting strong centrifugal flow field to obtain high particle recovery efficiency; while the prestripping zone is a dense gas–solid flow system, which emphasizes the importance of good interphase contacting. This greatly increases the coupling difficulties. Otherwise, low pressure drop and swift product vapor withdrawal geometry are also required in our RTD systems.

With these understandings in our R&D efforts since 1992, systematic R&D work, including laboratory bench-scale experiments, computational flow dynamics (CFD) analysis, large-scale cold model validations, and industrial validations and applications, was done. By now, there have already been four types of RTD system developed and commercialized, that is, fender-stripper cyclone (FSC) and circulating-stripper cyclone (CSC) for external-riser FCC units and vortex quick separator (VQS) and super vortex quick separator (SVQS) for internal-riser FCC units. Nearly 50 applications have been achieved in FCC units of different throughputs and geometrical schemes.

1.3.3 Development of the External-Riser FCC RTD Systems

1.3.3.1 FSC System FSC system is the first-generation RTD developed for external-riser FCC units, for example, Kellogg's Orthoflow FCC unit. This research program began in 1992 with its first industrial application in 1996. As illustrated in Figure 1.17, FSC system includes three main geometrical

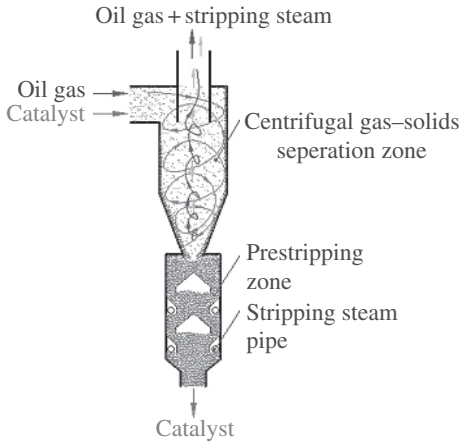

FIGURE 1.16 Schematic of an efficient RTD system.

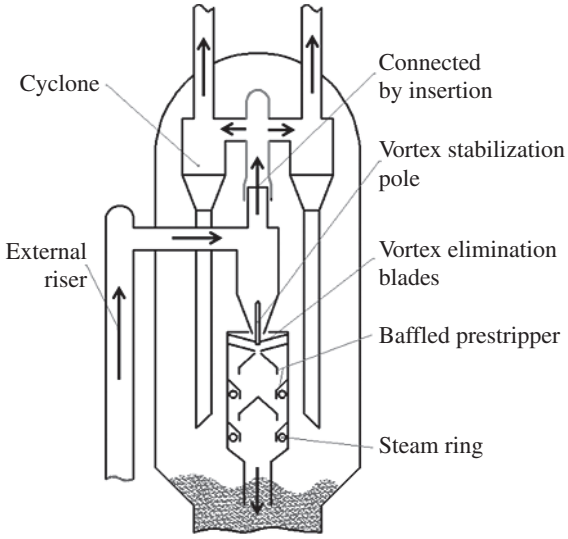

FIGURE 1.17 FSC system.

function structures: (i) a rough-cut cyclone for centrifugally separating gas–solid mixture, (ii) a baffled prestripper for quickly stripping the separated spent catalyst, and (iii) a special connection geometry between the RTD gas outlet tube and the inlet tube of downstream cyclones for quickly withdrawing the separated oil gas. FSC system was designed to replace a rough cyclone RTD (see Figure 1.18) usually used in external-riser FCC units. Despite high particle collection efficiency (usually ≥98%), its biggest defect is its long oil gas residence time in the reactor space, which results in degraded product yields and serious coking. In some modified designs, the oil gas exit tube of a rough cyclone is prolonged to the same level as the downstream cyclone inlets as shown by the dashed line in Figure 1.18. To some extent, this shortens the postriser oil gas residence time, but this problem is still not well solved. For Shell's DCC system, oil gas exit tube of the rough cyclone is connected directly with the inlets of the downstream cyclones, but there is still approximately 6 wt% oil gas entering into the reactor space from its dipleg due to its positive-pressure nature [25].

One of the proprietary geometrical features of FSC system is its specially designed baffled prestripper. As shown in Figure 1.19, it consists of a series of perforated disc-and-donut baffles. The prestripper design is to make the stripping gas and the spent particles flow in different routes and form high-efficiency cross-flow contacting. Ideally, it is required that (i) all gas goes through the holes in the baffles, countercurrent contacting with the particles flowing along the angling baffle surfaces and that (ii) gas velocities through the holes be large enough to avoid particle leakages through the holes. By experiments, we found that the key is to properly select an open area fraction of the holes in the baffles

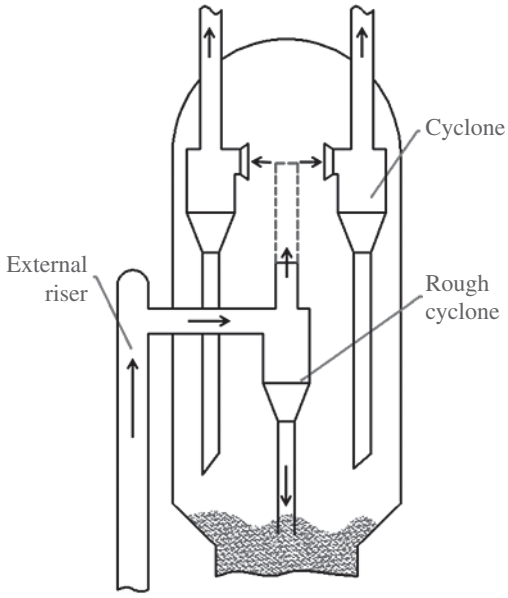

FIGURE 1.18 Rough cyclone RTD.

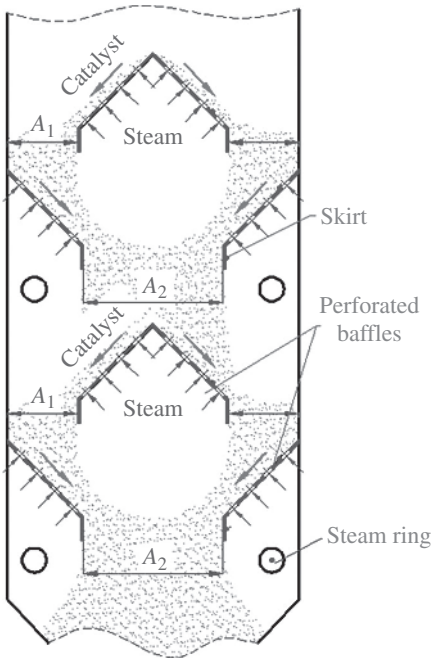

FIGURE 1.19 Cross-flow prestripper.

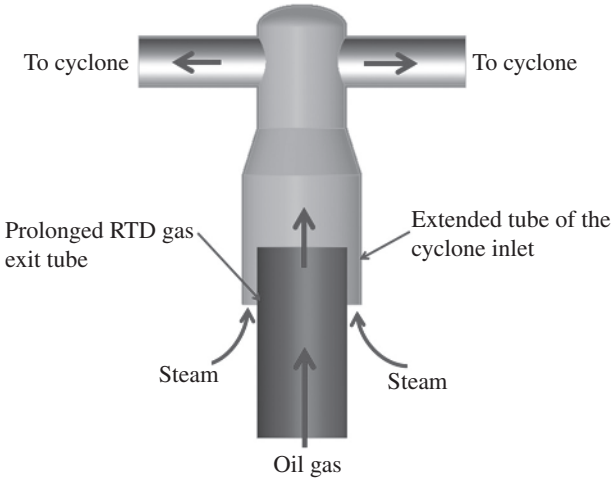

FIGURE 1.20 Venturi connection geometry between the RTD gas exit tube and the downstream cyclone inlet tube.

and solid fluxes through the annular area A1 and circular area A2. The baffled prestripper with cross-flow gas–solid contacting increases the downward flow resistance and prestripping efficiency, reducing the amount of oil gas flowing downward and entrained by the downward-flow particles.

Another different feature of FSC system is its connection geometry between its gas outlet tube and the inlet of the downstream cyclones. As shown in Figures 1.17 and 1.20, the inlets of several downstream cyclones are connected to a downward-extended tube. The RTD gas outlet tube is also prolonged to insert concentrically into the cyclone inlet tube. Due to the high velocity of oil gas in the RTD exit tube, a

local low-pressure region forms near the top of the RTD exit tube as in a Venturi tube, hence avoiding oil gas bypassing into the large reactor space. Other gases, mainly stripping steam, flow into downstream cyclones through the annular passage. By properly selecting the insertion depth of the RTD's oil gas exit tube and the annular flow area, FSC system can achieve minimized oil gas leakage without negative impact on particle recovery efficiency even at fluctuating operating conditions.

For FSC system, the coupling between the gas–solid separator and the prestripper is crucial to its successful development. For a gas–solid cyclone separator with a dust hopper and a tangential inlet, there are usually two factors that influence its separation efficiency most seriously. One is the downward gas flow into the dust hopper. The more the gas flows into the dust hopper, the more collected dust will be entrained into the separation zone again when it leaves, resulting in reduced particle separation efficiency. The other is the twisting inner vortex, which can reach the dust hopper and sweep off some collected dust into the separation zone, also reducing the particle separation efficiency. For FSC system, the introduction of the prestripping gas flow strengthens the negative impacts of the two factors on particle separation. In order to keep high particle recovery efficiency, as can be seen in Figure 1.17b, a vortex stabilization pole and several vortex elimination blades are installed in the cone section of the rough-cut cyclone and in the top of the prestripper, respectively. This is to stabilize the twisting inner vortex and weaken its strength in the prestripper, thus minimizing the negative impact on the particle recovery efficiency by the prestripping gas flow. Otherwise, the vortex elimination blades are to stabilize the operation of the prestripper.

Due to these unique geometrical features, FSC system can provide many advantageous properties over other previous RTD designs, including the following:

- **Shorter postriser residence time**. Oil gas stays in FSC system within 2 s, which corresponds to a postriser oil gas residence time less than 5 s in an FCC unit [29]
- **Higher oil gas containment approaching to 100%**. Oil gas enters into the reactor space through two outlets: the bottom particle dipleg outlet and the top gas outlet of an RTD. FSC's specially designed prestripper and connection geometry between the gas outlet and the inlet of the downstream cyclones reduce the amount of oil gas into the disengager significantly. Almost 100% oil gas containment can be achieved in most operating conditions.
- **Higher particle collection efficiency greater than 99%**. With good coupling geometry between the gas–solid separator and the prestripper together with other structural optimizations, FSC's measured particle collection efficiencies were greater than 99% in large-scale cold model tests [30].
- **Better operating reliability**. Due to the specially designed connection geometry between the gas outlet and the inlet of downstream cyclones, FSC system can maintain satisfactory particle recovery efficiency even during unit startups and pressure upsets [31].

In 1996, FSC system was first tested in a small FCC unit in Yanbian Refinery of China National Petroleum Corporation (CNPC) located in China's Jilin Province, which processed 0.15 Mton/annum Daqing AR feedstock. This commercial application was very successful [29]. After the revamp, dry gas yield decreased from 7.15 to 5.43% and coke yield decreased from 8.15 to 7.48%, corresponding to a 2.38% increase of liquid products (LPG + gasoline + diesel oil). Otherwise, the solid content in the slurry was lower than 1.65 g/l after the revamp, demonstrating FSC's high particle recovery efficiency. Even during unit startups, FSC still worked very well without significant catalyst loss, demonstrating its high reliability.

After this successful application, FSC was quickly commercialized in two larger FCC units in the next year. One was a 1.0 Mton/annum resid FCC unit in CNPC's Fushun #1 Refinery in China's Liaoning Province; the other was a 0.8 Mton/annum resid FCC unit in CNPC's Qianguo Refinery in China's Jilin Province. The two applications were also successful, further proving FSC's excellent performance. By now, FSC system has been commercialized in 15 industrial FCC units, including a 3.5 Mton/annum FCC unit in CNPC's Dalian Refinery, which is currently one of China's largest FCC units.

1.3.3.2 CSC System CSC system is the second-generation RTD developed for external-riser FCC units. Figure 1.21 shows its 3D model and installation schematic in an FCC unit. As can be seen, CSC's largest difference from FSC system lies in its different prestripper employed. This type of prestripper, as can be seen in Figure 1.21, is named as annular circulating prestripper (ACPS), which employs a different approach to achieve high-efficiency prestripping efficiency and high oil gas containment. Figure 1.22 gives a more detailed diagrammatic representation of the ACPS. It employs a cylinder partition column to separating the prestripper into two zones: core and annular. A perforated-plate distributor and a ring distributor are placed at the bottom of both the core zone and the annular zone, respectively. A high gas velocity is kept in the core zone, whereas a low gas velocity is kept in the annular zone. Unstripped spent catalyst is first directed into the core zone via a dipleg with a perforated cone on its top. The holes in the cone wall allow the prestripping steam and the stripped oil gas to flow through. When the dense bed in the disengager is high enough, the different particle concentrations in the two zones due to their different gas velocities make the catalyst particle circulating like the pattern shown in Figure 1.22. The spent

catalyst can thus get multiple stripping before it leaves the prestripper, resulting in high prestripping efficiency. Even when the bed height is low in the reactor, as can be seen in Figure 1.21, the spent catalyst can still go through the core zone and the annular zone in turn and undergo prestripping twice. Moreover, the dense bed in the ACPS's core zone acts as a seal to prevent oil gas from flowing downward and passing into the reactor space from CSC's dipleg outlet. This helps CSC system achieve higher oil gas containment. The structure of ACPS is much simpler than the baffled prestripper

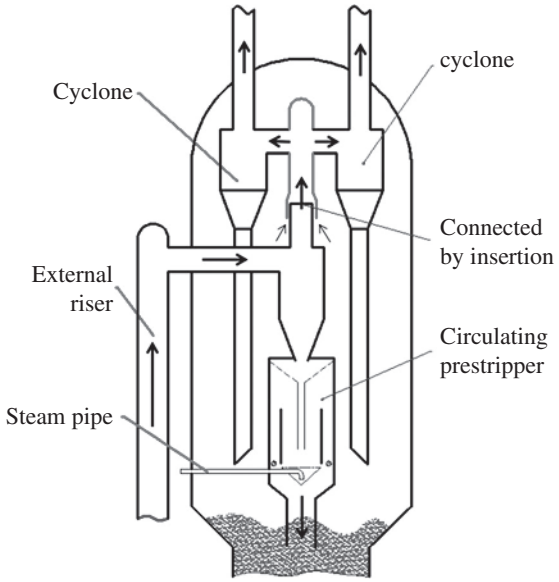

FIGURE 1.21 CSC system.

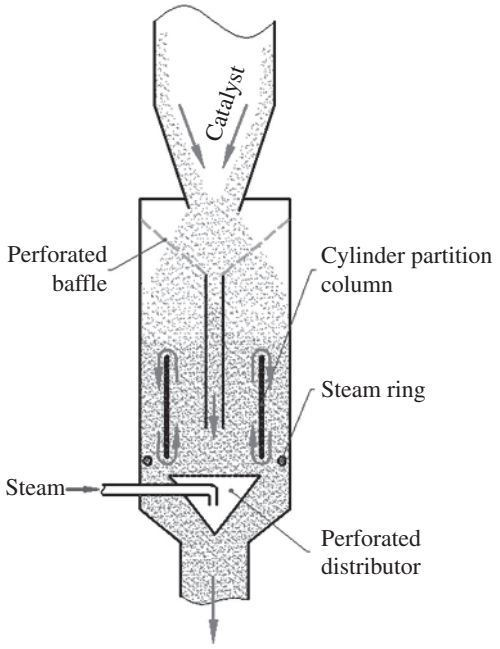

FIGURE 1.22 Annular circulating prestripper.

in FSC system, thus enabling it lower manufacturing cost and longer period reliability.

In 2000, CSC system was first commercialized in a 0.1 Mton/annum RFCC unit in Shenghua Refinery located in China's Shandong Province. A T-type RTD was replaced with a CSC. This successful revamp resulted in a 0.93% decrease in dry gas yield, a 0.21% decrease in coke yield, a 1.48% increase in gasoline yield, and a 1.14% increase in liquid products (gasoline + diesel oil + LPG). The solid content in the slurry was reduced to less than 2.0 g/l after the revamp, demonstrating CSC's high particle separation efficiency. Otherwise, this application also proved CSC's excellent reliability even under abnormal operating conditions such as startup period [32].

After this first successful application, CSC was also quickly commercialized in larger FCC units [33] and began to become a priority in the revamps of external-riser FCC units. By 2009, CSC has been commercialized in 13 commercial FCC units.

1.3.4 Development of the Internal-Riser FCC RTDs

1.3.4.1 VQS System For an internal-riser FCC unit, the riser usually inserts into the stripper and reactor vessel and is concentric with them. UOP's early straight-riser FCC units and later combustor-type FCC units as well as the S&W IFP RFCC units all belong to this category. To adapt to the symmetrical reactor layout, a compact RTD system was developed, that is, VQS system. The development of VQS system also began since 1992 until its first industrial application in 1998. As shown in Figure 1.23, a concentric cylinder column called "encloser" contains a top section of the internal riser. The top section of the encloser functions as a

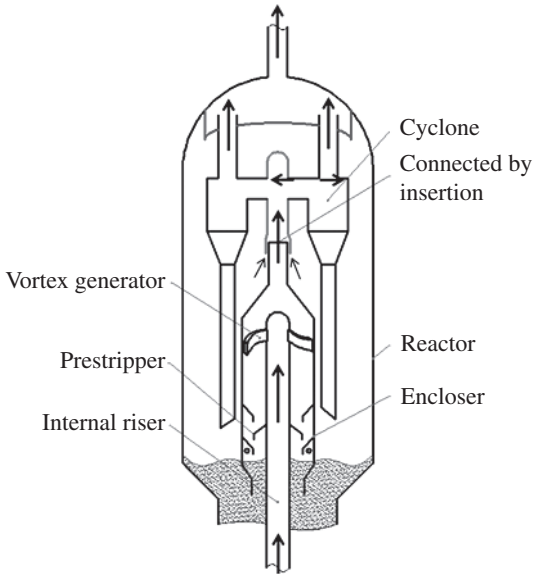

FIGURE 1.23 VQS system.

centrifugal gas–solid separation zone where swirling gas–solid flow is generated by the specially designed product vapor outlets in the riser top, namely, vortex generator. The bottom section of the encloser is a baffled prestripper for quick stripping oil gas entrained by the downward catalyst flow and sealing oil gas from flowing downward into the huge reactor space. This is an annular cross-flow prestripper with the same mechanism as in FSC system. A conical section connects the encloser top to withdraw the separated product vapor to the downstream cyclones. The RTD gas outlet tube is prolonged to insert into a large inlet tube that connects all the inlets of the downstream cyclones. Similar to FSC and CSC systems, this connection geometry facilitates to quickly withdraw the separated product vapor and maintain high containment of product vapor and high operating reliability. Whether the scale of a FCC unit is large or small, a VQS system is enough. By contrast, there are usually two or three FSC or CSC systems needed in a large-scale external-riser FCC unit.

The most distinct feature of VQS system is its design in gas–solid separation zone. The final structure shown in Figure 1.23 is a result of continuous improvement efforts. The vortex head of the earliest design is as shown in Figure 1.24. The top of the riser is sealed with a cover plate. Product vapor flows out through the several slots configured evenly around the circumferential wall near the riser end. Due to the enclosed outside arc wall and the two inclined top and bottom walls, product vapor flows in a downward spiral way, forming a centrifugal flow field favoring centrifugal gas–solid separation. Early results of laboratory experiments showed that the tangential gas velocity and the inclination angle, α, were the two key factors governing the collection efficiency. Finally, an optimized α between 15 and 25° and an optimized gas velocity in the range of 16–24 m/s were obtained. The resultant pressure drop is less than 2 kPa and acceptable [34].

Later, it was found in scale-up experiments that a modification of the vortex head shown in Figure 1.25 can further increase the particle collection efficiency [35]. Here, the gas–solid mixture is directed near the wall by several downward spiral arms. Particles do not need to cross the long distance between the outlet and the encloser wall before

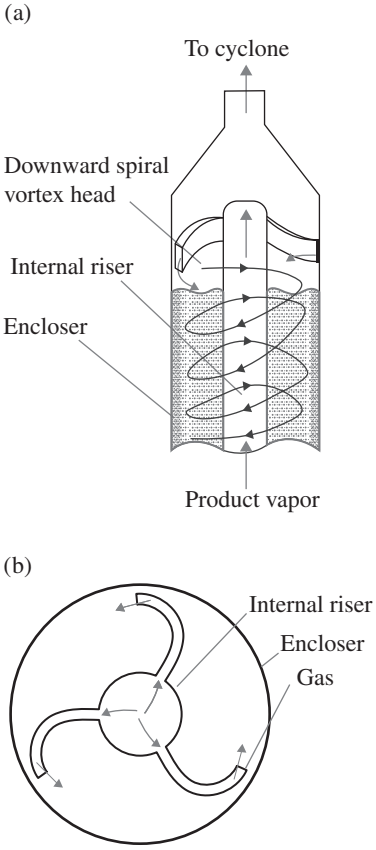

FIGURE 1.25 Second-generation vortex head: (a) side view and (b) top view.

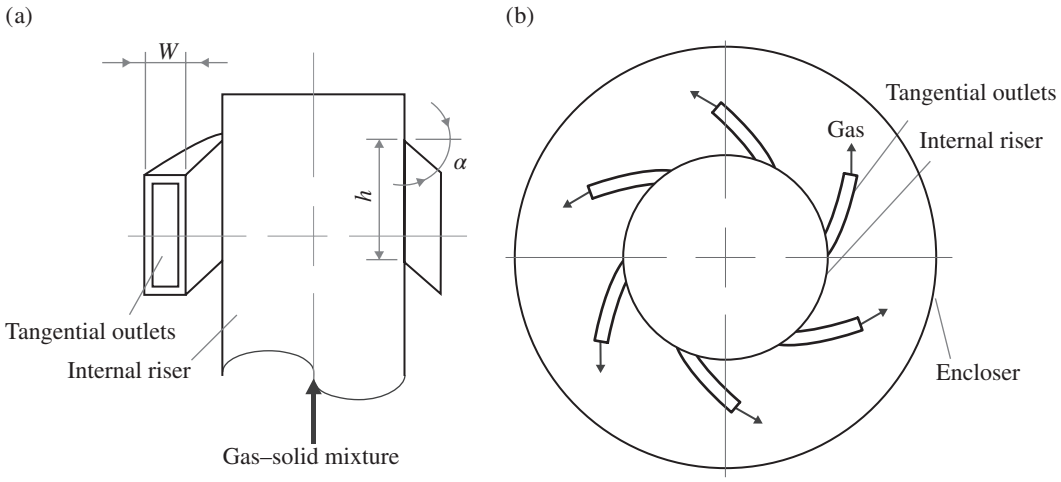

FIGURE 1.24 First-generation vortex head: (a) side view and (b) top view.

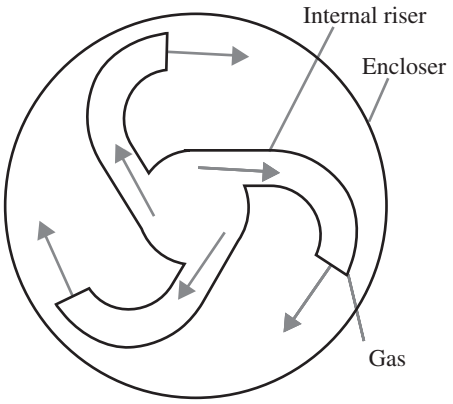

FIGURE 1.26 Third-generation vortex head.

separated, thus avoiding being carried away by the upward gas flow. This was also the structure when VQS system was first commissioned in industrial FCC unit in 1998. This gas–solid separation structure is similar to that in UOP's VSS system shown Figure 1.14b. However, the difference is the geometry of the vortex generator, which includes several downward spiral arms favoring higher particle recovery efficiency. The vortex generator of the VSS system has been settled with two horizontal arc arms. Particles ejected from one arm are possible to strike the frontal arm. This may influence its particle recovery efficiency negatively. Otherwise, erosion problems may also arise.

Even after successful industrial applications, the effort to improve VQS's particle recovery efficiency continued for many years. The latest version of the vortex generator in VQS system is that shown in Figure 1.26. Different from Figure 1.25b, the spiral arms connect tangentially with the internal riser, which makes a section of the riser with swirling gas–solid flow, acting as a preseparation zone before gas–solid mixture enters into the encloser space. It was proved that VQS's solid recovery efficiency could be further increased with this geometry [36].

The advantages of VQS system are summarized as follows:

- **Compact geometry**. In an internal-riser FCC unit, VQS system is installed concentrically to the reactor vessel. One VQS system is enough even for a very large FCC unit. Unlike FSC and CSC systems, two or more RTDs are needed when an FCC unit becomes large. This compact geometry design makes it the best choice of RTD system for an internal-riser FCC unit.
- **Short postriser residence time**. Compared to other RTD systems, the oil gas residence time in a VQS system is shorter. The postriser oil gas residence time can also be within 5 s in an FCC unit.
- **Higher oil gas containment approaching 100%**. Similar to the FSC system, the baffled prestripper in the bottom zone of the VQS encloser and the specially designed connection geometry between the gas outlet and the inlet of downstream cyclones prevent oil gas leaking into the huge disengager space, resulting in almost 100% containment of oil gas. The bed level of the stripper is recommended to submerge the annular particle outlet of the prestripper. If not, however, the prestripper can still maintain very high oil gas containment due to the cross-flow baffle structure in the prestripper. This gives higher operation flexibility to the VQS system.
- **High particle recovery efficiency greater than 98.5%**. The particle collection efficiency of the VQS system is also very high. The internal riser is a natural vortex stabilizer. Together with the optimized vortex head, strong centrifugal gas flow field forms in favorite of high-efficiency particle recovery. Large cold model test demonstrated that it had a greater than 98.5% particle recovery efficiency under all FCC operating conditions [35].
- **Better operating reliability**. The VQS system has similar connection geometry between the gas outlet and the inlet of downstream cyclones as FSC and CSC systems, which gives it better operating reliability in fluctuating operating conditions.

VQS system was first tested in an 80 Mton/annum RFCC unit in Sinopec's Yanshan Refinery. After revamp, the startup process was very smooth. Due to multiple technologies employed in that revamp, only the slurry solid content could be used to evaluate VQS's performance. When the unit operation stabilized, a calibration was conducted. The measured slurry solid content was less than 4 g/l, demonstrating VQS's satisfied particle recovery efficiency. The late application in Sinopec's Jiujiang Refinery in 1999 provided a better choice to examine the performance of VQS system thoroughly [37]. This RFCC unit had a 1.0 Mton/annum throughput. Only RTD was replaced in that revamp. A Tee inertial separator was replaced by a VQS system. The revamp was very successful. At the same throughput, dry gas yield decreased from 5.09 to 4.58 wt%; coke yield decreased from 7.97 to 7.41 wt%; the yield of gasoline and diesel oil increased from 66.92 to 68.12 wt%, that is, a 1.2% increase. This was the benefit of the shortened oil gas postriser residence time by the VQS system. VQS's prestripper further improved the stripping performance, resulting in decreased coke H/C ratio from 7.8 to 6.3 wt%. Otherwise, the decrease in the yield of coke and dry gas and the improved stripping performance enable the refinery further increase the residue-blending ratio in the feedstock from 33.8 to 42.3 wt%, further improving the unit profitability. After revamp, the coking in the reactor vessel was greatly alleviated, which helped prolonging the unit turndown period and decreasing the frequency of the unscheduled unit shutdown.

By now, there have been 18 VQS systems commercialized. The largest VQS system was used in a 3.0 Mton/annum RFCC unit in CNPC's Lanzhou Refinery.

1.3.4.2 SVQS System VQS system usually has very good performances in both particle recovery and restraining undesirable postriser reactions, but its particle recovery efficiency in larger FCC units with a throughput greater than 2.5 Mton/annum was found not to be good as in smaller units. This is due to the weakened centrifugal flow field in larger units, a similar mechanism in gas–solid cyclone separators. In order to further increase the particle recovery efficiency of VQS system, a series of laboratory researches were conducted to find its bottlenecks, which led to the development of the second-generation RTD system for internal-riser FCC units, that is, the SVQS system.

As shown in Figure 1.27, except for the vortex head design, other geometrical designs maintain the same as VQS system. A detailed schematic of SVQS's vortex head is shown in Figure 1.28. Compared with the vortex head of VQS system (see Figures 1.25 and 1.26), there are a partition column and an annular cover added. The spiral arms penetrate through the partition column. This idea of adding a partition column came from the findings by a series of CFD simulations and laboratory tests on the flow field of the VQS system [38–41]. It was found that a large fraction of gas bypasses, flowing upward and leaving the encloser directly, which results in some entrained particles incapable of entering the lower region with stronger centrifugal strength and lower particle recovery efficiency. When the encloser diameter is small, this problem is not very remarkable. However, when the encloser diameter increases as an FCC unit increases, the weakened centrifugal strength and the larger volume of bypassing gas can reduce the particle recovery efficiency considerably. With the partition column and the annular cover, all the gas–solid mixture has to flow spirally downward before having opportunity to leave the separation zone. Moreover, the centrifugal strength is stronger without bypassing and particles stay longer in a stronger centrifugal gas vortex, which is in favor of higher particle recovery efficiency. In a small-scale laboratory unit, its performance was systematically tested. The results show that its particle recovery efficiency had 20–30% increase, while the pressure drop only increased 0.2–0.8 kPa [42].

After a series of forward geometry optimizations and large continuous cold model validation, SVQS system was first applied in Sinopec's Jinling Refinery to replace an old VQS system in a 1.0 Mton/annum RFCC unit. Despite a slight increase in catalyst circulation rate, the average slurry solid content decreased from 5.9 to 4.0 g/l after unit revamp, demonstrating SVQS's higher particle recovery efficiency. Later, a replacement of VQS system by SVQS system was conducted in Sinopec's Yanshan Refinery in a 0.8 Mton/annum RFCC unit. A lower slurry solid content was also achieved after revamp. Unfortunately, an application in larger FCC units with a throughput greater than 2.5 Mton/annum is still lacking to better validate SVQS's performance.

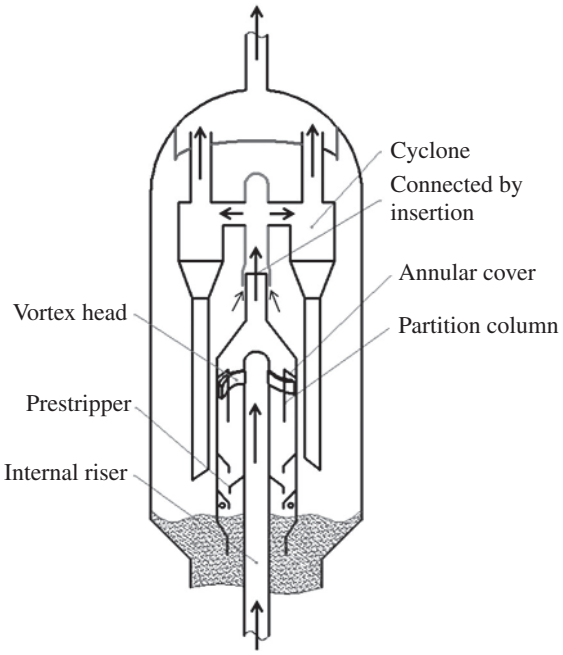

FIGURE 1.27 SVQS system.

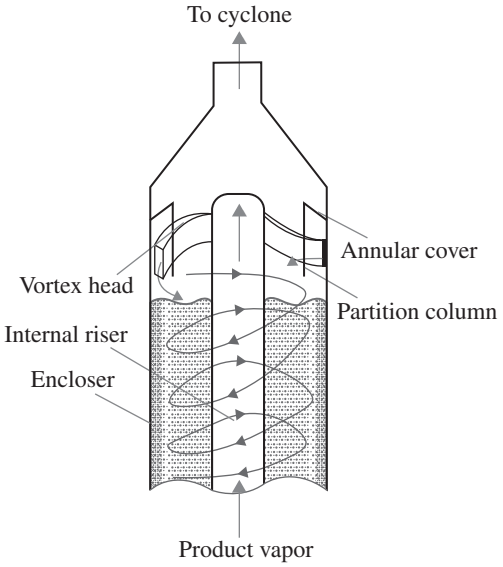

FIGURE 1.28 The vortex head for SVQS.

1.3.5 Conclusions and Perspectives

In order to accommodate with the increasing need for processing feedstock in China, an R&D program was initialized since the early 1990s to develop advanced RTD technologies to improve FCC product yields and restraining the more and more serious coking problems. The development guideline of three "quick"s and two "high"s embodies a balance among the multiple requirements of an RTD in particle recovery, postriser oil gas residence time, and reliability. After over 20 years of laboratory research, optimizations, and applications,

four advanced RTD systems were developed successfully for China's various types of FCC units. Both internal- and external-riser FCC units of different throughputs can benefit from this technology. By now, nearly 50 advanced RTD systems were applied in commercial FCC units. The sum of the throughputs of all these FCC units has already exceeded 40.0 Mton/annum, which is nearly one-third of China's total FCC processing capacity.

As these FCC RTD technologies become more and more mature and recognized in China, more applications of these technologies are expected in future. Future work should be devoted to further optimize and modify these technologies to accommodate with the changing FCC process technologies, for example, new FCC processes for producing light olefins and cleaner transportation fuels. Otherwise, these RTD technologies also have application potentials in other chemical processes needing quick termination of reactions or accurate control of reaction time Therefore, modification and optimization efforts are also needed in applying these technologies in these areas.

1.4 AN MZCC FCC PROCESS

1.4.1 Technology Background

Recently, improving the yields of light oil and liquid product of FCC unit is a perpetual impetus for developing FCC technology. However, the yield of coke and dry gas has been on a high level as the crude quality declines together with the increasing of blend ratio of residue during FCC process. Dry gas, a low valuable by-product during FCC process, contains the most hydrogen. The effective utilization of hydrogen in heavy feedstocks decreases with the increase in the yield of dry gas, resulting in low yields of light oil and liquid products. At present, the optimizing operation of unit and the use of new technologies and equipment, such as new type of prelifting, atomization nozzle, and quick separation for solid and liquid, have reduced the yields of nonaimed products. However, these technologies have partly revised the FCC equipment, and the effects are not sufficient due to the limitation of other reaction zones.

The FCC reaction system couples every reaction zones together from the feeding zone, to the reaction zone, to the exit zone, and finally to the lifting zone. If aiming at different reaction properties for different reaction zones and the sequence feature for these processes and their intereffects, one condition can be given to promote the cracking reactions but to prohibit the thermal cracking reactions. Plentiful researches have demonstrated that it is a desired technology to realize the effective contact for catalyst and feedstock under high oil–catalyst mixing energy, plug flow of reaction under higher C/O ratio, and further reaction for oil and gas heavy component based on high oil–catalyst mixing FCC. This MZCC FCC process can be described as follows: (i) high effective contact for oil–catalyst and high energy back-mixing for feeding zone, (ii) orderly proceeding and plug flow for the reaction zone, (iii) the quick separation for oil and catalyst for the exit zone, and (iv) re-reaction and chemical stripping for heavy component for the stripping zone. Therefore, an MZCC has been developed for CUPB [43].

The MZCC technology developed by CUPB can be selected by whether three zones (feeding zone, reaction zone, and exit zone) or four zones (feeding zone, reaction zone, exit zone, and lifting zone) to coordinated-control according to the properties of feedstock and catalysts, the operating scheme, and the operating period. The technology increases the yield of liquid products and light oil, but it decreases the yield of dry gas and coke.

1.4.2 Reaction Principle for MZCC

From the viewpoint of reaction principle, the essence of FCC reaction is to convert heavy feedstock into products with new chemical structure by re-distributing carbon and hydrogen [44]. The hydrogen contents of liquefied petroleum gas (LPG), gasoline, and diesel are higher than feedstock. The needs of the increasing hydrogen content for the above products require the decreasing generation of the low-hydrogen-content products such as coke and slurry. Therefore, maintaining optimal coke yield at a low level as well as decreasing yield of dry gas is an important direction for improving effective conversion of FCC reactions.

Aiming at the high yield of dry gas, the MZCC technology exploited by CUPB is based on high oil–catalyst mixing energy FCC reaction. The technology coordinated-controlled multireaction zones of FCC unit, and the principle chart is shown in Figure 1.29.

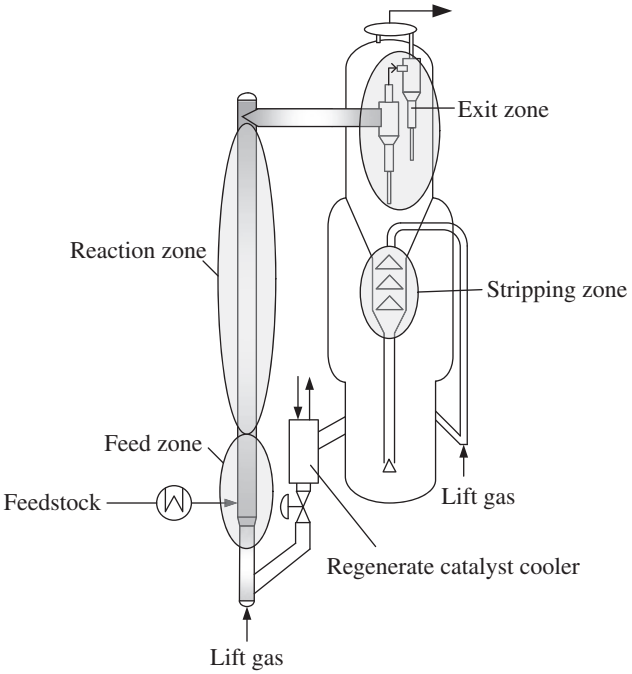

FIGURE 1.29 Schematic diagram of MZCC process.

1.4.2.1 High Oil–Catalyst Mixing Energy for Feeding Zone The oil–catalyst mixing energy refers to momentum and heat carried by feedstock and catalysts when the oil and catalyst contacted. Effective atomize nozzle can strengthen the transfer of momentum and make heavy oil atomize sufficiently, which could improve oil–catalyst mixing and transfer efficiency to same extent to improve the distribution of products. Meanwhile, the premise for realizing high oil–catalyst mixing energy is to solve the heat balance limit of FCC reaction and regeneration process and to flexibly adjust the regenerated catalyst circulating volume to adapt different feedstock and modulation for process [45].

1.4.2.2 High C/OCatalyst-to-Oil Ratio and Plug Flow for Reaction Zone The temperature of the reaction zone is above 500°C in the riser. There always exists a competition between catalytic cracking reaction and thermal reaction. Therefore, the increase in catalysts-to-oil ratio could improve the total reaction activity of the reaction zone so as to prohibit the thermal reaction in the backstage of the reaction zone due to the deactivation of catalyst.

1.4.2.3 Gas and Solid Super Short Quick Separation for Exit Zone Using or developing gas and solid separation system can realize quick separation of catalysts and oil gas under high catalyst circulation rate and reduce the overcracking reactions and thermal reactions [46], especially, reactions that are under the reaction condition of high C/O ratio.

1.4.2.4 High-Temperature Chemical Stripping Zone Chemical reactions still exist in the lifting zone of an FCC unit. The heavy components adsorbed on spent catalyst are removed by physical lifting with steam. It is necessary to strengthen the lifting zone to promote further conversion of heavy oil and as to avoid coking in the disengager. Therefore, a process is proposed: regeneration catalyst is introduced to increase the temperature of the lifting zone to 490–510°C to increase the average microactivity index with 2–5 units, and then realize the effective chemical lifting for heavy components adsorbed on spent catalyst.

1.4.3 Design Principle of MZCC Reactor

The key to implement the MZCC technology is to offer regenerated catalyst with low temperature and high circulate content. A cooler is needed for the technology to cool down a part of regenerated catalysts before they are contacted with the other part of regenerated catalysts with high temperature in riser. The process is shown in Figure 1.30 [47]. The reaction condition in the riser will be influenced by

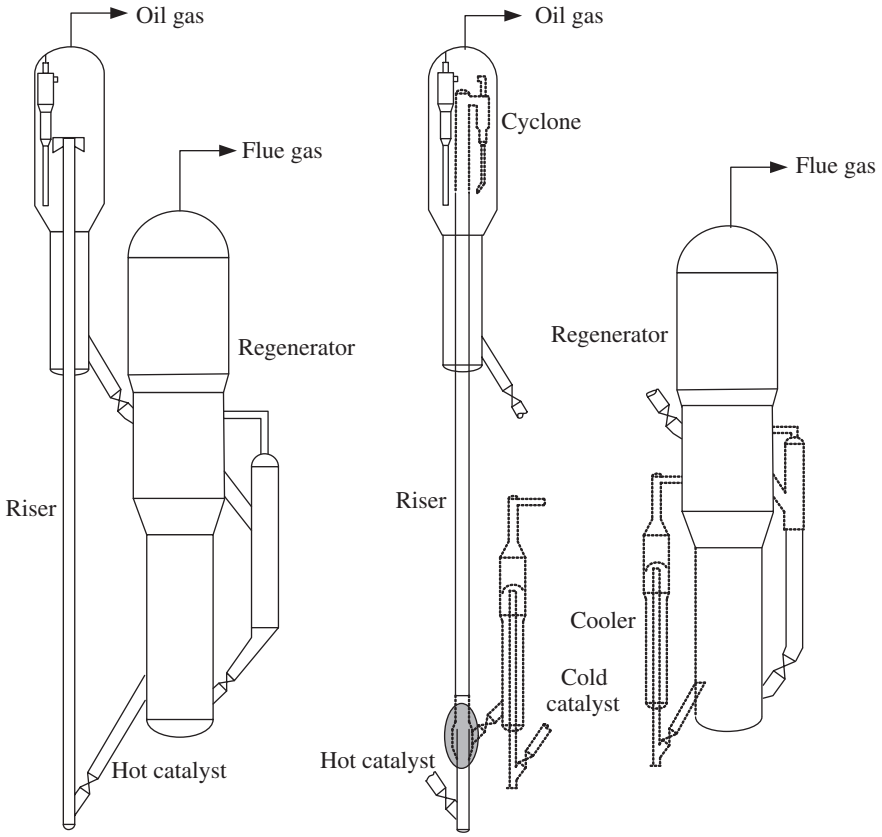

FIGURE 1.30 Comparison of prelift section between MZCC and routine FCC.

mixing effects of high- and low-temperature regenerated catalysts. Comparing the distribution of temperature in the prelifting stage of different structure as shown in Figure 1.31, one can find that the mixing effect could be improved by increasing the height of the prelifting stage. The difference in temperature between cold and hot regenerated catalysts could be eliminated by introducing high-temperature regenerated catalysts and low-temperature regenerated catalysts into the prelifting stage in the same side and removing the sleeve of the entrance for the low-temperature regenerated catalyst; thus, the mixing effects of cold and hot regenerated catalysts in the prelifting stage could be improved by a large margin.

The new feeding technology is able to realize the quick mixing of oil and catalysts in high oil–catalysts mixing energy. It can reach the goal of promoting quick and uniform mixing of feedstock and catalysts by installing two stage of feeding nozzle in the riser, setting the arrange angle and location of specific feeding nozzle. The arrangement of new feeding nozzle is shown in Figure 1.32.

In order to realize the plug flow of oil gas and catalysts in the riser, a new inner structure is installed in the riser [48]. It can retard the backfall effects of up-going catalysts in the riser and make the oil gas and catalysts with a plug flow reactor in the riser. The numerical simulation results of structure for new type reactor are shown in Figure 1.33. From Figure 1.33, one can see that the new type structure riser can eliminate the core-annulus flow of catalysts in the riser and make the distribution of catalysts more uniform in radial direction in the riser.

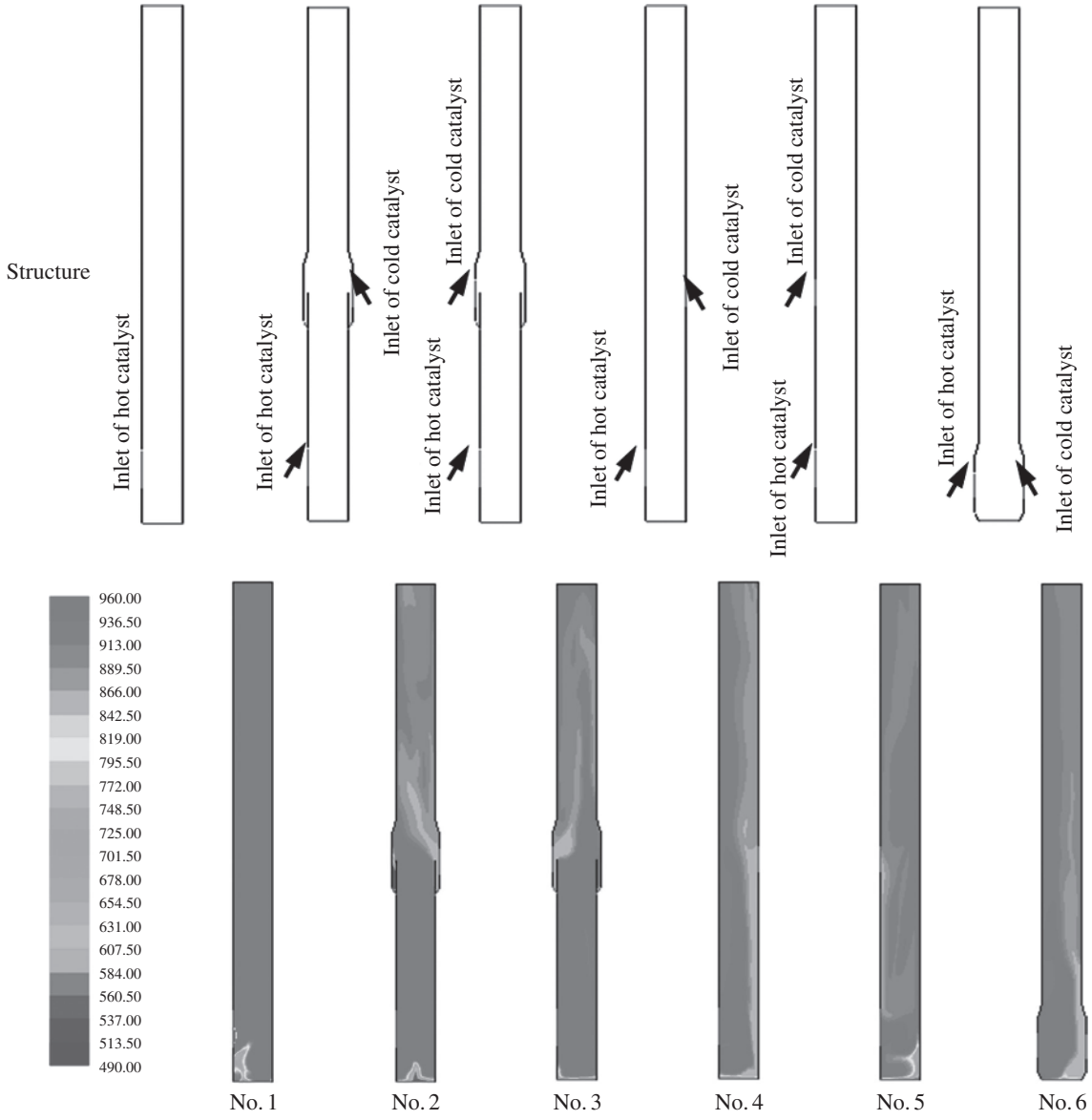

FIGURE 1.31 Temperature distributions in different preriser structures.

Aiming at the quick separation of oil gas and catalysts in the exit of riser, three new quick separation baffles have been developed: FSC, VQS, and CSC, and the structure of each of these systems is shown in Figure 1.34 [49, 50]. The average retention time of oil gas after reaction can be reduced to below 5 s and the problems of quick separation of oil gas and catalysts as well as the quick prelifting problem of oil gas carrying by catalysts can be solved once these three new quick separating systems are used. Therefore, the nonselective secondary cracking reaction and thermal cracking reaction in the disengager and the coking situation in the disengager can be solved.

In order to solve the industrial problem of coking in the disengager [51], the concept of chemical lifting vessel is proposed, and this is shown in Figure 1.35 [52]. By means of changing the structure of the lifting stage, the regenerated catalysts are induced into the lifting stage, and the transformation and flow properties are adjusted to create an environment under which the liquid heavy components are adsorbed on catalysts that have no time to react but can easily coke in the disengager, and thus the interfactor of coking within catalytic cracking disengager is eliminated. Moreover, based on the researches of different coking rule and course for gas and liquid components as well as the properties for gas–solid multiphase flow, heat transfer, and matter transfer, the joint method for the exit of first-landfall tropical cyclone and the entrance of top cyclone is determined and the external cause of coking in catalytic cracking disengager is overcome [53].

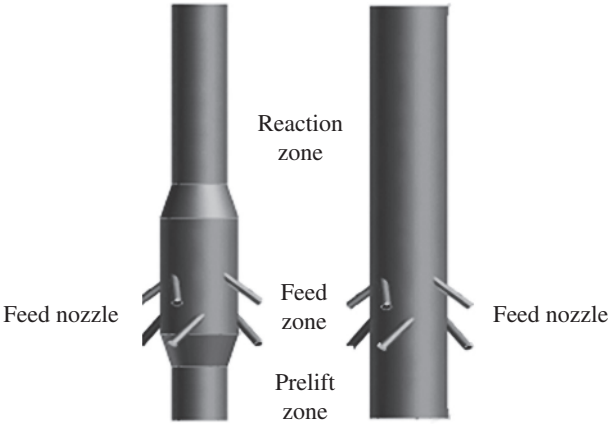

FIGURE 1.32 New array arrangement of FCC feed injectors.

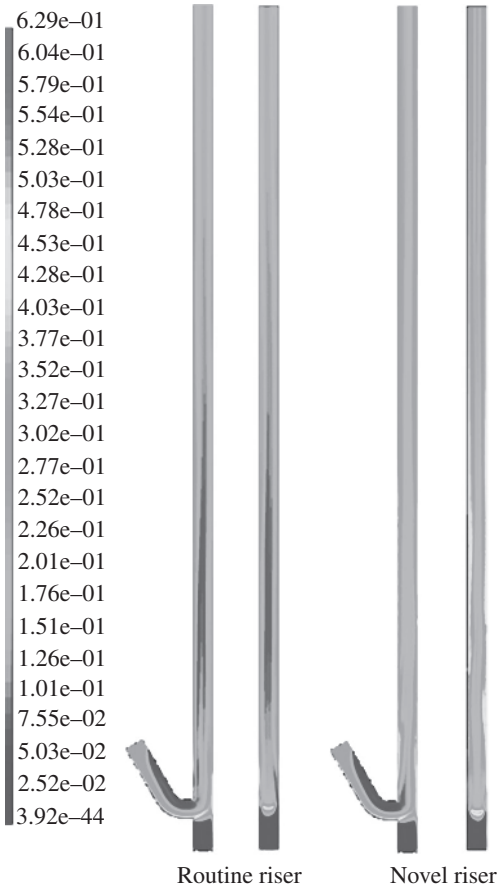

FIGURE 1.33 Comparison of gas–solid two-phase distribution within the conventional riser reactor with that of new array arrangement of feed injector.

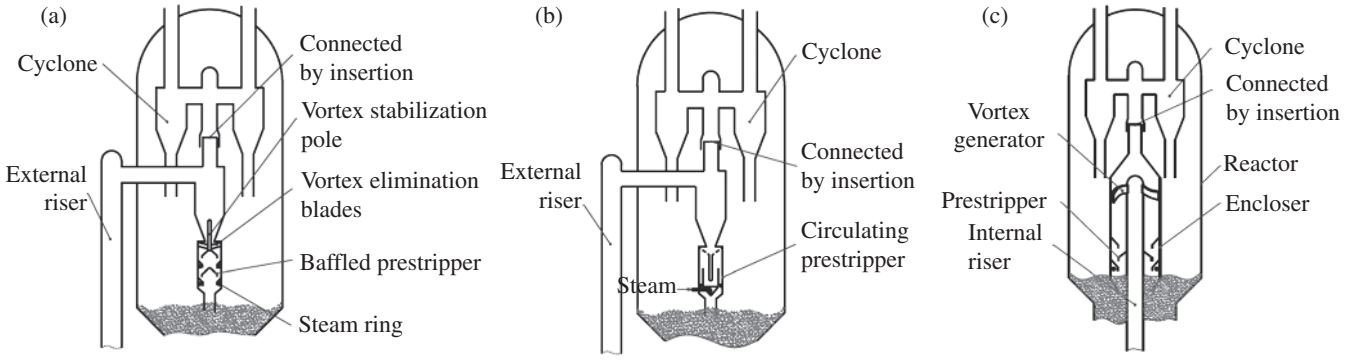

FIGURE 1.34 New configurations of rapid separation: (a) FSC, (b) CSC, and (c) VQS.

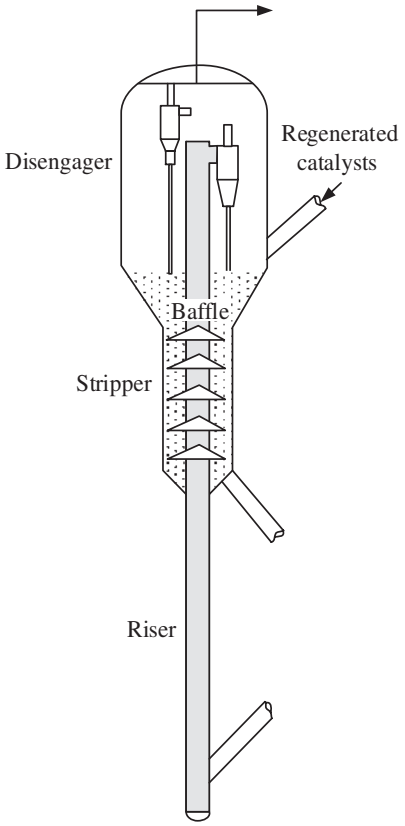

FIGURE 1.35 Schematic diagram of chemical strippers.

1.4.4 Key Basic Study

The flow field, temperature field, and concentration field of oil gas and catalyst are researched by numerical simulation. The results of the feeding model for conventional riser are shown in Figure 1.36, and that for new riser are shown in Figure 1.37. Compared with Figures 1.36 and 1.37, the new type array feeding technology can mix oil gas and catalysts uniformly at shorter distance and time, and thus promote the catalytic cracking reaction deeply.

In order to investigate the effects of high oil–catalyst mixing energy feeding, the heavy oil catalytic cracking reaction under high C/O ratio of higher oil–catalyst mixing energy and short contact time was investigated on the 2 kg/g pilot FCC unit, and a part of results are shown in Tables 1.7 and 1.8 [54, 55]. From Tables 1.7 and 1.8, one can find that compared with routine FCC reaction condition (reaction temperature is 500, oil–catalyst mixing temperature is 660°C, reaction time is 3.05 s, C/O ratio is 7), the distribution of product has improved dramatically under the reaction condition of high C/O ratio of higher oil–catalyst mixing energy and short contact time. Under the reaction temperature of 525°C and the C/O ratio of 15, the yield of dry gas decreases by 2.18%, that of light oil increases by 4.82%, and that of coke decreases by 1.43% compared to that of routine FCC reaction condition. Research found that the key for improving distribution of FCC product is to shorten the reaction time as well as increase the C/O ratio, maintain suitable reaction temperature and oil–catalyst mixing temperature. The optimal process conditions are obtained: reaction time of 1.1–1.5 s, C/O ratio of 12–15, reaction time of 530°C, and regenerant temperature of 630°C.

Based on the analysis of primary cause for FCC disengager coking, the model of FCC disengage coking is proposed: the heavy component that does not crack completely by condensating into oil drop in disengager coking after steam stripping [56–58]. To solve this problem fundamentally is to create a favorable reaction condition for converting this part of heavy component completely. Therefore, the chemical stripper and the preventing technology for FCC disengager coking are proposed and gained the national patent authorization [59]. When the regenerant is introduced into the stripping stage (shown in Tables 1.9, 1.10, and 1.11) [52], the re-reacting of heavy components in the stripping stage that adsorbed on spent catalyst is promoted, and thereby strengthen the heavy oil catalytic cracking reaction.

1.4.5 The Industry Application of MZCC

In order to improve product distribution and decrease the yield of dry gas and coke in Jinan Petrochemistry Company of SNOPEC 140 Mton/year RFCC unit, the MZCC technology with three zones coordinated-controlled scheme was adapted including the optimization of the feeding zone, reaction zone, and exit zone of the riser [47]. The main retrofit contents are as follows:

1. A catalyst cooler is added. It decouples the limit of thermal balance of FCC reaction–regeneration process. Therefore, limits of catalyst circulation ratio in riser are solved; mixing of thermal energy in the process is enhanced and reaction selectivity in riser is improved.
2. The original four-leaf-type quick separator is cancelled. The inner riser is increased by 6 m and fixed with four primary cyclone separators. The i-associated mode structure between vapor line of the primary cyclone separators and the single cyclone in the disengager is adapted to decrease the retention time of oil gas in the disengager.
3. Partial modification of semiregeneration inclined tube and addition of Φ600 gas recycling tube improves gas removal effect of semiregenerated catalyst.

The retrofit contents of unit according to the MZCC technology is shown in Figure 1.38. The feedstock properties before and after using the MZCC technology are shown in Table 1.12. The data in Table 1.12 show that the properties of feedstock are better in MZCC calibration than those in blank calibration.

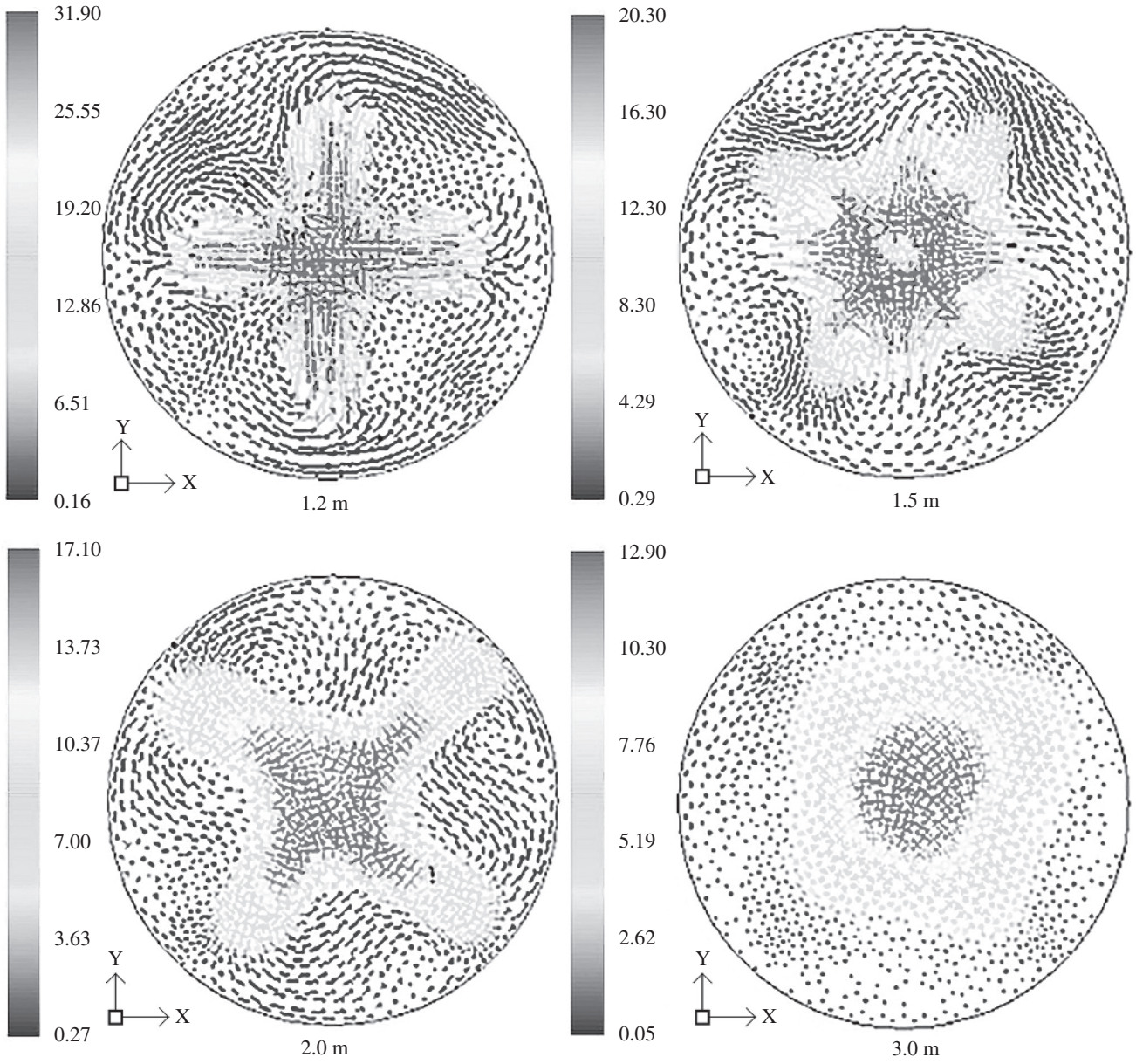

FIGURE 1.36 Numerical simulation results of gas–solid two-phase distribution within the conventional riser reactors.

Table 1.13 shows the process conditions before and after using the MZCC technology. From Table 1.13, one can see that the recycle ratio decreases from 0.2 to 0.08 due to the increase of reaction depth. The proportion of feedstock atomizing steam decreases from 9.8 to 9.45 wt%. The operational conditions of blank calibration are as follows: temperature is 501°C, regenerate temperature is 678°C, and the C/O ratio is 6.0, and those for MZCC calibration is 505°C, 671°C, and 7.65 separately.

Table 1.14 shows the material balance data before and after using the MZCC technology. From Table 1.14, one can see that after using the MZCC technology, the conversion increases from 63.84 to 72.52%. However, the selectivity of dry gas and coke decreases obviously due to the MZCC measure. Compared with blank calibration, under the operational condition the residue carbon of feedstock increases by 0.3 wt%, the density of feedstock increases and atomization effects of feedstock deteriorates: the yield of dry gas decreases by 0.2% and the yield of liquid product increases by 2.95% for the MZCC calibration period. This phenomenon demonstrates the advantages of controlling the product distribution by utilizing regenerator cooler to decouple the limit

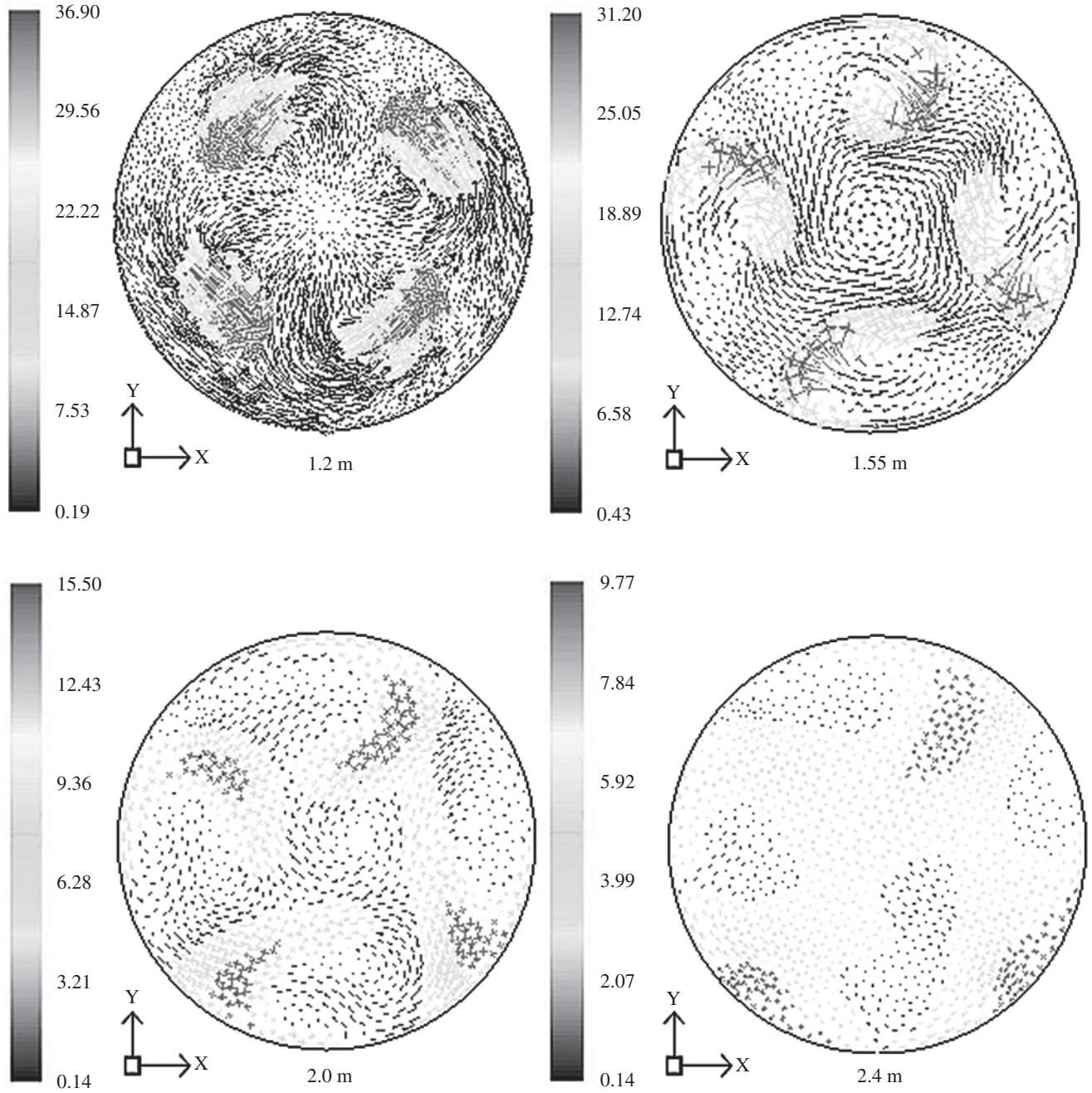

FIGURE 1.37 Numerical simulation results of gas–solid two-phase distribution within the riser reactor with new array arrangement of feed injector.

TABLE 1.7 Experiment Results of High Oil and Catalyst Mixing Energy and Short Contact Time RFCC (Temperature of Regenerated Catalyst is 660°C)

			Product Distribution, wt%							Yield, wt%	
Ton/°C	C/O[a]	Ton[b]/s	Dry Gas	LPG	Gasoline	Diesel	Heavy Oil	Coke	X^c, %	Light Oil	Liquid
500	7.0	3.05	4.45	16.14	37.23	19.25	14.43	8.50	66.32	56.48	72.62
520	10.0	1.37	2.52	14.69	39.47	19.31	16.50	7.50	64.19	58.78	73.48
550	15.0	1.24	3.05	19.52	39.63	18.64	11.66	7.49	69.70	58.27	77.79
550	15.0	1.07	2.34	16.54	39.63	19.89	14.81	6.79	65.30	59.53	76.07

[a] Catalyst-to-oil ratio.
[b] Reaction time.
[c] Conversion.

TABLE 1.8 Experiment Results of High Oil and Catalyst Mixing Energy and Short Contact Time RFCC (Temperature of Regenerated Catalyst is 630°C)

			Product Distribution, wt%							Yield, wt%	
Ton/°C	C/O[a]	Ton[b]/s	Dry Gas	LPG	Gasoline	Diesel	Heavy Oil	Coke	X^c, %	Light Oil	Liquid
500	7.00	3.05	4.45	16.14	37.23	19.25	14.43	8.50	66.32	56.48	72.62
500	9.56	2.38	3.65	12.60	38.58	19.85	16.91	8.41	63.24	58.43	71.03
525	15.0	1.31	2.89	17.95	40.40	20.03	11.64	7.10	68.33	60.43	78.38
525	15.0	1.11	1.65	17.90	41.02	21.16	11.24	7.04	67.61	62.17	80.08

[a] Catalyst-to-oil ratio.
[b] Reaction time.
[c] Conversion.

TABLE 1.9 Product Yields of Physical and Chemical Stripping

Item	Physical Stripping	Chemical Stripping			
R/S ratio	0	1:12	1:6	1:4	1:3
Product yield from reaction step, wt%	66.99	66.94	66.84	66.72	66.67
Product yield from stripping step, wt%	24.47	25.25	25.60	25.53	25.37
Coke yield after stripping, wt%	8.54	7.81	7.56	7.75	7.96

TABLE 1.10 Composition of Cracked Gas in Physical and Chemical Stripping

Item	Reaction Step	Physical Stripping	Chemical Stripping			
R/S ratio	—	0	1:12	1:6	1:4	1:3
H_2, wt%	0.16	3.95	4.02	4.09	4.11	4.13
(C_1+C_2), wt%	15.78	24.37	21.59	25.97	28.53	28.53
(C_3+C_4), wt%	84.06	75.63	74.39	69.94	67.36	67.34

TABLE 1.11 Changes in FBP and Heavy Components (Boiling Range >480°C) in the Liquid Product of Physical and Chemical Stripping

Item	Physical Stripping	Chemical Stripping			
R/S ratio	0	1:12	1:6	1:4	1:3
Yield of liquid product (>480°C), wt%	0.39	0.40	0.35	0.26	0.25
FBP of liquid product, °C	549.4	547.1	540.2	523.6	520.7

of thermal balance during FCC reaction–regeneration process and adopting the MZCC measures, which includes high C/O ratio, low oil, and catalysts contacting temperature, as well as ultrafast exit separation.

Table 1.15 shows the data analysis of dry gas and LPG before and after the MZCC technology used in FCC units. Analyzing the data from Table 1.15, one can see that the propylene content decreases but butene content increases by 1%, and the total contents of olefin increase by more than 2% due to the enhancement of C/O ratio when the MZCC technology is used.

From the data analysis of gasoline and diesel in Tables 1.16 and 1.17, respectively, one can see that the research octane number (RON) of gasoline is above 90, and olefin content is about 33 v%, while the cetane number decreases compared with the blank experiment for diesel.

1.4.6 Prospectives

Aiming at the different properties of reaction zones in FCC riser, MZCC technology developed by CUPB adopts creative process method and matched dedicated equipment. The main innovate includes the following:

1. The concept of MZCC FCC is proposed and reaction condition for MZCC FCC is realized.
2. The efficient regenerant temperature-regulated equipment and the super short quick separator for FCC riser terminator are required.
3. The high C/O ratio operational viewpoint under a small temperature difference of reaction condition between regenerant and reactant is adopted.

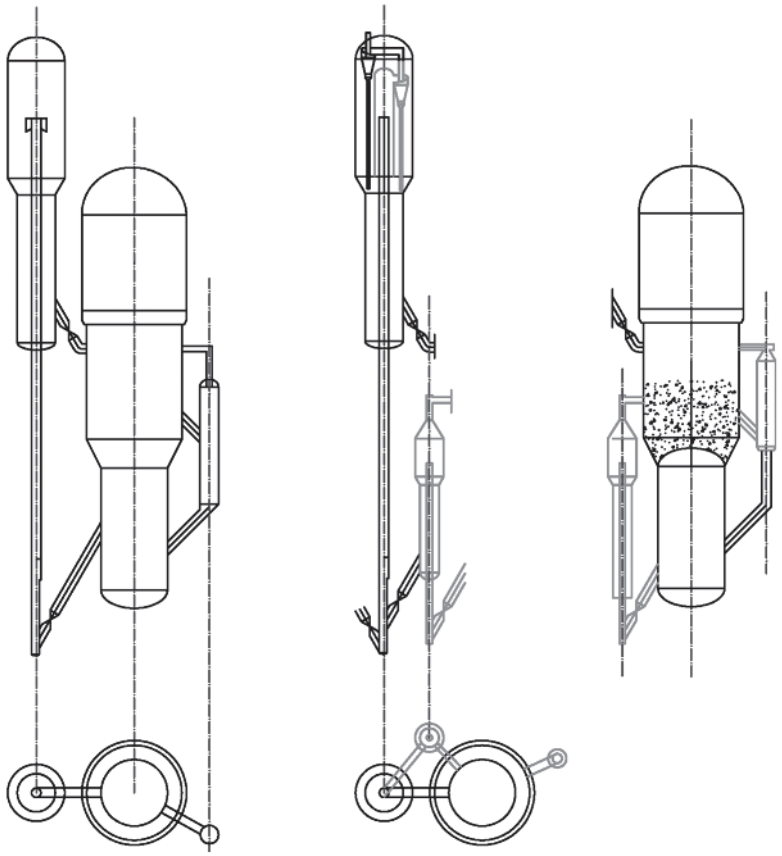

FIGURE 1.38 Reaction–regeneration system structures before and after MZCC application.

TABLE 1.12 Feedstock Properties Before and After MZCC Application

Item		Before MZCC Application	After MZCC Application
Density (20°C), kg/m^3		905.5	920.6
Viscosity (80°C), mm^2/s		18.76	23.3
Viscosity (100°C), mm^2/s		10.88	12.10
CCR, wt%		3.62	3.93
Condensation point, °C		35	30.5
Total nitrogen, μg/g		1985	2473
Sulfur, μg/g		3342	5111
Metal, μg/g	Fe	7.85	8.9
	Ni	5.45	12.5
	V	0.47	0.145
	Cu	<0.1	0
	Na	0.5	1.95
SARA, %	Saturates	65.38	54.8
	Aromatics	21.35	23.3
	Resins	12.28	21.4
	Asphaltenes	0.99	0.61

TABLE 1.13 Operating Conditions Before and After MZCC Application

Item	Before Application	After Application
Regenerated catalyst temperature, °C	678	671
Disengager pressure, kPa	179	163
Riser outlet temperature, °C	501	505
Feedstock preheating temperature, °C	223	212
Recycle ratio	0.20	0.08
Catalyst to oil ratio	6.0	7.65
Reaction time, s	3.32	3.48
Stripping steam/kg/ton catalyst	6.0	5.02
Feedstock atomizing steam, wt%	4.98	6.05

TABLE 1.14 Material Balance Before and After MZCC Application

Item	Before Application	After Application	Changes
Acid gas, wt%	0.45	0.47	+0.02
Dry gas, wt%	3.11	2.91	−0.20
LPG, wt%	17.11	14.15	−2.96
Gasoline, wt%	34.53	46.54	+12.01
Diesel, wt%	30.39	24.29	−6.1
Slurry oil, wt%	5.77	2.89	−2.88
Coke, wt%	8.64	8.45	−0.19
Loss, wt%	0.35	0.30	−0.05
Conversion, wt%	63.84	72.52	+8.68
Yield of light oil, wt%	64.92	70.83	+5.91
Liquid yield, wt%	82.03	84.98	+2.95
(Dry gas + coke) selectivity	0.18	0.16	−0.02

TABLE 1.16 Stable Gasoline Properties Before and After MZCC Application

Item		Before Application	After Application
Regenerated catalyst temperature, °C		678	671
Density (20°C), kg/m^3		708.0	733.9
Existent gum, mg/100 ml		1.2	1.2
Acidity, mgKOH/100 ml		0.37	0.095
Bromine number, gBr/100 g		78.6	83.0
Corrosion		Up to grade	Up to grade
Vapor pressure, kPa		90	63.02
Induction period, min		1084	1614
Total nitrogen, μg/g		53	78.97
Paraffins, v%		—	44.74
Olefins, v%		—	33.68
Aromatics, v%		—	21.58
Benzene, v%		—	0.32
Total sulfur, μg/g		388	586
Total sulfur declines, %		—	15.56
Octane number	RON	91.5	91.6
	MON	80.9	80.9
Distillation range, °C	IBP	31	35
	10%	43	53
	30%	59	72
	50%	82	98
	70%	116	132
	90%	158	173
	95%		184
	KK	178	199

From the fundamental research in the laboratory and the data from 140 Mton/year FCC unit in Jinan Petrochemical Company of SINOPEC, the MZCC technology can improve the yields of both liquid products and light oil as well as reduce the yield of dry gas and coke. The technology is superior to the existing FCC technologies and shows a better industrialized application prospect.

TABLE 1.15 Composition of Dry Gas and LPG Before and After MZCC Application

Item		Before Application	After Application
Regenerated catalyst temperature, °C		678	671
Dry gas, v%	Relative density	—	0.67
	H_2	20.48	25.47
	Air	25.71	28.33
	CH_4	23.65	23.69
	C_3 and C_3^+	1.26	0.73
	H_2/CH_4	0.87	1.07
LPG, v%	C_2^-	0.16	0
	C_3H_8	12.48	9.07
	C_3H_6	43.26	42.53
	i-C_4H_{10}	15.13	17.89
	n-C_4H_{10}	5.52	4.17
	C_4H_8	13.27	14.12
	C_5 and C_5^+	0.00	0.00
	∑Olefin	66.87	68.89

TABLE 1.17 Light Diesel Properties Before and After MZCC Application

Item		Before Application	After Application
Regenerated catalyst temperature, °C		678	670
Density (20°C), kg/m^3		887.8	938.6
Existent gum, mg/100 ml		95.6	418
Acidity, mgKOH/100 ml		1.44	1.24
Bromine number, gBr/100 g		14.8	11.79
Flash point, °C		56	81.5
Condensation point, °C		−7	−0.17
Cetane index		34	27.7
Total nitrogen, μg/g		1015	1460
Basic nitrogen, μg/g		0.0165	0.013
Sulfur, μg/g		2656	5298
Distillation range, °C	IBP	160	186
	10%	207	235
	30%	237	264
	50%	263	286
	70%	294	321
	90%	328	363
	95%	339	375.5

1.5 TWO-STAGE RISER FLUID CATALYTIC CRACKING PROCESS

1.5.1 Preface

Petroleum is perhaps the most important substance consumed in modern society. It provides not only fuel for industrial society but also raw chemical materials for the chemical industry. However, the workable reserves of conventional

crude oil are decreasing with the escalating demand of petroleum. Meanwhile, the crude oil feedstock for oil processing is becoming heavier and more inferior. Therefore, how to use the depletable petroleum resource efficiently has become a hot international issue. The properties of each crude oil vary greatly among different oil fields, but in general at least 50% of the crude oil is the heavy oil, so more efficiently converting heavy oil into lighter products is the key to improve the utilization ratio of oil resources. The FCC process continues to play a crucial role in an integrated refinery as the primary conversion process of heavy oil to lighter products in the global scale. A total processing capacity of FCC units in China is over 130 Mton/year, which provide over 75% of gasoline and approximately 30% of diesel in China fuel oil market. Therefore, increasing the light oil yield of the FCC process plays a pivotal role in improving economic performance of the oil refining industry, releasing the contradiction of light oil supply and demand, raising the utilization ratio of oil resources, saving energy, and reducing emissions.

FCC is the main process of catalytic cracking of heavy oil to gasoline, diesel, and LPG and some by-products (dry gas and coke) at high reaction temperature through gas–solid fluidization technology. In the conventional FCC process, the preheated high-boiling petroleum feedstock (at about 315–430°C) consisting of long-chain hydrocarbon molecules is combined with recycle oil from the bottom of the distillation column and injected into the bottom of riser reactor where it is vaporized and cracked into smaller molecules by contacting with the hot regenerated catalyst from the regenerator. All of the cracking reactions take place in approximately 3 s. The coked catalyst and oil vapor are separated through a set of two-stage cyclones, then the coked catalyst is sent to the regenerator after stripping, and the oil vapor is piped to the fractionator.

Since the startup of the first commercial FCC unit in 1942 [60], many improvements have been made in the field of catalysts, feed nozzles, and rapid gas–solid separation equipment. In order to reduce the olefin content of FCC gasoline, the flexible dual-riser FCC process, the SRFCC, and the FCC process for maximizing iso-paraffins (MIPs) were developed. However, the problem existed in the heart of the FCC unit—riser reactor is still not solved, which cause low yield of light oil, high yield of dry gas and coke, and poor quality of the FCC diesel. Especially with the heavier feedstock and higher operating severity for the FCC unit, these problems become more prominent and are urgently needed for the development of novel FCC process to increase the yield of light oil.

1.5.2 Reaction Mechanism of Heavy Oil in the Riser Reactor

At present, among the FCC units in China, the average yield of dry gas is about 4.0 wt%, including over 25 wt% hydrogen content, which is about two times of that in light oil. From the perspective of hydrogen balance, the reduction of 1.0 wt% of dry gas yield will contribute to the increase of 2.0 wt% of light oil yield. Therefore, it will be a reasonable method to increase the light oil yield by FCC technology innovation. The key to achieving this goal is understanding the mechanism of heavy oil cracking, determining the ideal reaction conditions, and realizing it in engineering by technology innovation.

1. Chemical reactions in the catalytic cracking process are complex, and the understanding of the reaction dynamics is based on the experimental study that needs further research. The heavy oil with complicated chemical structures and compositions cracks into multiple products, which are also very complicated in structures and compositions, by a large set of parallel–sequential reactions (shown in Figure 1.39). The reactions proceed fast coupled with catalysts deactivation, and the catalytic cracking and thermal cracking. As can be seen in Figure 1.39, if the yield of light oil (gasoline and diesel) and LPG are increased, the disadvantaged secondary reactions (i.e., the overcracking of the desired products, dehydrogenation, and condensation reactions) should be inhibited, and the yield of the ultimate products, such as dry gas and coke, should be reduced.
2. FCC is the typical multiphase fluidized reaction system with multiple process coupling with each other. To reveal the essence of this process quantitatively is a tough issue. The heavy oil feedstock in the multiregime riser reactor reacted undergo complex processes,

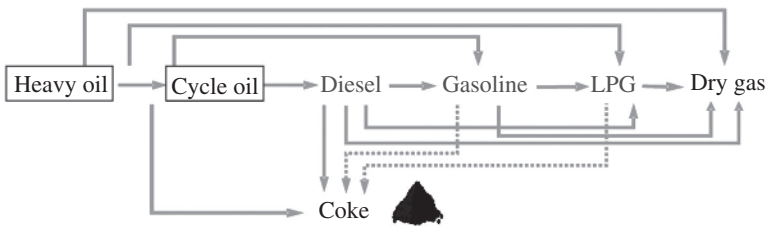

FIGURE 1.39 Parallel–sequential reaction network of heavy oil catalytic cracking.

such as multiphase fluid mixing, heat and mass transfer, adsorption process, and rapid parallel–sequential reactions, coupling with catalysts deactivation. These processes are interacted with each other. The flow and contact status of the multiphase fluid affect the heat and mass transfer, then the reactions will also be influenced, in contrast, the reaction results will affect the flow, heat, and mass transfer in the reactor.

Previous research in the complicated chemical reaction mechanism and the chemical reaction engineering during the FCC process mainly simplified the riser reactor as an isothermal plug flow reactor. Thus, in the process of developing novel FCC process, the cracking process in the riser reactor can only be simplified as the ideal plug flow, without considering the interaction of flow, heat transfer, and reactions.

It is a practical issue that the loss of light oil yield and the excessive yield of dry gas and coke. However, as the lack of a thorough understanding of the mechanism of the complex multiphase process, some technologies and methods for controlling the reactions of heavy oil in the riser reactor are carried out empirically or developed aimed at a particular problem. Thus, these implementation effects are undesirable and even have negative effect.

1.5.2.1 3D Gas–Liquid–Solid Three-Phase Flow–Reaction Coupled Simulation CFD method is introduced into the study of the FCC process through multidisciplinary innovation. On the basis of turbulent gas–solid two-phase flow theory and lumping kinetics of cracking reaction, the difficulty of the multiphase turbulent flow-heat transfer-parallel sequential reactions multiprocess coupled simulation is overcome, the 3D gas–liquid–solid three-phase flow–reaction model was first established and realized the detailed analysis of the numerical simulation for the flow, heat, and mass transfer, and cracking reactions in the industrial riser reactor.

1.5.2.2 Tracing Study of the Reaction Process in the Industrial Riser Reactor

Online Sampling Study of the Industrial Riser Reactor With the employment of the online sampling device (see Figure 1.40) we developed, gas–liquid–solid three-phase online sampling of high-temperature industrial riser reactor was realized for the first time, and both gas–liquid products and catalyst particles were obtained [61]. Further, the methods of treatment of catalyst particles containing oil, element analysis of porous catalysts, simulated distillation of crude oil containing light cut, and molecular weight estimation of oil fraction were all established. Based on the analysis of products and catalysts obtained from different axial positions, a new method for investigating the reaction process in industrial riser reactor was developed, which also facilitated the understanding of the essence of heavy oil catalytic cracking reactions.

Main Research Findings

1. Overcracking of light oil exists in the conventional riser reactor. Both results of simulation and online sampling can reflect the variation of product distribution and reaction temperatures along the riser quantitatively. Figure 1.41 illustrates the simulated results of product distribution along an industrial riser. Gasoline yield increased rapidly in the first 10 m above the feed inlet, then rose at a much lower rate and finally reached a plateau. In contrast, the maximum diesel yield was obtained at about 5 m above the feed inlet, and the total yield of gasoline and diesel achieved the

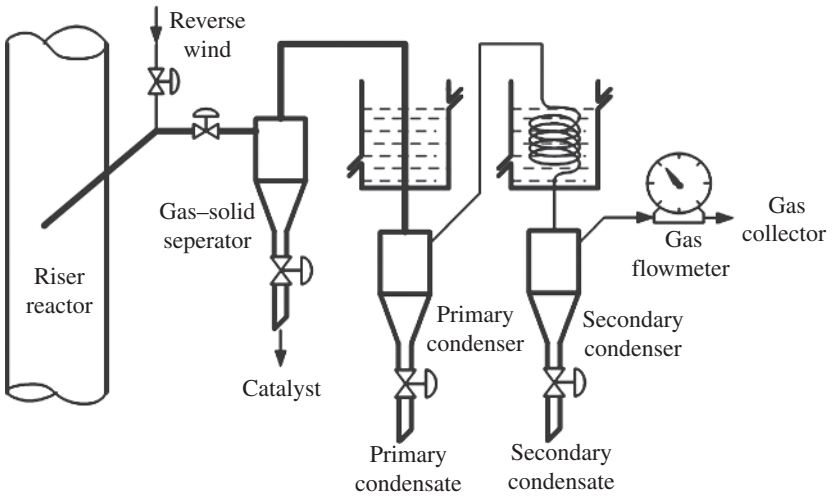

FIGURE 1.40 Online sampling device.

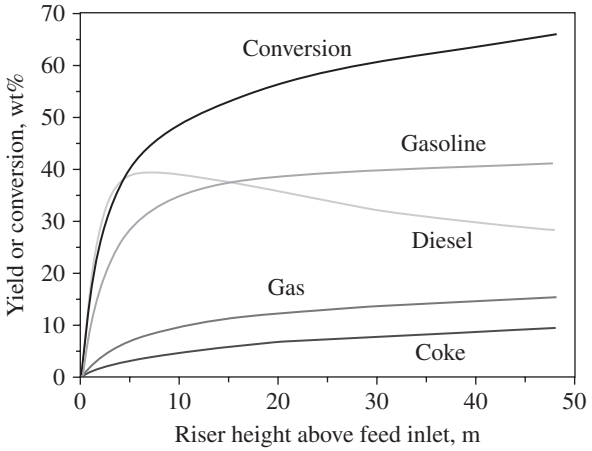

FIGURE 1.41 Product yield as a function of riser height.

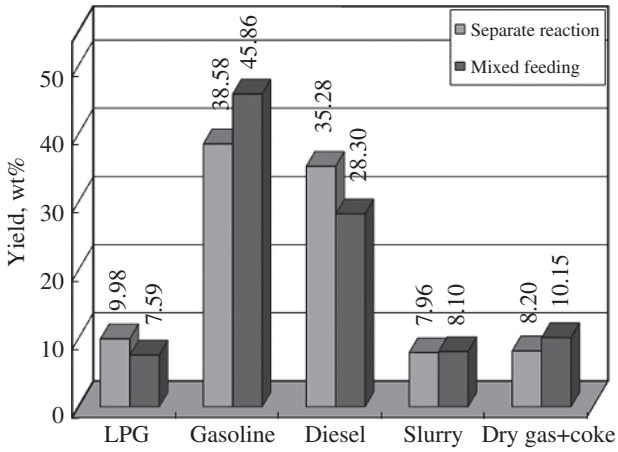

FIGURE 1.42 Effect of separate reaction on the product distribution.

maximum level at around 10 m above the feed inlet. Therefore, it can be inferred that gasoline and diesel are mainly generated at the feed entrance zone of the riser reactor (about 1 s of residence time); afterward, further cracking of gasoline and diesel happens. When the cracking rate of light oil is more than the generation rate, the decrease of light oil yield and increase of dry gas and coke yields can be seen.

2. Overall activity of the catalysts in the conventional riser reactor is seriously insufficient. Based on the online sampling study, axial variation of catalyst activity along the riser is obtained, which indicates that the catalyst activity decreased rapidly to 40–50% of the regenerated catalyst in the feeding zone and then decreased slowly in the second half of the riser reactor. This result suggests that the catalytic activity along the whole riser is extremely low. Consequently leading to aggravated thermal cracking reactions and decreased selectivity of desired products in the second half of the riser reactor. Besides, both the results of simulation and online sampling indicate that severe back-mixing flow exists in the feeding zone of the riser reactor.
3. Feeding and cracking fresh oil and cycle oil separately is obviously superior to mixed feeding and cracking. The different catalytic reactivity of fresh feedstock and cycle oil, and the inhibiting effect of competitive adsorption between fresh and cycle oil on desirable reactions, was studied in a continuously operated riser FCC apparatus. Fresh feedstock contains a considerable amount of high-boiling-point heavy components with large molecular weight, which are prone to crack. However, it is difficult for these components to gasify and diffuse to the internal pores of the catalyst. By contrast, the cycle oil containing a large amount of aromatics is difficult to crack. However, the cycle oil has a narrow boiling range, thus it is easy to gasify and diffuse to grab the active sites in catalyst micro-pores, and influenced the adsorption and reaction of the fresh feedstock. Figure 1.42 compares the weighted results of separated cracking of fresh feed and cycle oil with the results of the mixed cracking scheme. It can be found that, at the similar conversion level, when fresh feed and cycle oil were fed and cracked separately, the product distribution was significantly improved, lower yields of dry gas and coke, and higher yields of LPG and light oil can be achieved, compared to the mixed cracking scheme.

Three-Lump Kinetic Model of Two-Stage FCC Reactions

FCC process includes a large set of parallel–sequential reactions, and intermediates (gasoline, diesel, and LPG) are the desired products. We found that cokes on catalyst not only lead to the decrease of activity but also reduce the selectivity. When the coke content of the catalyst increased to 0.5 wt%, the selectivity of gasoline decreased from 45 to 33% and that of light oil reduced 8%. Thus, the yield of light oil would be decreased. The modified three-lump kinetic model was used to analyze the advantage of two-stage reactions on product selectivity.

In the three-lump kinetic model proposed by Weekman and Nace [62], the instantaneous gasoline yield (y_2) can be calculated as follows:

$$y_2 = r_1 \cdot r_2 \cdot e^{-r_2/y_1} \cdot \left[\frac{1}{r_2} \cdot e^{r_2} - \frac{y_1}{r_2} \cdot e^{r_2/y_1} - E_{\text{in}}(r_2) + E_{\text{in}}\left(\frac{r_2}{y_1}\right) \right] \quad (1.2)$$

Here, $r_1 = K_1/K_0$;

$r_2 = K_2/K_0$, the overcracking ratio;

$E_{\text{in}}(x) = \int_{-\infty}^{x} (e^x/x)dx$;

y_1 is the instantaneous weight fraction of feedstock;

K_0 is the reaction rate constant of feedstock;

K_1 is the reaction rate constant of feedstock to gasoline;

K_2 is the reaction rate constant of gasoline.

However, the equation was derived based on the assumption that after coking of the catalyst, the reaction rate constant of feedstock and gasoline declined at the same speed, keeping r_2 stable in the whole process, which does not tally with the actual situation. In the FCC process, the catalyst selectivity is declined as the reactions proceed, so r_2 should be increased. In the two-stage riser (TSR) FCC process, the coked catalyst is replaced by the regenerated catalyst in the second-stage riser, thus the value of r_2 is reduced and the product distribution can be improved.

As the Weekman three-lump kinetic model is not suitable for the TSR process, we derived a modified three-lump kinetic model with changeable r_2. The modified instantaneous gasoline yield (y_{22}) can be calculated as follows:

$$y_{22} = e^{\left(\frac{r_{20}+\beta y_{11}}{y_{12}}\right)} y_{12}^{-\beta} \left\{ y_{21} e^{\left(\frac{r_{20}}{y_{11}}+\beta\right)} y_{11}^{\beta} - r_1 \left[\frac{y_{12}^{\beta+1}}{\beta+1} - \frac{y_{11}^{\beta+1}}{\beta+1} + \frac{(r_{20}+\beta y_{11})}{\beta}\left(y_{12}^{\beta} - y_{11}^{\beta}\right) + \frac{(r_{20}+\beta y_{11})^2}{2!(\beta-1)}\left(y_{12}^{\beta-1} - y_{11}^{\beta-1}\right) + \frac{(r_{20}+\beta y_{11})^3}{3!(\beta-2)}\left(y_{12}^{\beta-2} - y_{11}^{\beta-2}\right) + \frac{(r_{20}+\beta y_{11})^4}{4!(\beta-3)}\left(y_{12}^{\beta-3} - y_{11}^{\beta-3}\right) + \cdots \right] \right\} \tag{1.3}$$

Here, y_{11} is the instantaneous weight fraction of feed in the first-stage riser;

y_{12} is the instantaneous gasoline yield in the first-stage riser;

y_{21} is the instantaneous weight fraction of feed in the second-stage riser;

y_{22} is the instantaneous gasoline yield in the second-stage riser;

$r_{21} = (r_{20} + \beta y_{11}) - \beta y_{11}$, the overcracking ratio in the first-stage riser;

$r_{22} = (r_{20} + \beta y_{21}) - \beta y_{21}$, the overcracking ratio in the second-stage riser;

r_{20} is the initial overcracking ratio;

β is the proportional constant.

Figure 1.43 shows the gasoline yield as a function of conversion, according to different models. The first line was calculated by Weekman model (Formula 1.2), the second line was calculated by modified Weekman model for TSR process (Formula 1.3), and the third line was calculated by Weekman model with changeable r_2. For one-stage reactions (line 3), the maximum yield of gasoline was 53.3 wt%, at the conversion of 74 wt%. By contrast, in the two-stage reactions (line 2), the gasoline yield can reach 56.1 wt% at the conversion of 76 wt%. As the increased overall catalyst activity and selectivity, the selectivity of gasoline increased from 72.0 to 73.8%, and a higher gasoline yield and feed conversion can be achieved. For other intermediates (diesel and LPG), the similar picture can also be drawn. Thus, two-stage reactions can increase the yield and selectivity of desired products.

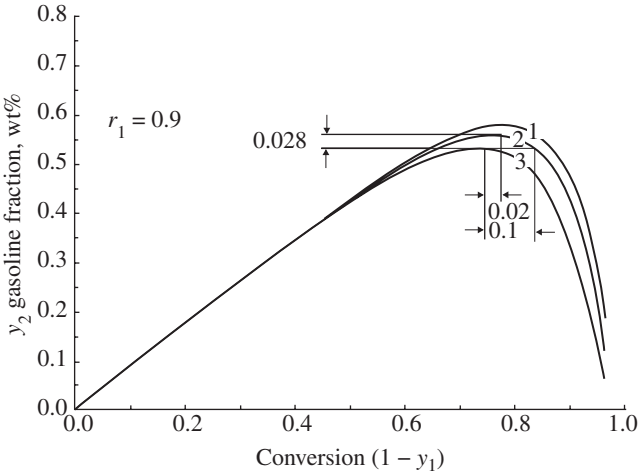

FIGURE 1.43 Effect of separate reaction on the product distribution.

1.5.3 The Proposed TSR FCC Process

On the basis of previous work, we established the enhancing catalytic cracking theory of "Effectively inhibiting the generation of dry gas and coke" and founded the novel "two-stage reactions, catalyst relay, short reaction time and high C/O ratio" idea of FCC process [63, 64]. The fresh feedstock and cycle oil react in two separate reactors. Thus, their competing adsorption and reaction effect can be avoided, and proper reaction conditions can be chosen for maximizing light oil yield. Moreover, the regenerated catalyst is also introduced into the second riser. Hence, the C/O ratio and the average activity of catalyst can be increased and the catalytic cracking reactions can be enhanced. In the TSR process, the residence time in each riser is shorter than in the conventional FCC process (about 3 s), based on the fact that the heavy oil is mainly cracked during the initial 1 s in the feed mixing zone where it has severe back-mixing. The TSR process achieved the connection of two reactors with severe back-mixing in series, making it closer to the plug flow reactor, which is beneficial to produce more intermediate products, such as gasoline, diesel, and LPG.

According to the novel idea (shown in Figure 1.44), we designed two structure-optimized riser reactors to replace the conventional riser reactor, formed a novel reaction–regeneration system with two-way catalyst circulation,

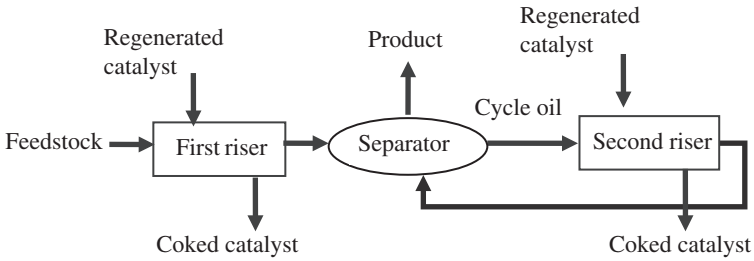

FIGURE 1.44 Diagram of the new idea.

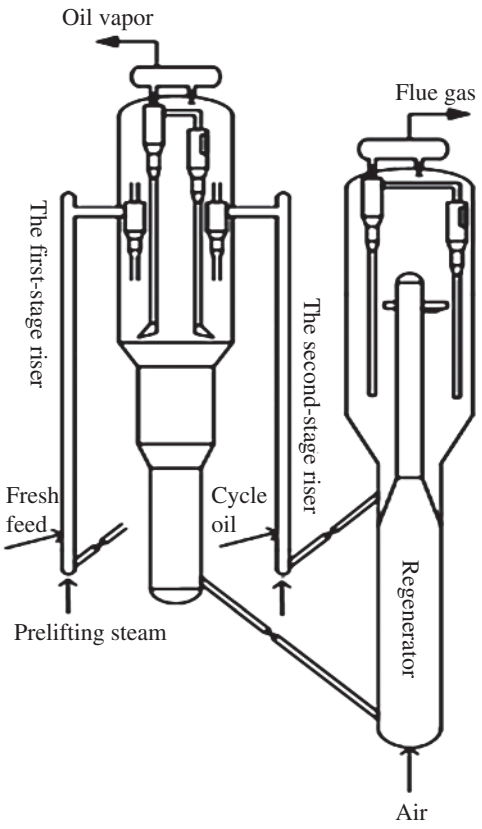

FIGURE 1.45 Schematic of the TSR FCC process.

successfully realized it in commercial scale, and finally developed the TSR FCC technology.

Figure 1.45 shows the schematic diagram of the reaction-regeneration system of the TSR process. The fresh feed after heat exchanging is injected from the bottom of the first-stage riser and contacts with the regenerated catalyst, rapid evaporation, and reaction. After approximately 1 s, the oil vapor and coked catalyst are separated. The coked catalyst was stripped by steam and then transported to the regenerator for regeneration. The oil vapor is piped to the fractionator and cut into dry gas, LPG, gasoline, diesel, and heavy cycle oil. The cycle oil is recycled to the bottom of the second-stage riser and reacts over the regenerated catalyst. The oil vapor and coked catalyst are separated at the riser exit. The coke catalyst is regenerated after steam stripping, and the oil vapor is piped to the fractionator with that from the first riser.

1.5.4 The Industrial Application of the TSR FCC Technology

In 2002, the TSR FCC technology was first applied in a 100 kton/annum industrial unit, which belongs to the Shtar Science & Technology Group. The conventional riser reactor (45.0 m) was replaced by a 16.0 m riser reactor for the first-stage reaction and a 10.7 m riser reactor for the second-stage reaction. After the transformation, under the same processing scheme, the dry gas and coke yields reduced 2.7 wt%, the liquid products yield increased 2.7 wt%, and the cetane number of diesel increased 7 units.

At present, there are 12 industrial units, in the process of transformation or new construction, applied the TSR technology. The accumulative processing capacity has reached 9 Mton/annum, the processing capacity of largest unit is 1.6 Mton/annum.

1.5.5 The Development of the TSR FCC Process

As with the rapid development of economy, the demand for propylene and ethylene is also growing rapidly. In recent years, the demand growth rate of propylene is even higher than ethylene. Steam cracking of hydrocarbons has been the major source of light olefins for more than half a century. As with the development of ethane steam cracking, the production of propylene reduced. The heavy oil catalytic cracking/pyrolysis process, which can not only reduce the energy consumption but also increase the P/E (propylene to ethylene) ratio, has become the important supplement for the production of propylene. Moreover, the resources of heavy oil are more abundant, and the price is lower. Compared with the naphtha steam cracking process, the heavy oil pyrolysis process has obvious advantages, such as wide resources, low cost, mild operating conditions, and low energy consumption. Nowadays, heavy oil pyrolysis process for light olefins has become an important objective of oil companies all over the world. The SINOPEC developed the ARGG,

MIP-CGP, DCC, and CPP processes, and the UOP, AXENS, and SHELL companies developed the PetroFCC, PetroRiser, and MILOS processes, respectively. However, the major problem for these processes is that high propylene yield always with high yield of dry gas and inferior quality of light oil. Thus, we developed a novel process to crack heavy oil for more propylene, less dry gas, and produce gasoline and diesel with better qualities.

1.5.5.1 TSR FCC Process for Maximizing Propylene (TMP) The TMP process was proposed based on the TSR FCC process; thus, the advantages of TSR FCC process were inherited, such as the higher operational flexibility and the higher conversion efficiency of heavy oil. But big challenges should be faced when producing more propylene from heavy oil, while maintaining the quality of light oil, and reducing the dry gas and coke yields.

In order to increase the propylene yield and selectivity, four measures were taken. (i) The special catalyst was developed, which has low hydrogen transfer reaction activity and high heavy oil cracking activity, thus high propylene selectivity and feed conversion can be achieved. (ii) The C_4 and light naphtha were selectively recycled from the bottom of the first riser and the second riser, respectively. On the one hand, the C_4 and light naphtha can crack under higher operating severity. As with the low reactivity of C_4 and light naphtha, it can enhance the conversion of C_4 and light naphtha into propylene. At the same time, the olefin content of gasoline can be reduced. On the other hand, with the injection of C_4 and light naphtha, more heat should be provided by the catalyst, according to the heat balance, and it requires a larger catalyst circulation. The higher the catalyst circulation, the larger the C/O ratio. Thus, the conversion of C_4, light naphtha, and heavy oil can be enhanced. (iii) On the basis of the previous studies, we found that with an enlarged section the solid density can have a significant increase. Therefore, we developed a novel reactor with higher catalyst density, which can enhance the contact and reaction of oil with catalyst, and further increase the conversion of C_4 and light naphtha. In previous work, we found that propylene is also the intermediate product, thus a relatively short reaction time should be taken to avoid the further conversion of propylene. Research [65] also found that when operated under a shorter residence time, more diesel with higher quality can be obtained.

In the catalytic pyrolysis process of heavy oil, how to reduce the dry gas and coke yields is an acknowledged challenge, as it is commonly operated at high operating severity. It has been well established that both thermal cracking and catalytic cracking can generate dry gas. For thermal cracking, free radical chain reaction, which has a much higher activation energy than catalytic cracking, is the main mechanism [66]. Haag and Dessau [67] proposed that H_2, CH_4, and C_2 hydrocarbons also could be created by monomolecular protolytic cracking route, and they also found that the activation energy for the protolytic cracking was higher than that for the β-scission. Thus, both the thermal cracking and the monomolecular cracking are favored at higher temperatures. In the TMP process, as with the injection of C_4 and light naphtha, the C/O ratio can be increased significantly without increasing the riser outlet temperature, and higher feed conversion and propylene yield can be achieved. Thus, the ratio of thermal cracking and monomolecular cracking can be reduced. Moreover, after the reaction of C_4 and light naphtha, the temperature of catalyst is lowered significantly, but the activity can keep at a high level, thus the thermal cracking of heavy oil can be restrained. On the other hand, the injection of heavy oil can control the high temperature reactions of C_4 and light naphtha at a proper reaction time, and restrains the thermal cracking of C_4 and light naphtha. In addition, the increased catalyst density in the novel reactor also can enhance the catalytic cracking of C_4 and light naphtha, and help to reduce the dry gas can coke yields.

Figure 1.46 shows the schematic diagram of the TMP process (the reaction–regeneration system). On the basis of the TSR reactor, two reaction zones for C_4 and light naphtha are added at the bottom of the two risers with two high catalyst density reactors. The regenerated catalyst first contacts with C_4 (in the first riser) and light naphtha (in the second riser) and then reacts with AR and cycle oil, respectively. The riser outlet temperature of the first riser is commonly operated between 480 and 520°C, while that for the second riser is 520–550°C, only slightly higher than the conventional FCC process.

1.5.5.2 Experimental Study

1. *Effect of catalyst on propylene yield* Figure 1.47 shows that a certain amount of HZSM-5 in the catalyst system is essential for increasing the propylene yield. The rising rate of the propylene yield first increased fast and then slowed down when the ratio of HZSM-5 exceeds 60% [68]. By contrast, the conversion decreased as the increasing of HZSM-5 ratio. Therefore, the ratio of HZSM-5/USY(or Y) should be proper to ensure the conversion of heavy oil.
2. *Stratified injections of 1-C4= and AR* In the first-stage riser, the 1-$C_4^=$ is injected from the lower position and first reacted with the regenerated catalyst under higher operating severity, then the AR is injected and reacts on the temperature-lowered catalyst. The experimental results show that under the stratified injection mode, the yield of dry gas reduced by about 40% and the liquid product increased 2.45 wt%, compared with that AR and 1-$C_4^=$ reacted separately. The injection of 1-$C_4^=$ only slightly influenced the conversion of AR, but the 1-$C_4^=$ can be

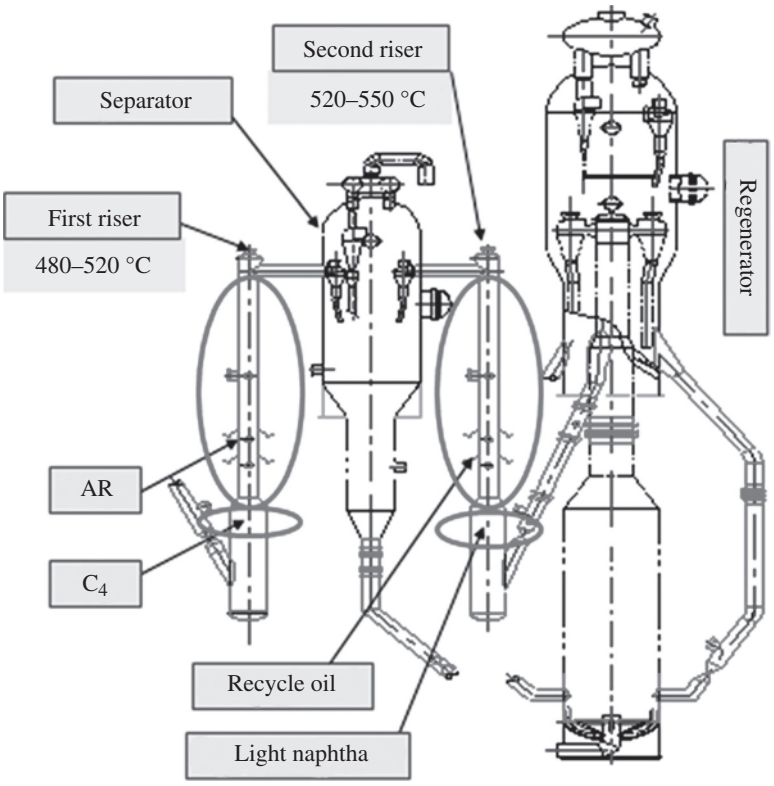

FIGURE 1.46 Schematic of the TMP process.

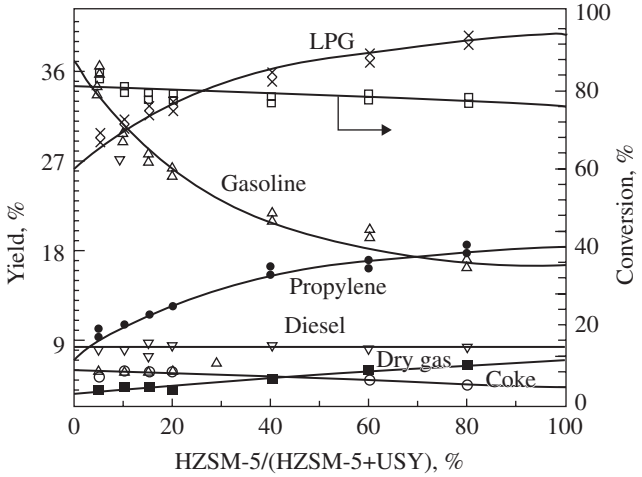

FIGURE 1.47 Effect of catalyst on product distribution.

further converted into propylene without increasing the yield of dry gas significantly (Table 1.18).

3. *Stratified injections of LCN and HCO* In the second-stage riser, the recycle ratio of LCN reached to 83%, compared to HCO feed; therefore, after the reaction of LCN, the temperature of catalyst would decrease sharply. Moreover, HCO is more difficult to be cracked than the fresh feedstock. Thus, the reaction temperature of the second-stage riser was higher than the first one. The stratified injection results of the LCN and the HCO according to the ratio of their yield in the first-stage riser are listed in Table 1.19. Compared with the calculated results, the yield of dry gas under the stratified injection mode decreased by around 32%, and the yield of liquid products increased by approximately 10%. In addition, after the reaction of LCN, most of the olefins are converted into light olefins or other hydrocarbons, such as iso-paraffins and aromatics. Thus, the olefin content of gasoline can be reduced without octane loss.

1.5.5.3 The Industrial Application of the TMP Technology

In 2006, the TSR FCC technology was first applied in a 120 kton/annum industrial unit belonging to the China Petroleum Natural Gas Co., Ltd Daqing Refining and Chemical Branch Co. Taking Daqing AR as the feedstock, the propylene yield reached 20.31 wt%, the liquid products yield was 82.66 wt%, and the yields of dry gas and coke were 14.28 wt%. Moreover, the RON of gasoline can be up to about 96.

At present, there are eight industrial units that applied the TMP technology in the process of transformation or new construction. The accumulative processing capacity has reached 6.6 Mton/annum, and the processing capacity of largest unit is 2.0 Mton/annum.

TABLE 1.18 Comparison of FCC Product Distributions Between the Stratified Injection of 1-$C_4^=$ and AR in the First-Stage Riser and Their Separate Reaction Process

Items	1-$C_4^=$+AR	AR	1-$C_4^=$	Calculation	Δ[a]
Mass ratio	16.26 : 100				
Reaction temperature, °C	510	510	510		
Catalyst/oil, kg/kg	8.5	7	8		
Residence time, s	1.21	1.38	1.45		
Product distribution, wt%					
Dry gas	3.85	3.70	15.71	6.25	–2.40
LPG	33.13	35.98	65.76	30.41	2.72
Gasoline	27.05	25.04	14.75	27.44	–0.39
Diesel	14.52	14.40	0.00	14.40	0.12
Heavy oil	15.23	15.03	0.00	15.03	0.20
Coke	6.22	5.85	3.78	6.46	–0.24
Light oil yield	41.57	39.44	14.75	41.84	–0.27
Liquid products yield	74.70	75.42	80.51	72.25	2.45
Conversion	84.77	84.97	—	84.97	–0.20
Ethylene	2.77	2.65	7.35	3.85	–1.08
Propylene	18.63	16.44	28.65	21.10	–2.47
Butene	9.80	16.26	22.94	3.73	6.07

[a] Item Δ is the values of stratified injection minus that of calculation.

TABLE 1.19 Comparison of FCC Product Distributions Between the Stratified Injection of LCN and HCO in the Second-Stage Riser and Their Separate Reaction Process

Items	LCN + HCO	HCO	LCN	Calculation	Δ
Mass ratio	12.68 : 15.23				
Reaction temperature, °C	530	530	530		
Catalyst/oil, kg/kg	10.5	8.5	9.5		
Residence time, s	1.85	1.93	1.72		
Product distribution, wt%					
Dry gas	8.30	4.44	21.76	12.31	–4.01
LPG	39.63	24.75	44.03	33.51	6.12
Gasoline	23.15	16.37	30.33	22.71	0.44
Diesel	8.57	16.26	0.00	8.87	–0.30
Heavy oil	16.27	33.43	0.00	18.24	–1.97
Coke	4.07	4.74	3.88	4.35	–0.28
Light oil yield	31.72	32.63	30.33	31.59	0.13
Liquid products yield	71.35	57.38	74.36	65.09	6.26
Conversion	83.73	66.57	—	81.76	1.97
Ethylene	6.84	2.76	16.00	8.78	–1.94
Propylene	19.65	12.39	26.68	18.88	0.77
Butene	15.22	9.89	12.46	11.06	

1.6 FCC GASOLINE UPGRADING BY REDUCING OLEFINS CONTENT USING SRFCC PROCESS

1.6.1 Research Background

With the development of environmental concerns and increasingly stringent regulations on the control of emissions from motor vehicles, changing transportation fuel (e.g., gasoline and diesel oil) composition will be required. Compositional changes to gasoline dictated by environmental considerations mainly include the reduction in olefin content which is considered as the key quality specification of gasolines. According to the new Chinese national standard, GBI 7930–2009, the content of olefins in motor gasoline should be lower than 30 v% [69–71]. Further, to satisfy the international motor fuel regulations, the content of olefins needs to be controlled at even lower level of below 20 v% with octane number of above 95 and lower sulfur content specified by Euro IV for commercial vehicles. Currently, in China, FCC process plays a key role in most refineries to provide approximately 30% of the diesel pool and almost 80% of the

gasoline pool as a whole to supply the Chinese fuel market. FCC gasoline directly originated from FCC units usually contains excessive olefins as high as 45–65 v% which can cause serious air pollution. Therefore, measures must be taken to control the olefin, sulfur, and aromatic contents with minimum octane number loss in FCC as one of the most effective way to improve gasoline quality to meet with the corresponding international standard.

To produce high quality gasoline, blending gasolines manufactured by different processes with "additives" to produce reformulated gasoline (RFG) has become the major method in most Western countries. On the other hand, nowadays, FCC naphtha is the dominant component of China's gasoline pool, and this situation is hard to change remarkably due to the lack of the catalytic reforming, alkylation, isomerization, and oxygenous compounds producing units as well as other secondary processing units. Therefore, it is unsuitable to employ "blending method" to offer "new" gasolines with lower concentrations of olefins, less sulfur, and high octant rating that burn more cleanly and have less impact on the environment [72, 73].

The sum of the aforementioned issues to date presents an unprecedented technological challenge to the petroleum industry in China to produce gasoline that maintains high octane value and is economically acceptable in the marketplace. As catalytically cracked gasoline forms a major part of the gasoline product pool in China, focusing on further improvement of product distribution in FCC process as well as FCC gasoline reformation is the appropriate approach to obtain higher economic benefit for refineries. To this viewpoint, a novel process named SRFCC for gasoline reformation was developed at the CUPB. In SRFCC process, using the classical FCC unit with regular catalyst, FCC gasoline is upgraded by removing the olefins in it. Olefins undergo specific reactions including hydrogen transfer, aromatization, isomerization and kinds of cracking reactions, and so on. After the upgrading process, the FCC gasoline quality can satisfy the new regulations with less olefins, maintaining unchanged octane number. In addition, SRFCC technology can be also used to maximize LPG and propylene by flexibly changing the operating conditions and upgrading ratio of FCC gasoline [74–76].

1.6.2 Reaction Principle of Gasoline Upgrading

The performance of an FCC unit, product distribution, and selectivity in such system are dependent on a large number of parameters including feed composition, catalyst property, residence time (RT), C/O ratio, temperature, and so forth. For heavy oil catalytic cracking, it needs high temperature, short residence time, and moderate catalyst activity. On the other hand, to upgrade the FCC gasoline, chemical reactions including hydrogen transfer, aromatization, and isomerization are the main reactions. The optimal reaction conditions for gasoline upgrading are relatively low temperature, long residence time, and high catalytic activity. Obviously, cracking heavy oil and upgrading gasoline optimally occur with opposite conditions. That is to say, heavy oil cracking and naphtha upgrading follow completely a different chemical reaction mechanism.

Based on the reaction chemistry discussed earlier, it is difficult to simultaneously optimize heavy oil cracking and naphtha upgrading in one FCC riser reactor using the same catalyst which has also been verified by previous researches [70]. In addition, it had been reported that using certain olefin reduction catalyst would result in the increase of capital cost, the reduction of the liquid yield up to 2.0%, as well as the worst product distribution [71].

According to the typical analysis of PONA and the chemical reaction mechanism, it is better to control the reactions when upgrading FCC naphtha by reducing olefins without decreasing octane values. That is to say, certain reactions need to be promoted while some reaction should be restrained. Ideal reaction mechanism of FCC gasoline in a heavy oil FCC unit is shown as Figure 1.48.

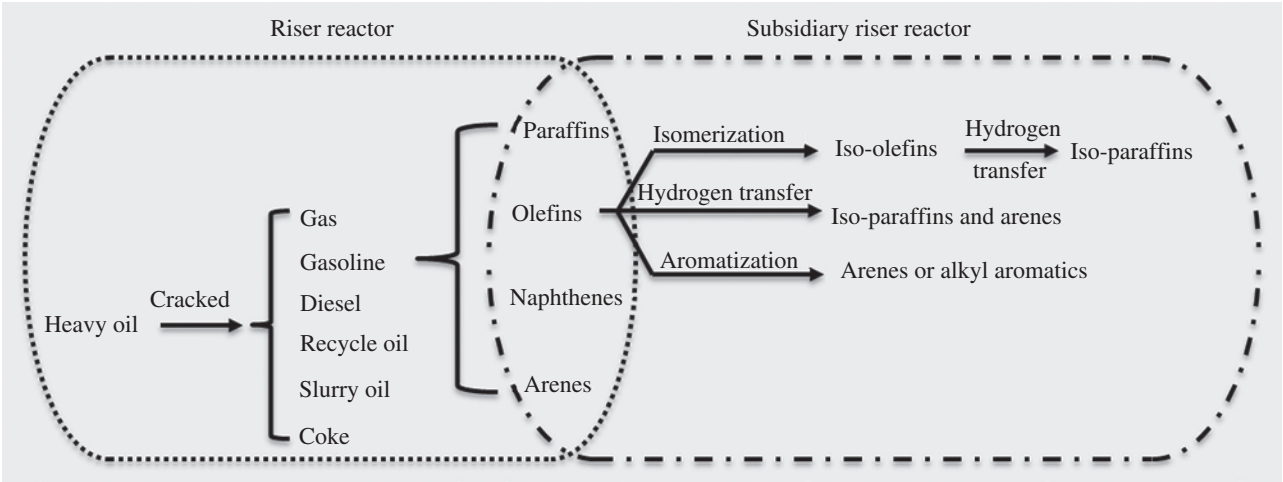

FIGURE 1.48 Schematic diagram of reaction mechanism of naphtha olefin reduction.

As shown in Figure 1.48, in order to enhance the FCC gasoline, isomerization, hydrogen transfer, cyclization, aromatization, and dealkylation reaction (i.e., the desired reactions) should be promoted. On the other hand, the reactions including initial cracking and condensation (i.e., the undesired reactions) must be restrained [77–80].

On the basis of the conversional FCC technology and the regular heavy oil cracking catalyst, SRFCC process [81–83] provides a secondary riser reactor in an original FCC unit to upgrade FCC naphtha. This "different upgrading location" could supply an independent reaction area with optimal operating conditions designed in SRFCC process with two riser reactors. This process can minimize gasoline olefins without reducing octane numbers by encouraging the desired reactions and restricting the undesired reactions. In addition, reprocessing FCC naphtha in a separated riser reactor in SRFCC process can also allow operating the second reaction zone at a higher severity to promote olefin cracking, aromatization, and dealkylation reactions and maximize propylene and LPG yields.

1.6.3 Design and Optimization on the Subsidiary Riser

Based on the earlier general idea and the chemical reaction mechanism of reducing gasoline olefins and activity to promote the desired reactions including hydrogen transfer, aromatization, and isomerization and restrain the adverse reactions such as initial cracking and condensation reactions, the upgrading reactor should be operated under low temperature and long residence time with moderate catalyst [84, 85]. Considering that the residence time is only 2.0–3.0 s in a conversional FCC riser reactor, it is better to design a special reactor combining transport fluidized bed and turbulent fluidized bed. Typical FCC riser reactor and the "transport fluidized bed plus turbulent fluidized bed" reactor are schematically shown in Figures 1.49 and 1.50, respectively.

The experimental results of the two kinds of reactors are listed in Tables 1.20 and 1.21.

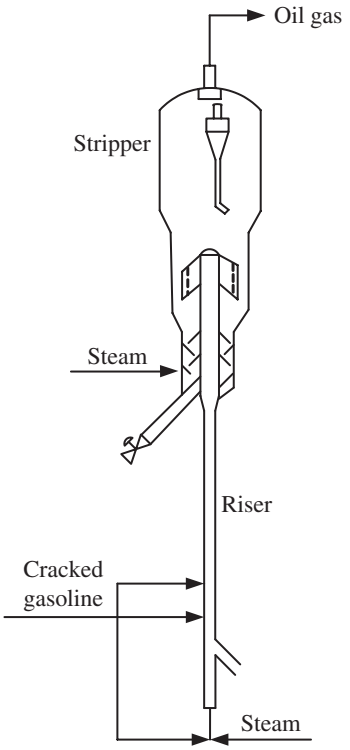

FIGURE 1.49 Riser reactor.

1.6.4 Key Fundamental Researches

1.6.4.1 Fundamental Researches Table 1.22 shows the experimental results in a pilot-scale gasoline upgrading riser [81–83, 86–88]. The data in Table 1.22 and Figure 1.51 indicate that due to the selective promotion and inhibition of the reactions during the upgrading process, the upgraded gasoline satisfies the new motor fuel standard with high gasoline yield of up to 85 wt%. At relatively low reaction temperature, the yield of gasoline can be up to 90 wt% with 98.5 wt% of liquid products' yield. The octane number of the upgraded gasoline is also increased.

Table 1.23 shows the group compositions of gasoline before and after upgrading. Compared with the data before

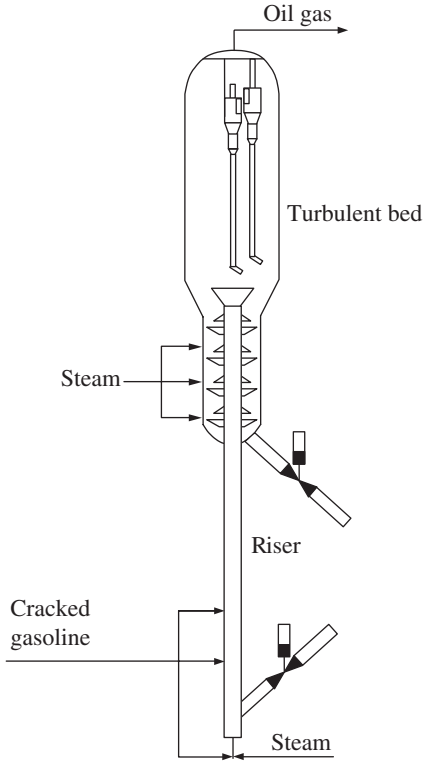

FIGURE 1.50 Riser reactor + turbulent bed.

TABLE 1.20 Results of Adopting Riser Reactor

Temperature,°C		Gasoline Feeding	420	450
Product distribution, wt%	Dry gas		0.1	0.2
	LPG		8.9	10.6
	Gasoline		85.6	83.1
	Diesel		4.1	4.6
	Coke		1.3	1.6
Group composition after upgrading, v%	Saturates	35.6	44.1	45.9
	Olefins	46.2	33.5	29.1
	Aromatics	18.2	22.4	25.0
Olefin conversion, %			27.5	37.4

RT: 2.0 s, C/O: 6, MAT: 62.
Data used herein obtained by averaging three parallel experimental results.

TABLE 1.21 Results of Adopting Riser + Turbulent Bed

Temperature, °C		Gasoline Feeding	420	450
Product distribution, wt%	Dry gas		0.1	0.2
	LPG		2.9	4.0
	Gasoline		90.5	88.3
	Diesel		4.6	5.1
	Coke		2.1	2.4
Group composition after upgrading, v%	Saturates	38.7	57.5	56.4
	Olefins	46.6	19.3	17.5
	Aromatics	14.7	23.2	26.1
Olefin conversion, %			61.6	62.4

RT: 200.0 s, C/O: 6, MAT: 63.
Data used herein obtained by averaging three parallel experimental results.

TABLE 1.22 Results of Pilot Plant of Naphtha Olefin Reduction Technology in Dagang Petrochemical Company (Micro-Activity 56, Reaction Time 3 s, Catalyst-to-Oil Ratio 6)

Items	Gasoline Feedstock	Upgrading Gasoline				
Temperature, °C		400	425	450	475	500
Residence time, s		03.01	2.96	2.88	2.80	2.93
Coke, wt%		00.54	00.57	00.58	00.51	00.59
Dry gas, wt%		00.27	00.30	00.33	00.42	00.41
LPG, wt%		11.34	11.53	12.17	15.03	16.72
Gasoline, wt%		87.85	87.60	86.92	84.04	82.28
C_3 + liquid yield, wt%		99.19	99.13	99.09	99.07	99.00
nP	04.49	04.68	04.84	04.82	04.84	04.96
iP	20.60	26.44	24.32	26.25	26.71	28.27
O	51.15	44.34	37.97	39.05	37.91	37.70
N	05.45	05.60	06.72	06.59	05.48	04.94
A	18.34	18.95	26.15	23.30	25.06	24.12
Olefin conversion, %		13.31	25.77	23.66	25.88	26.30
RON (calculated)	92.74	94.14	95.25	94.72	94.64	96.92

A, arene; iP, iso-paraffin; N, naphthene; nP, paraffin; O, olefin; the same later.

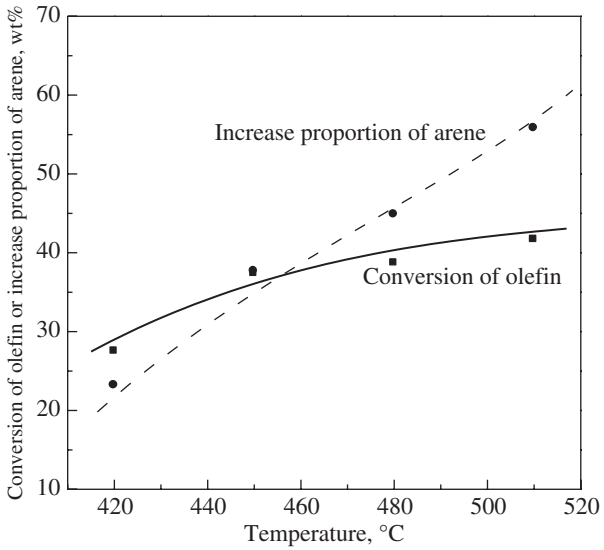

FIGURE 1.51 Effect of temperature on conversion of olefin and increase proportion.

TABLE 1.23 Composition of PONA Before and After Naphtha Olefin Reduction (Reaction Time 3 s, Catalyst-to-Oil Ratio, Reaction Temperature 450°C)

Carbon Number		3	4	5	6	7	8	9	10	11	12	13	Total Value
nP	Before upgrading		0.4	1.1	0.8	0.8	1.0	0.4	0.3	0.2			5.0
	After upgrading		0.2	1.1	1.0	0.9	0.9	0.4	0.4	0.2	0.1		5.2
iP	Before upgrading		0.4	5.7	5.8	3.2	3.2	1.9	1.4	1.3	0.2		23.1
	After upgrading		0.4	6.2	8.5	4.9	3.9	1.7	1.3	1.2	0.3	0.2	28.5
	Difference		0.0	0.5	2.7	1.7	0.7	−0.2	−0.1	−0.1	0.1	0.2	5.4
	Increment		−5.3	9.0	46.8	51.9	21.1	−11.5	−6.5	−8.7	50.0		23.4
O	Before upgrading		2.6	12.5	11.3	8.9	6.3	2.9	2.2	0.3			46.9
	After upgrading	0.2	2.4	10.4	10.0	6.0	3.1	1.0	0.9				33.8
	Difference		0.4	2.1	1.2	2.9	3.2	1.9	1.3	0.2			13.1
	Conversion		15.3	17.1	10.9	32.7	50.6	65.9	57.3	84.0			27.9
N	Before upgrading			0.1	0.2	3.0	1.5	1.3	0.5	0.1			6.8
	After upgrading			0.1	0.2	4.1	1.0	1.2	0.4		0.2		7.3
A	Before upgrading					2.3	5.8	5.3	4.1	0.8			18.3
	After upgrading					3.1	7.7	8.1	5.2	1.2			25.2
	Difference					0.8	1.9	2.7	1.1	0.4			6.9
	Increment					34.8	32.1	50.9	26.5	52.6			37.6

upgrading, the group composition of the upgraded gasoline has considerably changed. Olefins in the upgraded gasoline have significantly decreased with apparent increase of aromatic and iso-paraffin content. The reduction of gasoline olefins mainly results from the hydrogen transfer and the catalytic cracking reaction. The cracking of olefins would lead to the loss in gasoline yield which is undesirable during the upgrading process. When the upgrading process operates at lower temperature, the olefin cracking is effectively inhibited while more hydrogen transfer reaction occurs.

During the upgrading of gasoline, there are two reaction paths for olefins: (i) olefins are converted to paraffins (mainly iso-paraffin) via hydrogen transfer and isomerization, and (ii) olefins are transformed to aromatics via cyclization, aromatization, and hydrogen transfer. The iso-paraffin and aromatics are high octane number products so that the octane value of the upgraded gasoline would not decrease which is corresponding to the calculated RON.

There are considerable differences in compositions between light fractions of FCC naphtha and the whole gasoline products shown in Figure 1.52. Therefore, the upgrading mechanism between the two products is significantly different. In light fractions of FCC naphtha, C_5 and C_6 olefins account for most of the components. Those small molecular olefins first oligomerize to higher carbon number olefins and then form naphthenes or aromatics via hydrogen transfer, isomerization, cyclization, and aromatization.

The effects of olefin conversion on main product yields including C_3^+ liquid products, upgraded gasoline, liquefied gas, coke, and dry gas yields are shown in Figures 1.53, 1.54, 1.55, 1.56, and 1.57, respectively. There is a clear mutual suppression between the yields of C_3^+ liquid products and upgraded gasoline and the conversion increment of gasoline olefins.

Results obtained using various experimental apparatus with regular FCC catalyst show that operating conditions

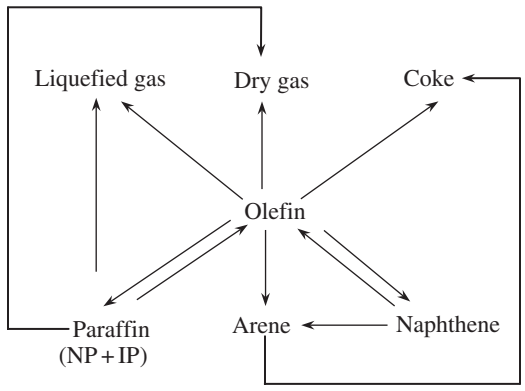

FIGURE 1.52 Reaction network diagram of full-range cracked gasoline olefin reduction.

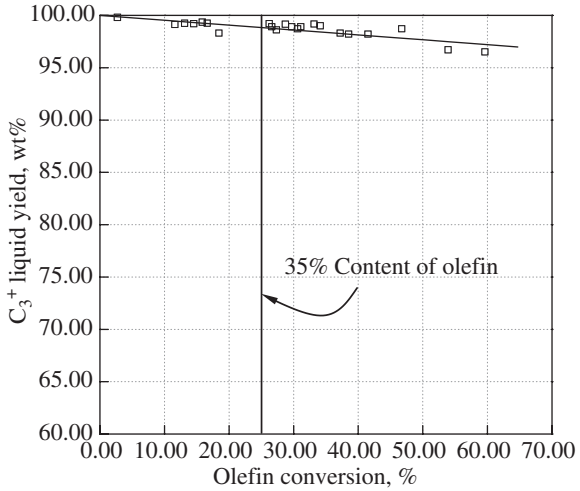

FIGURE 1.53 Effect of olefin conversion on C_3^+ liquid yield.

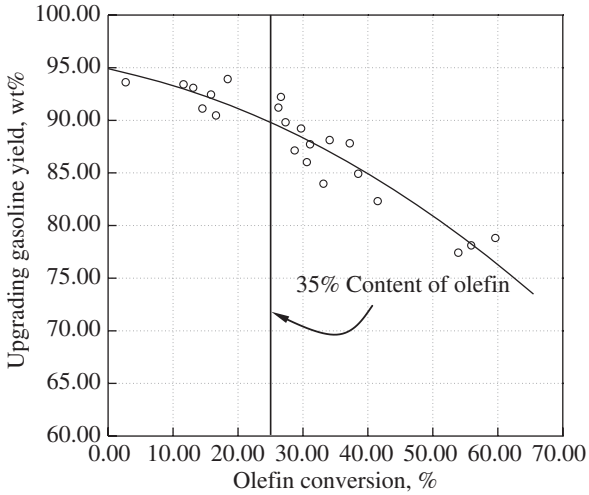

FIGURE 1.54 Effect of olefin conversion on upgrading gasoline yield.

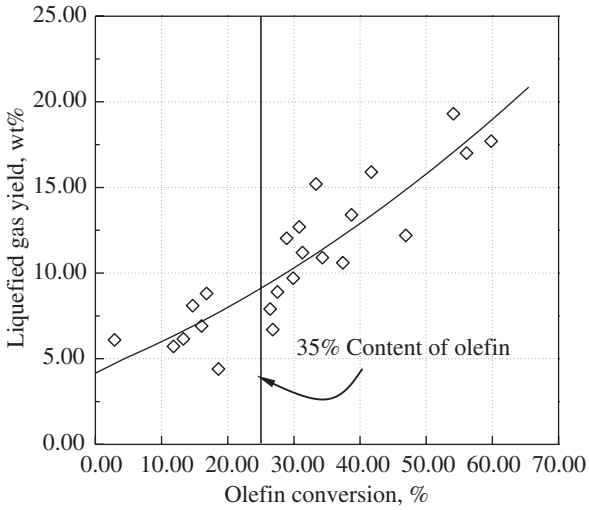

FIGURE 1.55 Effect of olefin conversion on liquefied gas.

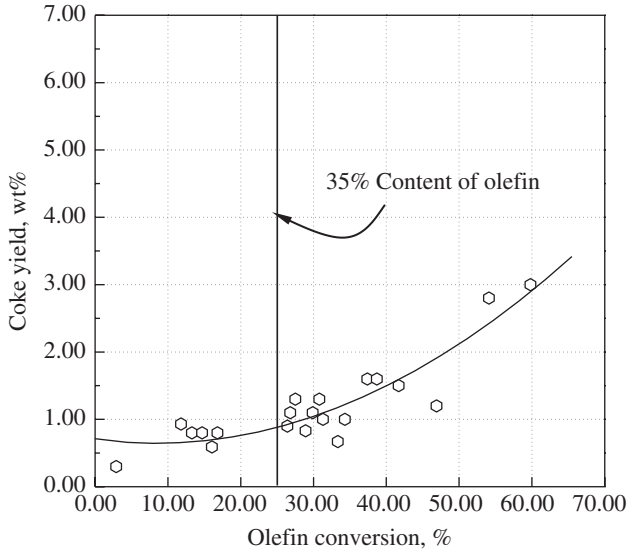

FIGURE 1.56 Effect of olefin conversion on coke yield.

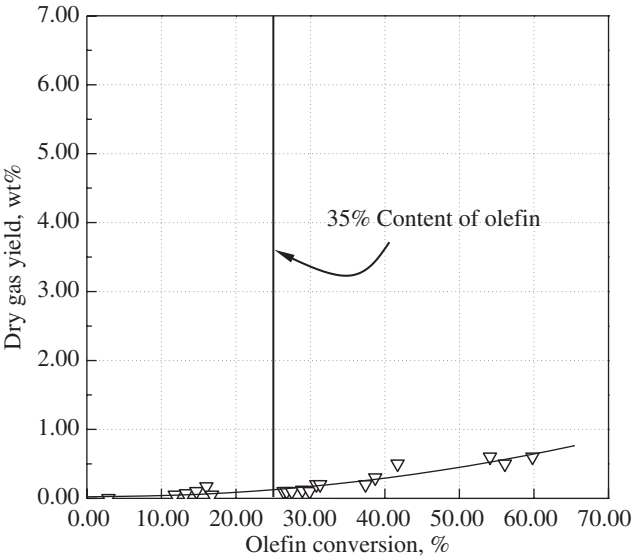

FIGURE 1.57 Effect of olefin conversion on dry gas yield.

have significant effects on the magnitude of the reduction in olefins, octane numbers of upgraded gasoline, and product distribution. The optimal operating conditions for SRFCC process is concluded as follows:

- Temperature: 420–480°C
- C/O ratio: 4–8
- Microactivity of catalyst: >58
- Residence time of transport fluidized bed (riser): 2.0–3.0 s
- Residence time of turbulent fluidized bed: 200–400 s

1.6.4.2 Technical Process According to the experimental results and with the consideration of the operating condition in regular FCC unit, a special fractionating tower is designed to separate oil gas of upgrading gasoline individually. Based on this aspect, separation technology of oil gas for FCC gasoline upgrading process is formed and thereafter the SRFCC process is developed.

Figure 1.58 shows the details of the SRFCC process. An additional reactor based on an FCCU is employed to upgrade naphtha. This auxiliary riser reactor is a combined reactor with a transport fluidized bed (riser) and a turbulent fluidized bed fixed at the riser's outlet. In addition, the special fractionating tower with an individual desuperheating section is used to separate the oil gas after the upgrading.

The process is briefly described as follows:

In the SRFCC unit, the riser reactor is operated at classical FCC conditions. Fresh heavy oil, recycle oil, and the slurry atomized by the water steam are injected into the bottom of the riser and contact with the hot regenerated catalyst with the prelifting steam. Conversion of the feedstock with suitable preheated temperature takes place in the presence of catalyst under certain temperature, C/O ratio, catalyst activity, as well as the reaction temperature and pressure while the mixture comprising catalyst and hydrocarbons passes upward through the riser. At the outlet of the riser, hydrocarbon vapors and catalyst are separated in an efficient gas–solid separation device and the cyclone located in disengaging space. The separated catalyst is sent to the stripper mounted inside the disengager where the steam is used to remove the entrained hydrocarbon vapors. The stripped catalyst passed downward through the dipleg flows into the generator, in which the coke on the catalyst is burned off by excess air. The hydrocarbon vapors flow out of the disengager and separate into cracking rich gas, crude gasoline, light diesel fractions, recycle oil, and slurry by the product recovery unit.

For the auxiliary riser operating, a portion of hot regenerated catalysts is introduced into the bottom of the upgrading transport fluidized bed (riser) through an inclined pipe joined with the regenerator. FCC gasoline from the main fractionators is injected through a nozzle and onto the hot catalysts at the base of the auxiliary riser. After contacting, vaporizing, mixing, and reacting, the oil gas and the catalysts flow into an auxiliary disengaging system and are separated by the cyclone separator at the top of the disengager. The spent catalysts flowing in a downward direction pass through catalyst stripper and are stripped of adsorbed and interstitial hydrocarbons by a countercurrent stripping steam. Stripped catalyst leaves the stripper through the new spent catalyst standpipe and flows into the regenerator. Reaction products separated with the catalysts flow into the upgrading product recovery system.

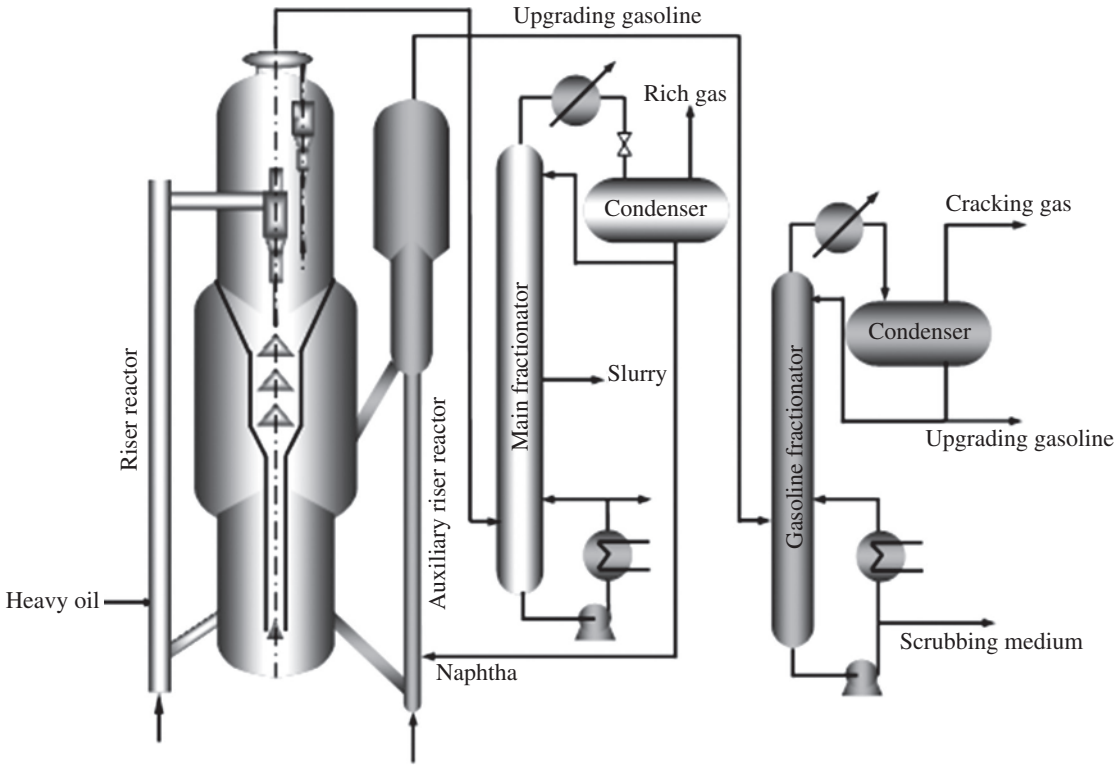

FIGURE 1.58 Overview flowchart of auxiliary riser FCC for naphtha olefin reduction technology.

1.6.5 Industrial Applications of the SRFCC Process

1.6.5.1 Numbers and Scale of the Commercial SRFCC Units The SRFCC technology is rapidly developing right now [89, 90]. There are now five industrial SRFCC units in China including the commercial runs of Fushun Petrochemical Company with the capacity of 1,500,000 tonne/year, Harbin Petrochemical Company as well as North China Petrochemical Company with the capacity of 1,000,000 tonne/year, Hohhot Petrochemical Company with the capacity of 900,000 tonne/year, and Binzhou Petrochemical Company with the capacity of 200,000 tonne/year. The industrial application results show that SRFCC process is simple and easy to be carried out by which it can produce clear gasoline meeting with Euro III standard (Figures 1.59 and 1.60).

1.6.5.2 Typical Examples of the Commercial SRFCC Unit In 2004, Fushun Petrochemical Company revamped its RFCC unit with the capacity of 1.5 Mton/annum using SRFCC process. The originally existing residue fluid catalytic cracking unit (RFCCU) is a side-by-side pattern with two-stage regenerator employing Daqing AR, VR, and mixing gas oil (GO) as the feedstock developed by Sinopec Engineering Incorporation. The content of olefins in FCC gasoline before revamping is high up to 50–55 v%.

Based on the effects of the olefin reduction and the mass balance after the upgrading process, the magnitude of reduction in gasoline olefins is to some extent large with

FIGURE 1.59 Profile of SRFCC in Fushun Petrochemical Company.

FIGURE 1.60 Profile of SRFCC in Harbin Petrochemical Company.

olefin content decreasing from 44.7 to 15.2 v% and the corresponding conversion of olefins is up to 66%. Meanwhile, aromatics content increases by 6.6%. The upgraded gasoline contains only 33.8 v% of olefins with minimizing increment in dry gas and coke yield of only 0.5%. Therefore, using SRFCC technology, good effects of the reduction in olefins are obtained with better product distribution and less increment of energy consumption by only 10 kg standard oil/ton feed (Tables 1.24, 1.25, 1.26, 1.27, 1.28, 1.29, and 1.30).

1.6.6 Outlook

On the basis of the existing FCC unit and the regular FCC catalyst, using SRFCC technology, the content of gasoline olefins can be reduced to 35 or 20 v% and below. Clean FCC naphtha can be produced in SRFCC process achieving the upgrade of gasoline products. In addition, the SRFCC process can be used to maximize the yield of LPG and propylene by flexibly adjusting operating conditions which can promote the integration of refining and chemical industry.

The successful commercialization of the SRFCC technology shows at least three incredible advantages versus conventional FCC units as follows:

1. Gasoline olefins can be reduced lower than 20–25 v%, maintaining the octane values to satisfy the increasingly stringent environmental regulations;
2. Less loss in yields of dry gas plus coke accounting for only 0.5–1.0 wt% in the total mass balance in the SRFCC unit;
3. Flexible operating and adjusting is of important in SRFCC unit. Propylene yield can increase by 3–4%.

SRFCC process can be used to deal with naphtha feedstock containing high olefin content of up to 40 v%. The content of olefins can be decreased to 18 v% when treating

TABLE 1.24 Mass Balance Before and After Plant Revamping

Items		Before Revamping	After Revamping	Comparison
Inlet	VR	22.47	23.45	
	GO	20.38	19.27	
	AR	57.14	57.28	
	Sum	100.00	100.00	
Outlet	Dry gas	6.03	6.11	0.08
	LPG	14.57	15.73	1.16
	Gasoline	43.26	41.60	−1.66
	Diesel	23.32	23.92	0.60
	Slurry	3.86	3.23	−0.63
	Coke	8.59	9.01	0.42
	loss	0.37	0.40	0.03
	Sum	100.00	100.00	

TABLE 1.25 Main Operation Parameters

Item	Designed Value	Actual Value
Outlet temperature of main riser, °C	500–505	502
Feed rate of main riser, ton/h	187.5	200
Outlet temperature of auxiliary riser, °C	430	405
bed temperature of turbulent reactor, °C	420	~400
Regenerated temperature, °C	690	686
Feed rate of auxiliary riser, ton/h	75	35
Feed temperature of auxiliary riser, °C	40	40
Main/auxiliary disengager pressure, MPa (g)	0.225/0.215	0.215/0.193
New fractionators top/bottom temperature, °C	120/350	136/243
New fractionators top/bottom pressure, MPa (g)	0.175/0.20	0.144/—

TABLE 1.26 PONA Analysis of Gasoline (Fluorescence, %)

Items	Saturates	Olefins	Aromatics
Crude gasoline feed	40.6	46.2	13.2
Upgrading gasoline	57.8	22.7	19.5
Stabilized gasoline	50.8	33.8	15.4

TABLE 1.27 Properties of Gasoline

Items	After Revamping: Crude Gasoline Feed	After Revamping: Upgrading Gasoline	After Revamping: Stabilized Gasoline	Before Revamping
Density (20°C), kg/m^3	731	727	723	720
HK, °C	39	35	38	37
KK, °C	193	188	190	187
Mercaptan sulfur, PPM	34	28	31	42
Induction Period, min			718	442
ON MON			78.9	78.7
RON			89.3	89.5
Vapor pressure, kPa			64.6	55.7
Total sulfur, wt%	0.012	0.009	0.01	0.01

TABLE 1.28 Properties of Diesel

Items		After Revamping	Before Revamping
Density (20°C), kg/Nm^3		873.9	875.4
Distilling range	HK, °C	183	181
	KK, °C	343	341
Cetane number, —		34.7	35.3
Total sulfur, wt%		0.17	0.18
Flash point, °C		65	65
Condensation point, °C		−10	−10
Viscosity	50°C, mm^2/s	1.95	1.85
	20°C, mm^2/s	3.709	3.47

TABLE 1.29 Composition of Liquefied Gas, wt%

Items	After Revamping	Before Revamping
Propane	12.53	12.96
Propylene	42.64	40.82
Isobutane	19.71	18.67
n-butane	4.23	4.26
1-$C_4^=$ + *i*-$C_4^=$	10.39	11.99
trans-$C_4^=$	4.12	4.55
cis-$C_4^=$	2.9	2.86
i-C_5 + *n*-C_5	3.48	3.98
H_2S, ppm	3500	3000

TABLE 1.30 Energy Consumption Before and After Plant Revamping

Items	Before Revamping, kg Standard Oil/Ton Feed	After Revamping, kg Standard Oil/Ton Feed	Comparison
Electrics	6.93	8.21	1.28
Steam	−45.26	−39.89	5.37
Coke	85.9	90.25	4.35
Energy consumption	66.89	76.12	9.23

gasoline of 45–55 v% olefin content with minimizing gasoline loss of below 1.0 wt% in the total feeding. Therefore, the SRFCC process has a good application prospect.

According to the environmental legislation, olefin content has become a crucial specification. The content of olefins in motor gasoline should be lower than 30 v% by referring the new Chinese national standard, GBI 7930–2009. To further satisfy the international motor fuel regulations, the content of olefins needs to be controlled at even lower degrees. SRFCC process can effectively reduce the olefin content to 18 v% and below with reduction in gasoline loss. SRFCC technology will help strengthen the competitive ability of the refineries and will yield remarkable economic as well as social benefits.

1.7 FCC PROCESS PERSPECTIVES

Since the first commercialization of FCC process in 1942, the FCC process has a remarkable history of adapting to continual changes in market demands. Many improvements have been made. In the future, it is projected that there are as much improvements will be enhanced as follows:

1. The pretreatment of heavy oil with lower quality. With the increment of heavy oil with lower quality, which cannot be fed into the conventional FCC units because of higher Conradson Carbon Residue, higher heavy metal contents, and higher nitrogen and sulfur contents, effective pretreating process will be required imminently.
2. Energy consumption reduction. The energy consumption of FCC units is very large and then the potential to reduce the energy consumption is large as well. The major direction is to reduce the coke yield, to utilize the combustion heat of CO within regenerator flue gas, and to develop novel process to utilize the flue gas heat.
3. Pollutant emissions reduction. The main pollutants from the FCC units are fine catalyst dust, CO, SOX, and NOX. They took up the most of pollutant emissions in most refineries. With the development of environmental concerns and increasingly stringent regulations on the control of emissions from refining processes, pollutant emission reduction will be required as well.
4. The variety of catalyst and process to meet the market demands. For instance, the maximum production of diesel and light olefins.
5. The process simulation and integrating optimization. The FCC processes are complex so that the integrating optimization has to be carried out for the whole FCC unit and novel processes, and supporting facilities have been developed in order to increase the riser reactor efficiency.

REFERENCES

1. True W. R, Koottungal L. Asia, middle east lead modest recovery in global refining. Oil & Gas Journal, 2012, 110(12): 32–42.
2. Gao J., Xu C., Lin S., et al. Advanced model for turbulent gas–solid flow and reaction in FCC riser reactors. AICHE Journal, 1999, 45(5): 1095–1113.
3. Gao J., Xu C., Lin S., et al. Simulations of gas-liquid-solid 3-phase flow and reaction in FCC riser reactors. AICHE Journal, 2001, 47(3): 677–692.
4. Lan X., Xu C., Wang G., et al. CFD modeling of gas–solid flow and cracking reaction in two-stage riser FCC reactors. Chemical Engineering Science, 2009, 64(17): 3847–3858.
5. Gao J., Lan X., Fan Y., et al. Hydrodynamics of gas–solid fluidized bed of disparately sized binary particles. Chemical Engineering Science, 2009, 64(20): 4302–4316.
6. Lan X., Xu C., Gao J., et al. Influence of solid-phase wall boundary condition on CFD simulation of spouted beds. Chemical Engineering Science, 2012, 69(1): 419–430.
7. Gao J., Xu C., Lin S., et al. A gas-solid two-phase flow-reaction model of the FCC riser reactions and numerical simulation I. Development of the gas-solid two-phase flow-reaction model. Acta Petrolei Sinica, Petroleum Processing Section, 1998, 14(1): 27–33.
8. Gao J., Xu C., Lin S., et al. A gas-solid two-phase flow-reaction model of the FCC riser reactions and numerical simulation II. Numerical simulation on the gas-solid two-phase flow and reaction of commercial riser reactors. Acta Petrolei Sinica, Petroleum Processing Section, 1998, 14(2): 55–60.
9. Gao J., Xu C., Lin S., et al. Numerical simulation on the gas-liquid-solid three phase flow-reaction in FCC riser reactors I. Development of the gas-liquid-solid three-phase flow-reaction model. Acta Petrolei Sinica, Petroleum Processing Section, 1999, 15(3): 16–23.
10. Gao J., Xu C., Yang G., et al. Numerical simulation on the gas-liquid-solid three phase flow-reaction in FCC riser reactors II. Numerical simulation on the flow and evaporation of the feed spray. Acta Petrolei Sinica, Petroleum Processing Section, 1999, 15(4): 16–21.
11. Gao J., Xu C., Lin S., et al. Numerical simulation on the gas-liquid-solid three phase flow-reaction in FCC riser reactors III. Numerical simulation on the flow, heat transfer and reaction. Acta Petrolei Sinica, Petroleum Processing Section, 1999, 15(5): 28–36.
12. Gao J., Xu C., Lin S., et al. Numerical simulation on the gas-solid two phase turbulent flow. Journal of Chemical Engineering of Chinese Universities, 1999, 13(3): 199–204.
13. Gao J., Xu C., Lin S., et al. Turbulent gas-solid two-phase flow-reaction model. Journal of Chemical Engineering of Chinese Universities, 1999, 12(3): 259–264.
14. Wang H., Xu C., Gao J., et al. A gas-solid two-phase flow-heat transfer-reaction model for FCC riser. Journal of the University of Petroleum, China, 1998, 22(6): 87–91.
15. Gao J., Zhen X., Dong W., et al. Determination of location of reaction-terminating medium in FCC riser reactor. Journal of the University of Petroleum, China (Edition of Natural Science), 2000, 24(6): 1–3.
16. Gao J., Xu C., Lin S., et al. A gas-solid two-phase flow-reaction model of FCC riser reactions and its numerical simulation III. Numerical modeling on the reaction-terminating technique. Acta Petrolei Sinica, Petroleum Processing Section, 1998, 14(3): 38–46.
17. Wang Y., Zhang H., Gao J., et al. Numerical modeling on the reaction-terminating technique in commercial RFCC riser reactor. Journal of Daqing Petroleum Institute, 2000, 23(1): 35–40.
18. Dong W., Xu C., Gao J., et al. Industry experiment of reaction terminating technique in FCC riser reaction. Journal of the University of Petroleum, China (Edition of Natural Science), 2000, 24(6): 4–7.
19. Letzsch W. Fluid catalytic cracking. In: Handbook of Petroleum Processing, Eds. D. S. J. Jones and P. R. Pujadó. Dordrecht: Springer, 2006, p. 253.
20. Song J., Sun G., Chao Z., Wei Y., Shi M. Gas flow behavior and residence time distribution in a FCC disengager vessel with different coupling configurations between two-stage separators. Powder Technology, 2010, 201: 258.
21. Wei Y., Yan H., Shi M. Flow analysis of reason for coking on riser wall of cyclone in disengager in RFCC unit. Petroleum Processing and Petrochemicals, 2000, 31(12): 33 (in Chinese).
22. Avidan A., Owen H., Schipper P. Fluid-catalytic cracking-past and future challenges. Oil & Gas Journal, 1990, 88: 56.
23. Chen Y. M. Recent advances in FCC technology. Powder Technology, 2006, 163: 2.
24. Meyers R. A. Handbook of Petroleum Refining Processes (3rd Ed). New York: McGraw-Hill, 2003.
25. Couch K. A., Seibert K. D., Van Opdorp P. Proceeding of NPRA Meeting. San Antonio, TX, March 2003.
26. Gauthier T., Andreux R., Verstraete J., Roux R., Ross J. Industrial development and operation of an efficient riser separation system for FCC units. International Journal of Chemical Reactor Engineering, 2005, V3, A47.
27. Andreux1 R., Ferschneider G., Hémati M., Simonin O. Experimental study of a fast gas-particle separator. Chemical Engineering Research and Design, 2007, 85, 808.
28. Xie C. Recent development of FCC technologies-30. Internal report of RIPP, Sinopec. Beijing, China, 2010.
29. Lu C., Cao Z., Shi M. Proceeding of the Seventh FCC Annual Meeting of China. Shanghai, China, September 2000 (in Chinese).
30. Cao Z., Lu C., Shi M. Study of a new rough cyclone with a stripper attached. Petroleum Processing and Petrochemicals, 1997, 28(3): 47 (in Chinese).
31. Liu W., Bian X., Wei S. Commercial application of shed stripping cyclone. Petroleum Refinery Engineering, 2000, 30(3): 45.
32. Lu C., Xu G., Lu S., Shi M. Study and industry application of a pre-stripping separation system for riser termination of FCCU. Petroleum Processing and Petrochemicals, 2002, 33(1): 33 (in Chinese).

33. Xu K. Revamping of FCC unit with CSC rapid separation technology. Petroleum Refinery Engineering, 2005, 35(5): 11 (in Chinese).
34. Cao Z., Shi M. Study on\votex type fast separation system at FCCU riser outlet. Petroleum Processing and Petrochemicals, 1996, 27(10): 10 (in Chinese).
35. Cao Z., Lu C., Shi M. Votex type fast separation system at FCCU riser outlet. Petroleum Refinery Engineering, 1999, 29(3): 14 (in Chinese).
36. Hu Y., Lu C., Shi M. Performance comparison of two newly developed disengager arms in vortex quick separator for FCC disengager. Journal of Chemical Industry and Engineering (China), 2008, 59(10): 2478 (in Chinese).
37. Lu C., Cao Z., Shi M. Experimental study and industry application of a new vortex quick separation system at FCCU riser outlet. Acta Petrolei Sinica (Petroleum Processing Section), 2004, 20(3): 24 (in Chinese).
38. Zhou S., Lu C., Shi M. Study on the flow field of gas-solid vortex quick separator with different structure. Petroleum Processing and Petrochemicals, 2004, 35(3): 12 (in Chinese).
39. Sun F., Lu C., Shi M. Modification of the 3-dimension gas flow field in the vortex quick separation system of FCC disengager. Petroleum Processing and Petrochemicals, 2004, 35(2): 51 (in Chinese).
40. Sun F., Lu C., Shi M. Numerical simulation and analysis of gas flow field in vortex quick separation system of FCC disengager. Journal of Chemical Industry and Engineering (China), 2005, 56(1): 16 (in Chinese).
41. Sun F., Lu C., Shi M. Numerical simulation of gas-particles flow field in new vortex quick separation system for FCC disengager. Journal of Chemical Industry and Engineering (China), 2005, 56(12): 2280 (in Chinese).
42. Hu Y., Wang Y., Lu C., Shi M. Improvement of the isolate cylinder in vortex quick separation system at FCCU riser outlet. Acta Petrolei Sinica, Petroleum Processing Section, 2008, 24(2): 177 (in Chinese).
43. Gao J., Wang G., Xu C., et al. A multi-zone coordinated-enhanced method for heavy oil catalytic cracking: CN200910162648.8. 2009-08-17.
44. Gao J., Xu C., Lu C., et al. Future understanding of the reaction pathway of residue fluid catalytic cracking—a new multi-zone cascade-control FCC process. Petroleum Refinery Engineering, 2006, 36(12): 1–6.
45. Wang G., Gao J., Xu C., et al. A flexible adjusting method of heat balance for FCC reaction-regeneration system: CN200910162649.2. 2009-08-17.
46. Wang G., Gao J.,Xu C. Evolutionary design on FCC reactors driven by the high temperature and short contact time demands. Petroleum Science and Technology, 2004, 22(11–12): 1581–1594.
47. Wang G., Li Z., Li Y., et al. Laboratory-scale experiments and industrial practice of low-temperature contact and high ratio of catalyst to oil in the FCC process. Energy & Fuels, 2013, 27(3): 1555–1563.
48. Mao Y., Gao J., Xu C., et al. An improved method for FCC riser reactor: CN200810055684.X. 2008-01-07.
49. Cao Z., Shi M. Study of a vortex rough cut separation system for FCC riser outlet. Petroleum Processing and Petrochemicals, 1996, 27(10): 10–13.
50. Lu C., Zhang Y., Shi M. A historic review on R&D of China's FCC riser termination device technologies. International Journal of Chemical Reactor Engineering, 11(1): 1–18.
51. Wei Y., Song J., Zhang K., et al. Analysis of microstructures of coke and coking mechanism in the reactors of fluid catalytic cracking units. Journal of Fuel Chemistry and Technology, 2005, 33(4): 445–449.
52. Wang G., Wen Y., Gao J., et al. On-site sampling at industrial fluid catalytic cracking strippers and laboratory-scale experiments on chemical stripping. Energy & Fuels, 2012, 26(6): 3728–3738.
53. Wang J., Mao Y., Wang J., et al. Optimization of linkage structure between primary and secondary cyclone separator in the FCC disengagers. Acta Petroleum Sinica (Petroleum Processing Section), 2008, 24(3): 251–255.
54. Wang G., Lan X., Xu C., et al. Study of optimal reaction conditions and a modified residue catalytic cracking process for maximizing liquid products. Industrial & Engineering Chemistry Research, 2009, 48(7): 3308–3316.
55. Wang G., Yang G., Xu C., et al. A novel conceptional process for residue catalytic cracking and gasoline reformation dual-reactions mutual control. Applied Catalysis A: General, 2008, 341(1): 98–105.
56. Gao J., Xu C., Gao D., et al. Coking mechanisms within RFCC disengagers. Petroleum Science and Technology, 2004, 22 (5–6): 601–615.
57. Gao D., Gao J., Xu C., et al. Research progress of coking in disengagers of resid fluid catalytic cracking units. Modern Chemical Industry, 2003, 23(7): 23–26.
58. Gao D., Gao J., Xu C., et al. Analyzing of coking within RFCC disengager. Petrochemical Industry Technology, 2003, 10(3): 54–56.
59. Gao J., Mao Y., Xu C., et al. A coking inhibiting method for RFCC disengager: CN200310121301.1. 2003-12-11.
60. Sadeghbeigi R. Fluid Catalytic Cracking Handbook: An Expert Guide to the Practical Operation, Design, and Optimization of FCC Units. Amsterdam: Elsevier, 2012; 1.
61. Yang C. H., Shan H. H., Zhang J. F., et al. Shortcoming of conventional RFCC reactor and advantage of TSRFCC technology. Journal of China University of Petroleum (Edition of Natural Science), 2007, 31(1): 127–131.
62. Weekman V. W., Nace D. M. Kinetics of catalytic cracking selectivity in fixed, moving, and fluid bed reactors. AICHE Journal, 1970, 16 (3): 397–404.
63. Shan H. H., Dong H. J., Zhang J. F., et al. Experimental study of two-stage riser FCC reactions. Fuel, 2001, 80(8): 1179–1185.
64. Shan H. H. Fundamental Studies on the Technology of Fluid Catalytic Cracking with Two-Stage Risers. Dongying: University of Petroleum, 2004.
65. Zhang J. H., Shan H. H., Chen X. B., et al. Multifunctional two-stage riser catalytic cracking of heavy oil. Industrial & Engineering Chemistry Research, 2013, 52(2): 658–668.

66. Kossiakoff A., Rice F. O. Thermal decomposition of hydrocarbons, resonance stabilization and isomerization of free radicals. Journal of the American Chemical Society, 1943, 65(4): 590–595.
67. Haag W. O., Dessau R. M. Duality of Mechanism in Acid Catalyzed Paraffin Cracking. The Eighth International Congress on Catalysis, Verlag Chemie, Berlin, Germany, July 2–6, 1984, pp. 305–315.
68. Li C. Y., Yang C. H., Shan H. H. Maximizing propylene yield by two-stage riser catalytic cracking of heavy oil. Industrial & Engineering Chemistry Research, 2007, 46(14): 4914–4920.
69. Feng Y., Gao J., Xu C. The production technologies of clean gasoline. Petrochemical Industry Technology, 2002, 4: 238–242.
70. Zhang Y., Gao J., Liu Z. C., Xu C. High quality gasoline production technology. Petrochemical Industry Technology, 2003, 4: 65–69.
71. Wang G., Gao J., Xu C. The modified FCC process for production of low-olefin clean gasoline. Petrochemical Industry Technology, 2004, 4: 39–43.
72. Wang J.-L., Ren K., Gao J.-S., Xu C. Technology on the reduction of alkenes from FCC gasoline. Yunnan Chemical Technology, 2004, 6: 31–35.
73. Zhang G., Gao J., Liang Y., Xu C., Liu Y. The technology situation and progress of decreasing olefins of FCC gasoline. Chemical Industry Times, 2003, 8: 1–4.
74. Yao A.-Z., Gao J.-S., Xu C.-M. Studies on upgrading of FCC gasoline for olefin reduction and more propylene production. Contemporary Chemical Industry, 2005, 5: 17–21.
75. Wei Q., Yang G.-F., Wang G., Xu C.-M., Gao J.-S. Commercial application of FCC naphtha reformulation for olefin reduction and more propylene production. Modern Chemical Industry, 2007, 11: 55–58+60.
76. Dai J., Yang G.-F., Wang G., Xu C.-M., Gao J.-S. Kinetic model of FCC naphtha reformulation for reducing olefin and enhancing propene production. Journal of Fuel Chemistry and Technology, 2008, 4: 431–436.
77. Yan P., Liu Z., Gao J., Xu C. Orthogonal experimental research on catalytic upgrading of cat cracked gasoline in presence of compounded catalyst. Refining and Chemical Industry, 2006, 1: 11–13+22+68.
78. Yan P., Gao J., Xu C. Catalytic conversion of C_4 hydrocarbon mixtures. Modern Chemical Industry, 2006, S2: 320–323+327.
79. Yang G.-F., Wang G., Tian G.-W., Gao J.-S. Kinetic model of FCC naphtha olefin reformulation. Journal of Fuel Chemistry and Technology, 2007, 3: 297–301.
80. Yang G.-F., Tian G., Gao J. Reaction behavior and reaction heat of FCC naphtha olefin reformulation. Journal of Chemical Industry and Engineering (China), 2007, 6: 1432–1438.
81. Gao J., Xu C., Bai Y. Test and study on the reaction rule of FCC naphtha olefin-decrement upgrading. Petroleum Refinery Engineering, 2004, 5: 11–15.
82. Gao J., Xu C., Bai Y. Study on the reaction rules of FCC naphtha upgrading for olefin decrement. Petroleum Processing and Petrochemicals, 2004, 8: 41–45.
83. Bai Y., Gao J., Xu C. Study on reaction rules of different processes for decreasing FCC gasoline olefin content. Petroleum Refinery Engineering, 2004, 6: 7–10.
84. Wei Q., Yang G., Wang G., Xu C., Gao J. Performance of the commercial subsidiary reactor for FCC naphtha upgrading. Chemical Reaction Engineering and Technology, 2007, 5: 398–403.
85. Wang G., Yang G.-F., Gao J.-S. Effects of the operating conditions in the mix zone on FCC naphtha olefin upgrading. Journal of Fuel Chemistry and Technology, 2009, 3: 311–317.
86. Sun R., Wang G., Xu C., Liu W., Gao J. Effect of gasoline hydrocarbon composition on the performance of catalytic pyrolysis. Petrochemical Technology and Application, 2008, 5: 405–409.
87. Yang G.-F., Wang G., Gao J.-S., Xu C.-M. Coke formation and olefins conversion in FCC naphtha olefin reformulation at low reaction temperature. Journal of Fuel Chemistry and Technology, 2007, 5: 572–577.
88. Yang G.-F., Xu C.-M., Gao J.-S. Coke formation and its influence on olefin conversion in FCC naphtha upgrading. Acta Petrolei Sinica, Petroleum Processing Section, 2008, 1: 15–21.
89. Bai Y., Gao J., Li S., Xu C. Commercial application of subsidary riser for FCC naphtha olefin reduction. Petroleum Processing and Petrochemicals, 2004, 10: 17–21.
90. Gao J., Xu C., Lu C., Mao Y., Shi Q., Wang A., Liu H. Commercialization of auxiliary riser FCC for naphtha olefin reduction technology in Binzhou petrochemcal company. Petroleum Refinery Engineering, 2005, 6: 8–10.