

**MULTIPHASE
REACTOR
ENGINEERING** *for*
**CLEAN AND LOW-CARBON
ENERGY APPLICATIONS**

EDITED BY
**YI CHENG
FEI WEI
YONG JIN**

WILEY

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Edited by

YI CHENG, FEI WEI, and YONG JIN

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PREFACE

A multiphase reactor accommodates more than one phase (gas, liquid, or solid) coming into contact and resulting in a change in chemical composition of one or more phases. Almost all of the fuels, chemicals, and materials are produced through chemical transformations in multiphase reactors. Multiphase reactor engineering actually integrates fundamentals of transport phenomena and chemical reactions with reactor modeling, design, scale-up, and process optimization quantitatively, and will continue to play a key role in the development of industrial processes.

This book pays special attention to the applications of multiphase reactor engineering in the energy-related processes, especially to the emerging processes of clean, highly efficient conversion of fossil fuels as well as biomass to chemical products. The goal in editing the book is to provide the state-of-the-art review on the historical development and characteristics of conventional and non-conventional multiphase reactors with the updated knowledge linked with the basic principles of some novel processes. In particular, for the limited reserves and poorer quality of oils nowadays, conventional refining processes meet new challenges, which calls for the new revolution in multiphase reactor technologies, for example, for clean

coal utilization processes. Some emerging processes, such as coal to liquid fuels, coal to chemicals (e.g., acetylene, olefins, and aromatics) and the newly updated coal pyrolysis, gasification, and combustion, are being commercialized in industry. In parallel to the aforementioned processes, a perspective view on the CO₂ capture and storage is also included as CO₂ emission has become the bottleneck for sustainable future of the earth. The chapters are organized as follows: petroleum refining (Chapter 1), coal direct conversion (Chapters 2–5), syngas conversion (Chapters 6 and 7), methanol conversion (Chapters 8 and 9), natural gas conversion (Chapter 10), biomass conversion (Chapter 11), and CO₂ control based on chemical looping technology (Chapter 12).

The editors would like to acknowledge the great efforts from all the contributors in preparing the chapters and their expertise in the specific areas. We anticipate that the book would help readers to deeply understand the fundamentals of multiphase reactors and the sophisticated applications related with key solutions to cleaner conversion techniques of fossil fuels and biomass.

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NOVEL FLUID CATALYTIC CRACKING PROCESSES

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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 $40\text{--}45 \times 10^8$ 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 $60 \mu\text{m}$ (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 $1050\text{+}^\circ\text{F}$ ($330\text{--}550^\circ\text{C}$) range.

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

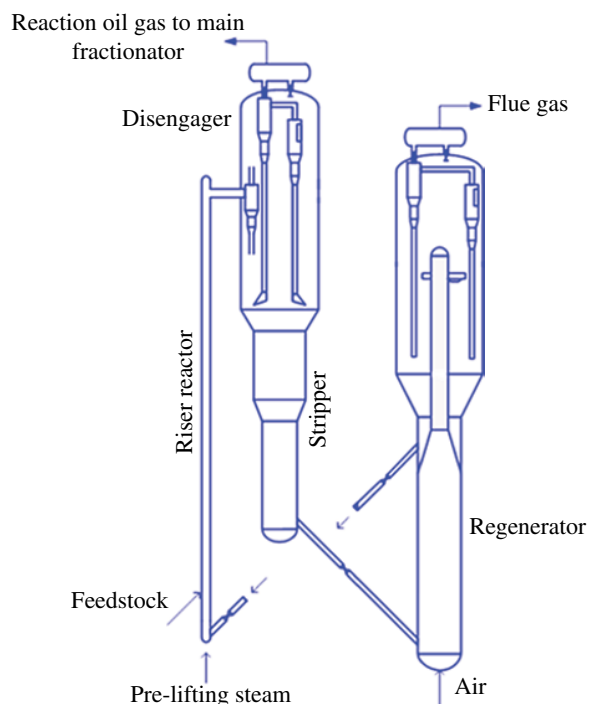


FIGURE 1.1 The basic “side-by-side” type FCC unit configurations.

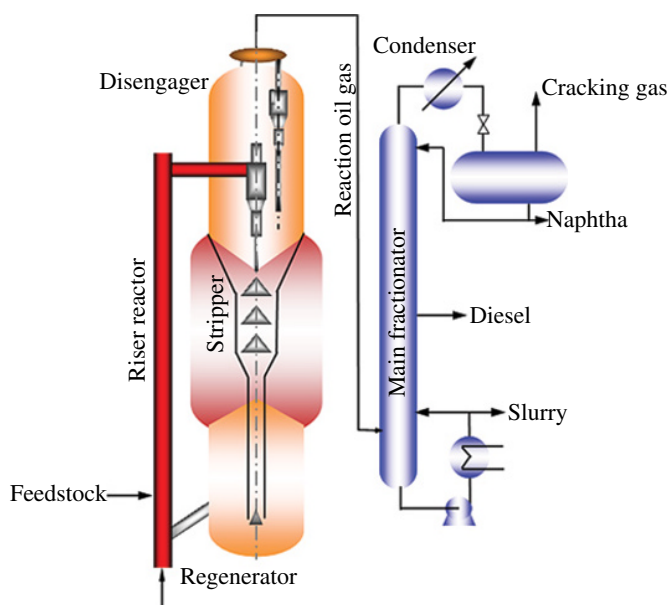


FIGURE 1.2 The basic Orthoflow or stacked-type FCC unit configurations.

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

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

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.

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 CO₂) 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

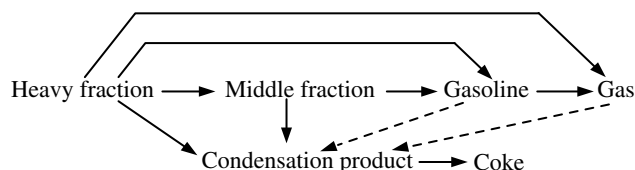


FIGURE 1.3 Catalytic cracking reaction mechanisms for hydrocarbons in petroleum.

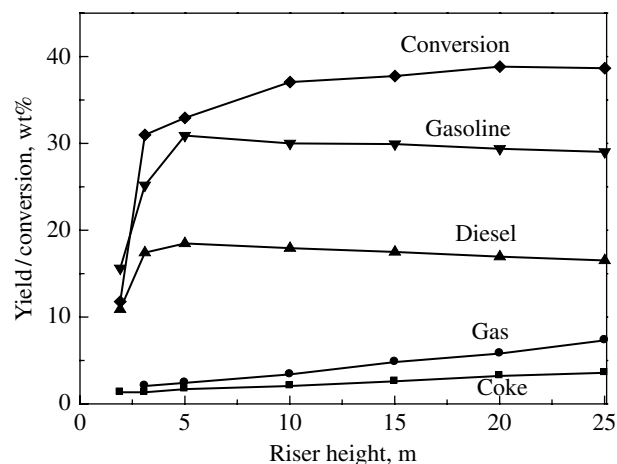


FIGURE 1.4 Product yield along the riser.

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

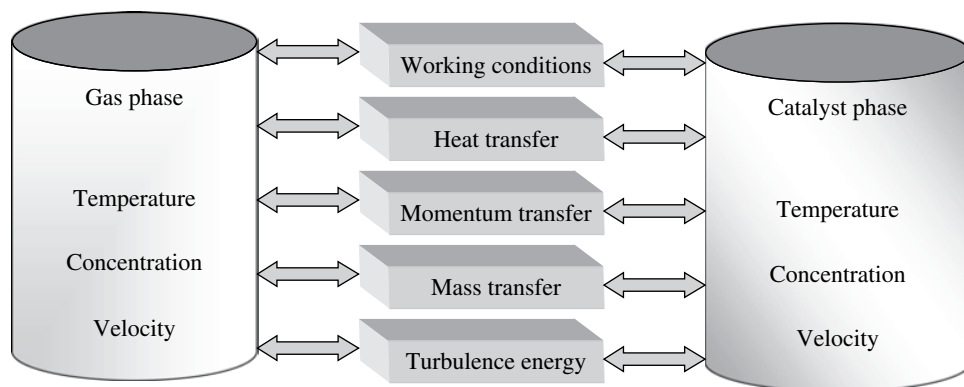


FIGURE 1.5 Gas–solid flow and reaction model in FCC riser.

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]:

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

where x , r , and θ 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

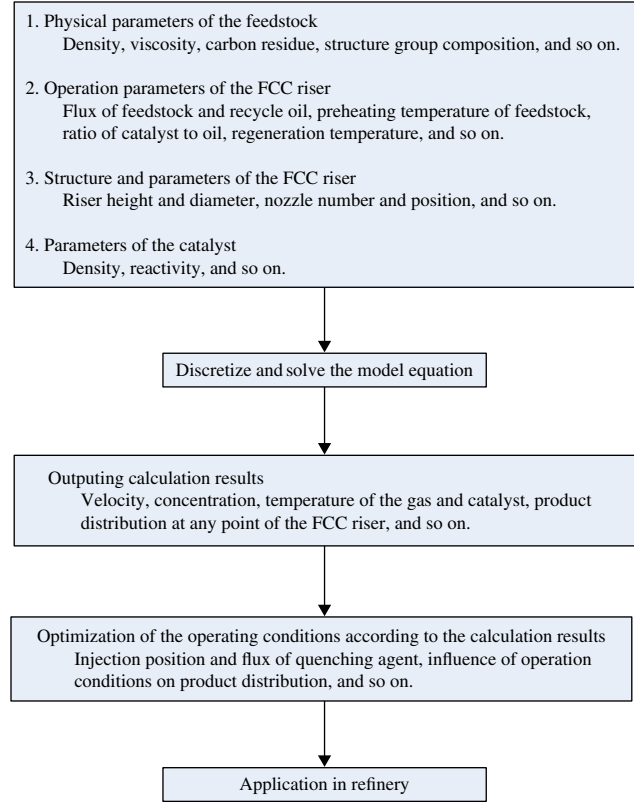


FIGURE 1.6 Overview diagram for simulation calculation.

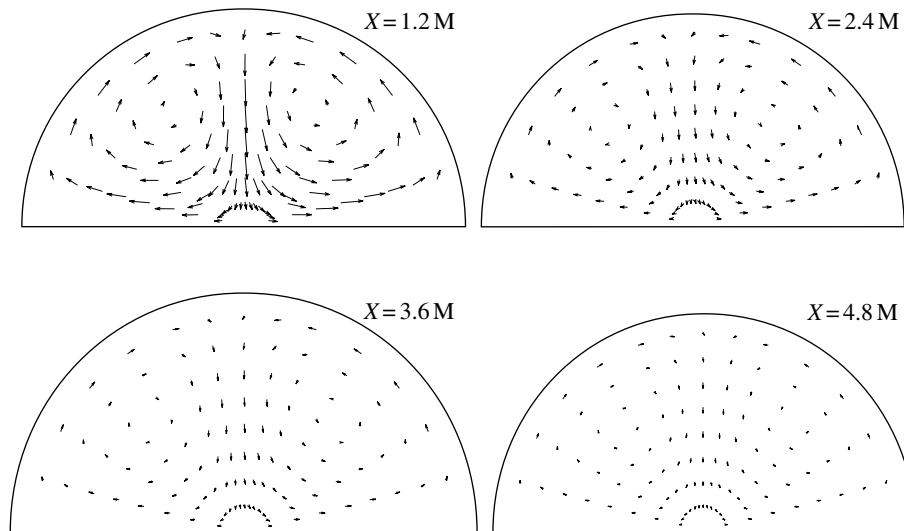


FIGURE 1.7 The gas-phase flow diagrams for different sections in FCC riser.

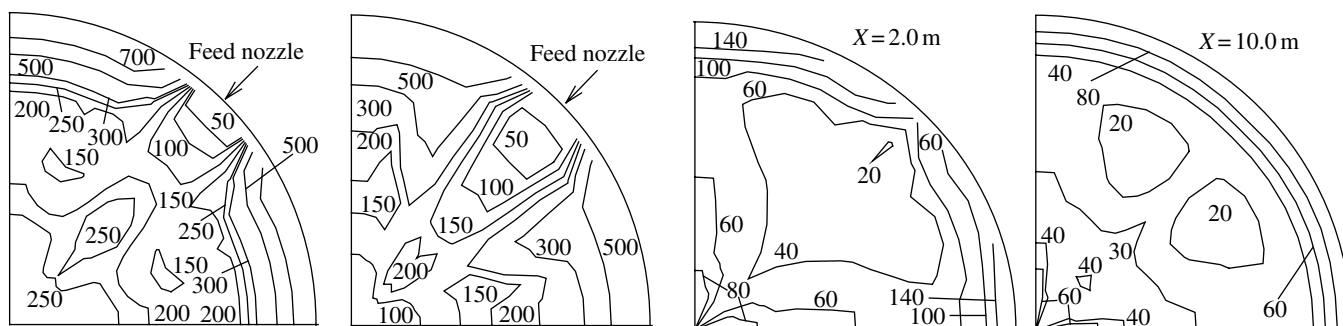


FIGURE 1.8 Catalyst concentration contour plots for different sections in FCC riser (kg/m^3).

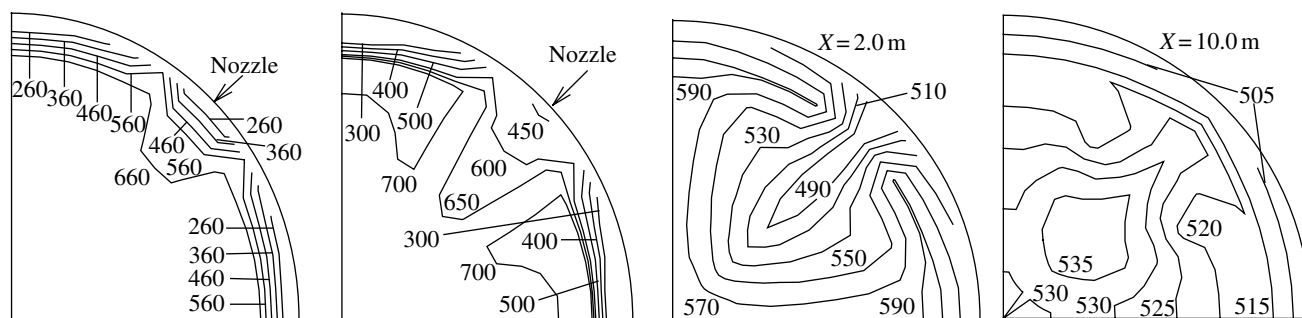


FIGURE 1.9 The gas-phase temperature contour plots for different sections in FCC riser ($^{\circ}\text{C}$).

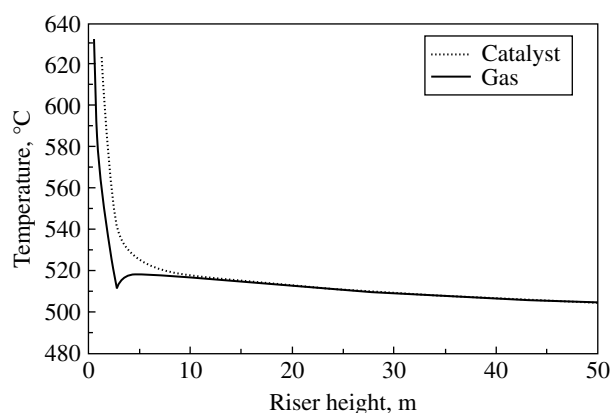


FIGURE 1.10 The gas and catalyst temperature along FCC riser.

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

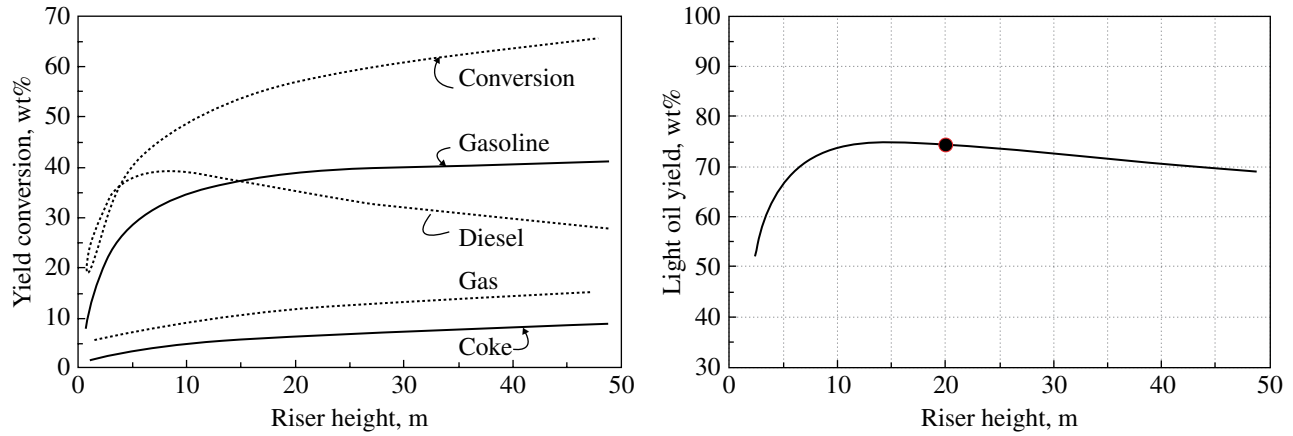


FIGURE 1.11 Product yield, conversion, and the light oil yield along FCC riser.

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.

- 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 20.0m 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 20.0m. 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

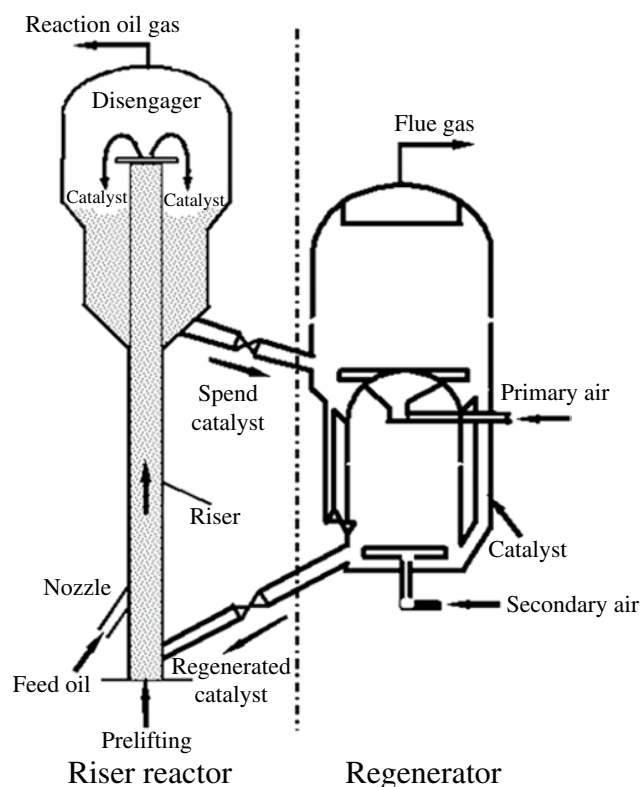


FIGURE 1.12 The schematic diagram for reaction-regeneration system in FCCU in Petrochemical Factory of Shengli Oilfield Company Ltd.

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 1.5m (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
Slurry 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 pre-stripping 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.

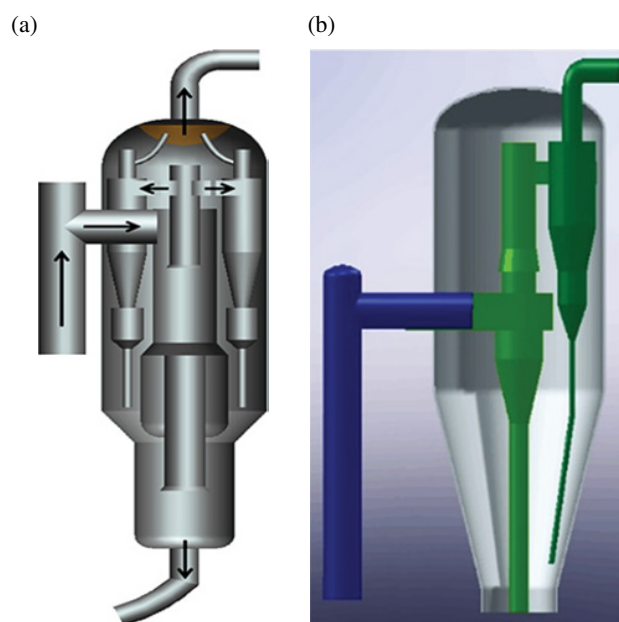


FIGURE 1.13 Close-coupled cyclone systems: (a) Shell's internal close-coupled cyclone system and (b) KBR's closed cyclone.

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-

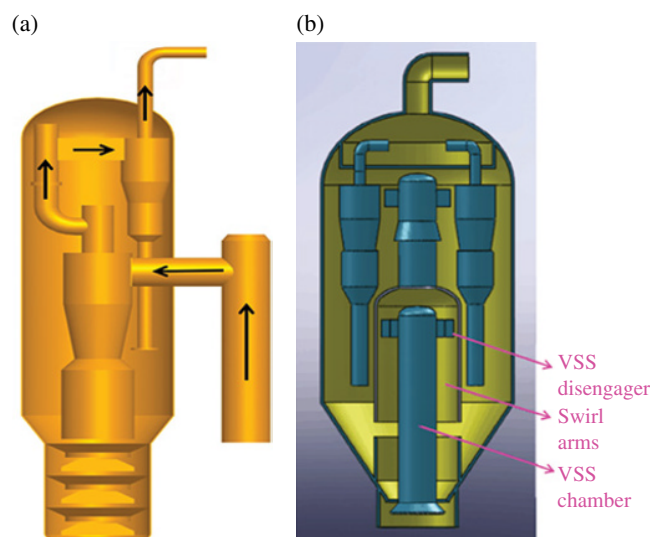


FIGURE 1.14 UOP's (a) VDS and (b) VSS.

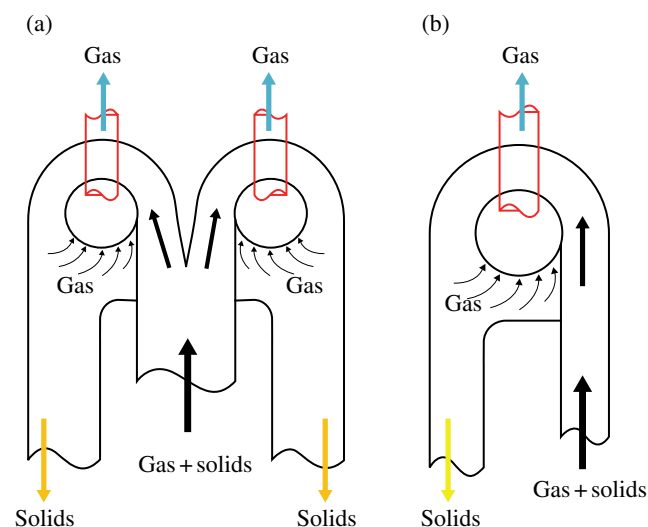


FIGURE 1.15 (a) RS² and (b) LD2.

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.

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 valve 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

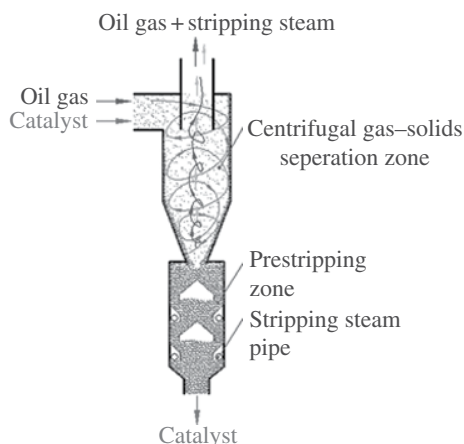


FIGURE 1.16 Schematic of an efficient RTD system.

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

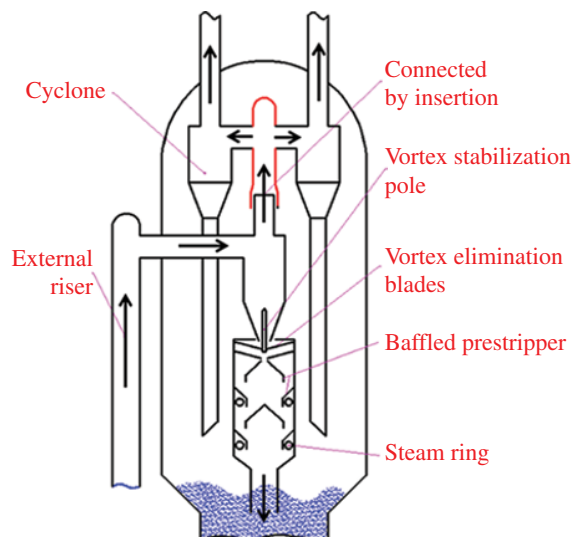


FIGURE 1.17 FSC system.

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 $\geq 98\%$), 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, counter-current 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

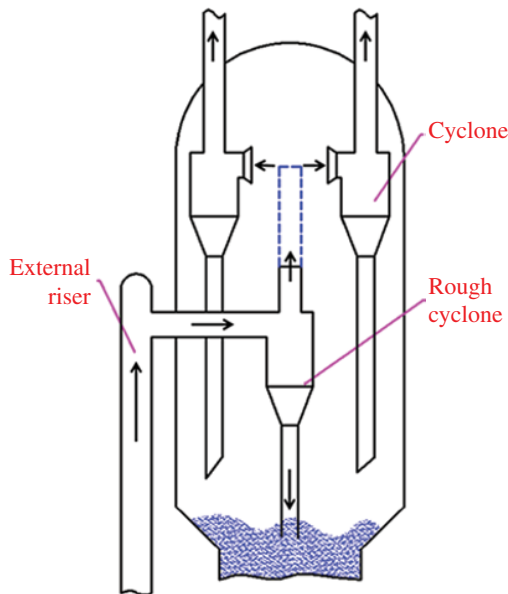


FIGURE 1.18 Rough cyclone RTD.

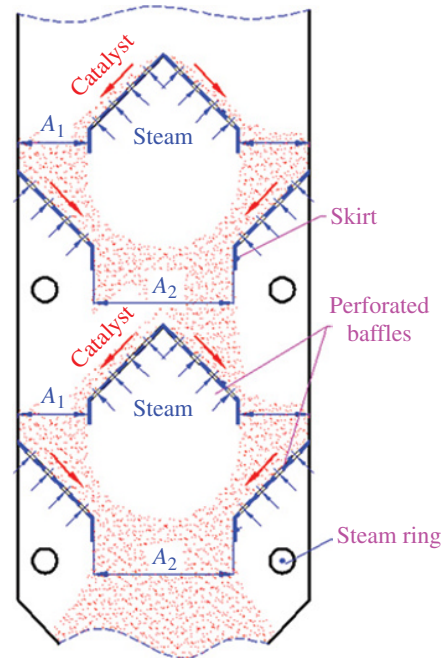


FIGURE 1.19 Cross-flow prestripper.

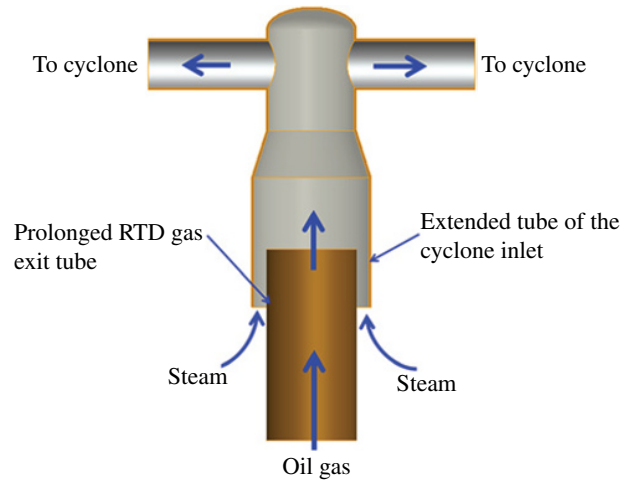


FIGURE 1.20 Venturi connection geometry between the RTD gas exit tube and the downstream cyclone inlet tube.

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 pre-stripping 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

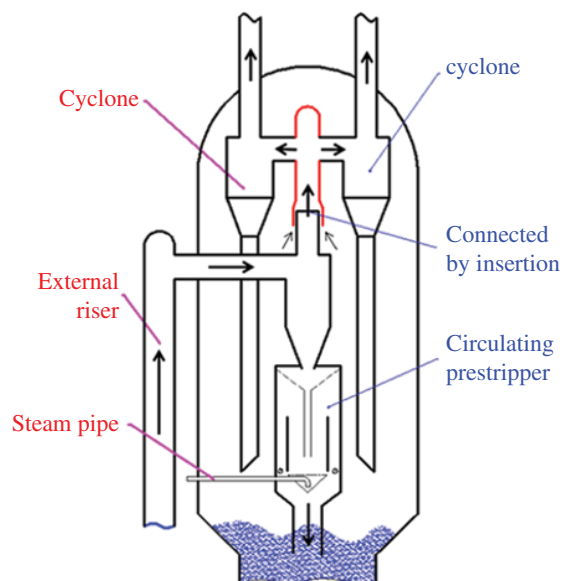


FIGURE 1.21 CSC system.

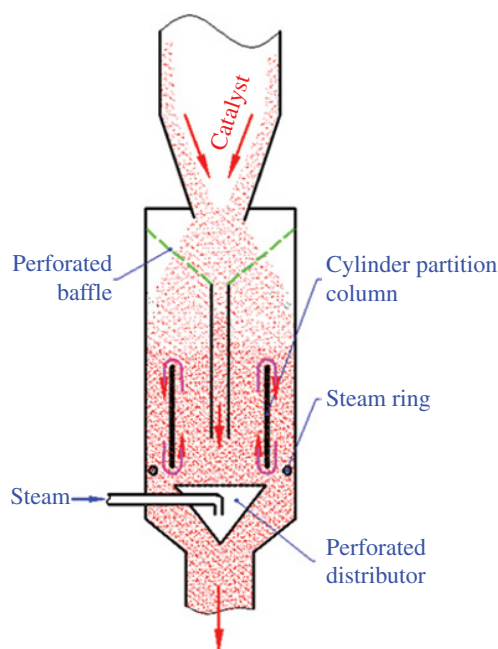


FIGURE 1.22 Annular circulating prestripper.

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

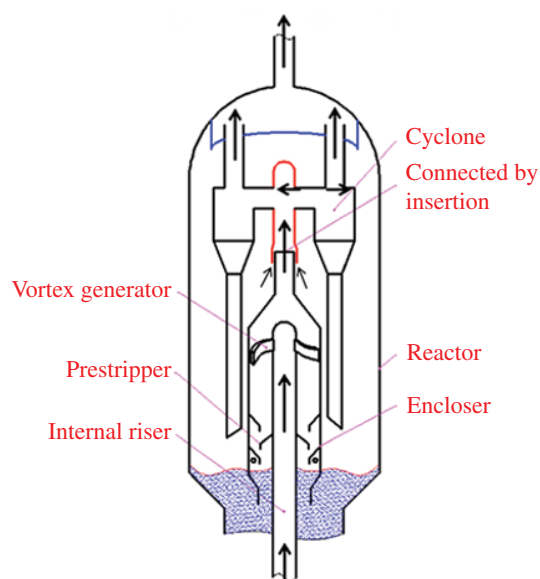


FIGURE 1.23 VQS system.

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 enclosure 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 enclosure 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 enclosure wall before

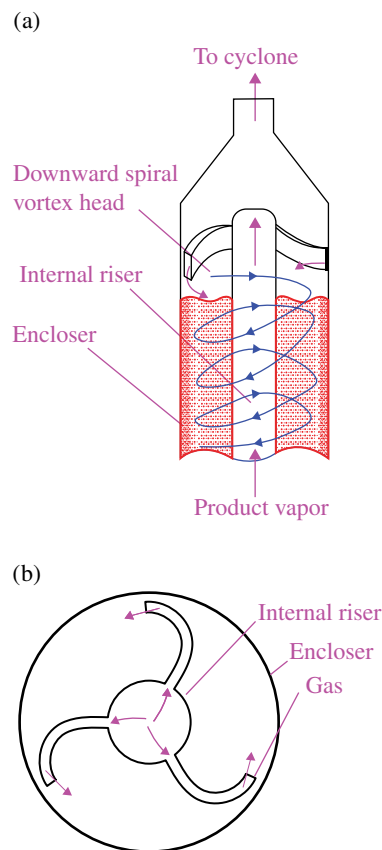


FIGURE 1.25 Second-generation vortex head: (a) side view and (b) top view.

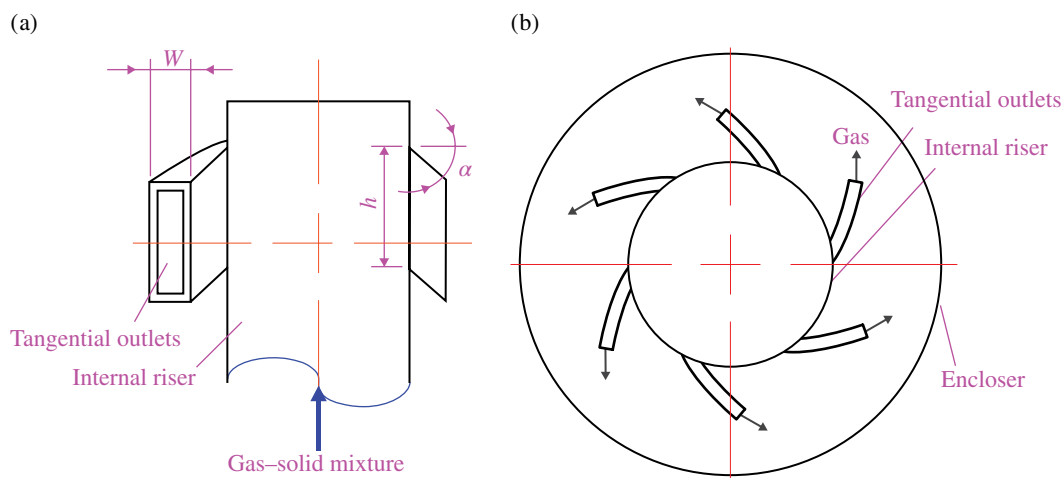


FIGURE 1.24 First-generation vortex head: (a) side view and (b) top view.

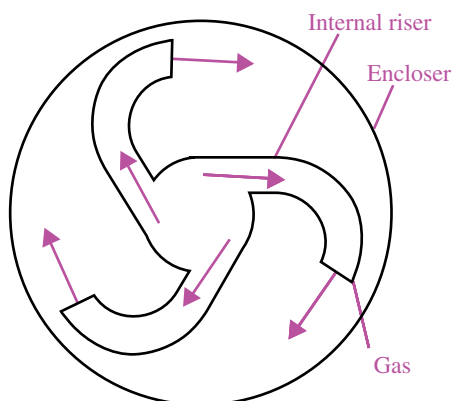


FIGURE 1.26 Third-generation vortex head.

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 favor 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 80Mton/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 1.0Mton/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 3.0Mton/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 2.5Mton/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 SVOS 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 enclosure directly, which results in some entrained particles incapable of entering the lower region with stronger centrifugal strength and lower particle recovery efficiency. When the enclosure diameter is small, this problem is not very remarkable. However, when the enclosure 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.

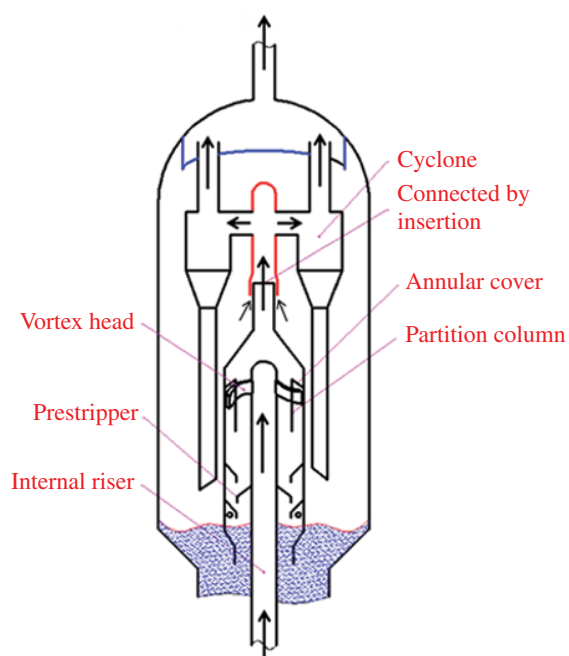


FIGURE 1.27 SVQS system.

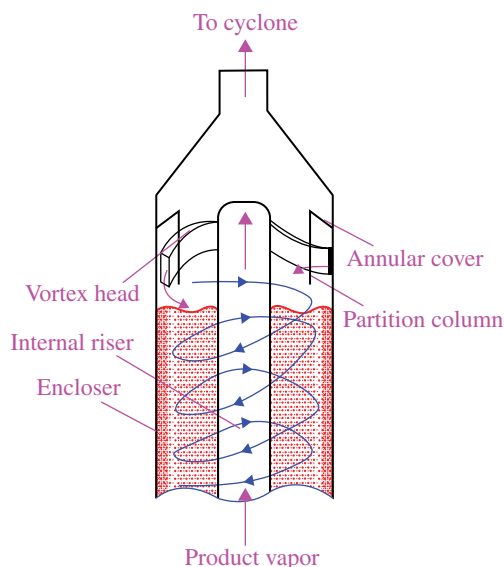


FIGURE 1.28 The vortex head for SVQS.

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.

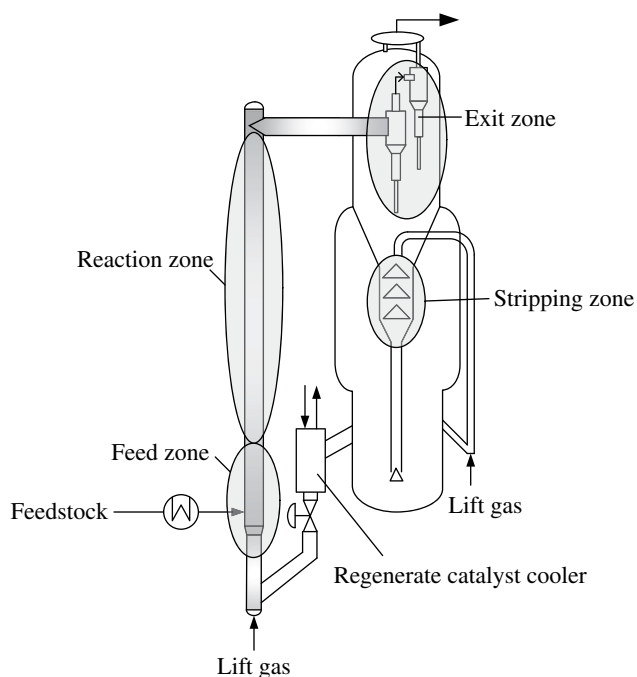


FIGURE 1.29 Schematic diagram of MZCC process.

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/O Catalyst-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

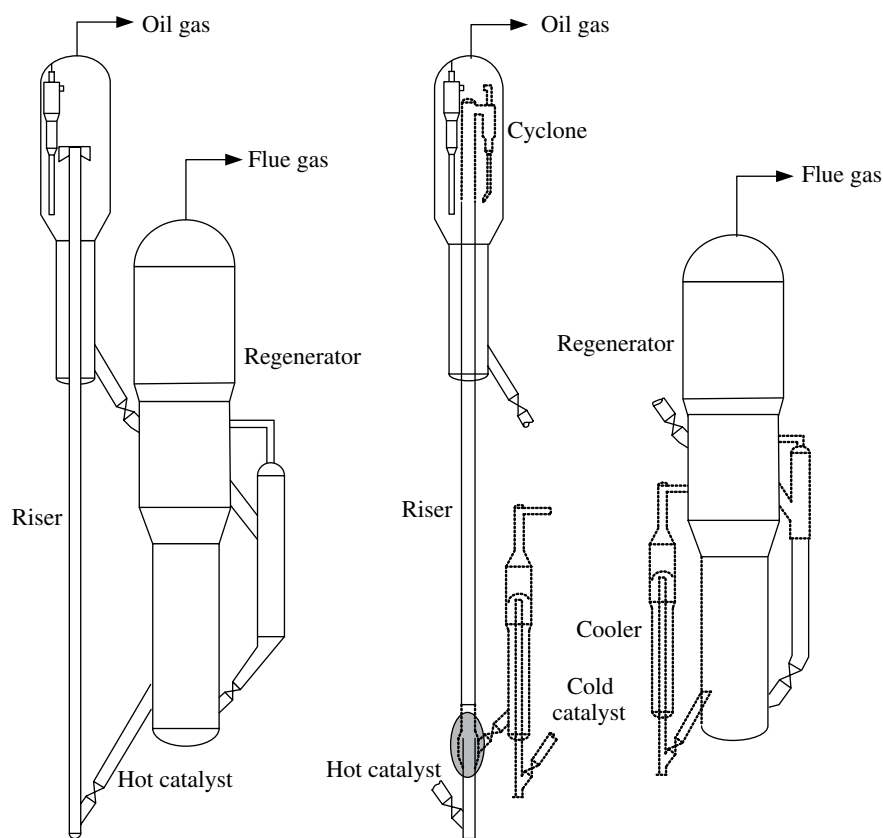


FIGURE 1.30 Comparison of prelift section between MZCC and routine FCC.

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 structure 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.

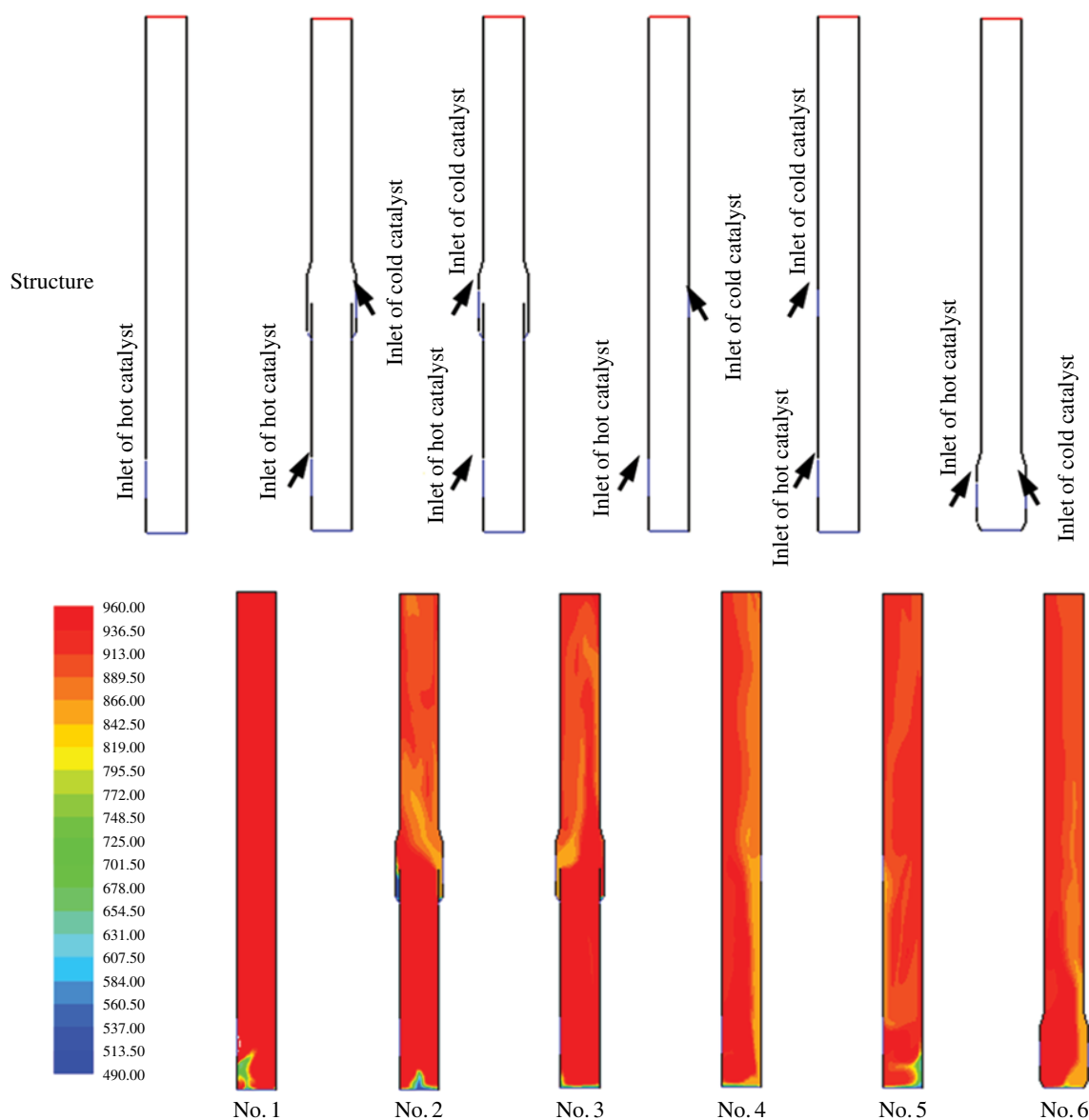


FIGURE 1.31 Temperature distributions in different pre-riser structures.

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

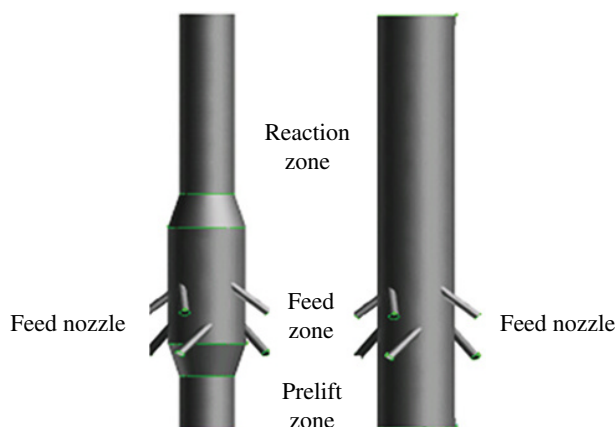


FIGURE 1.32 New array arrangement of FCC feed injectors.

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].

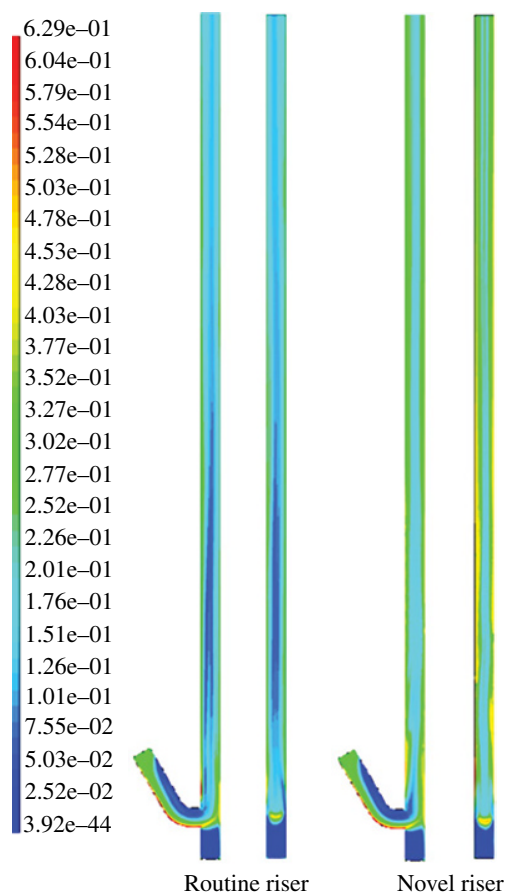


FIGURE 1.33 Comparison of gas–solid two-phase distribution within the conventional riser reactor with that of new array arrangement of feed injector.

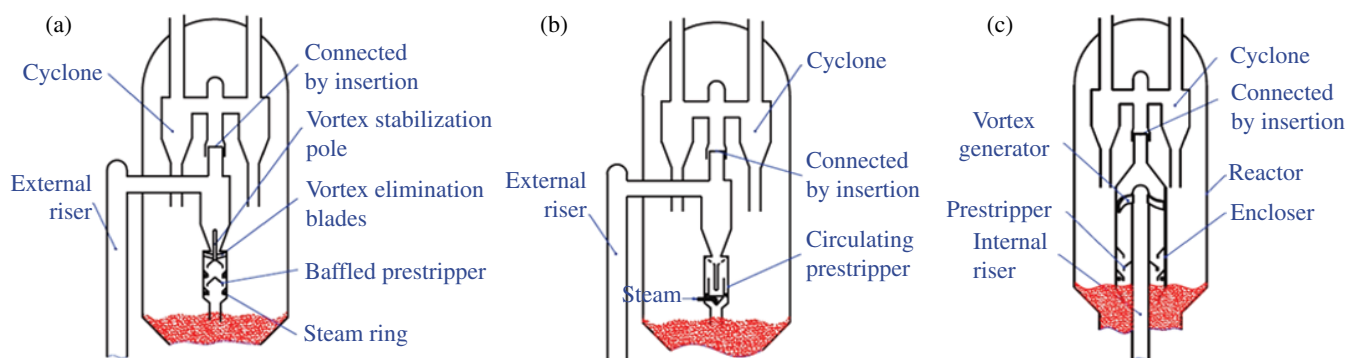


FIGURE 1.34 New configurations of rapid separation: (a) FSC, (b) CSC, and (c) VQS.

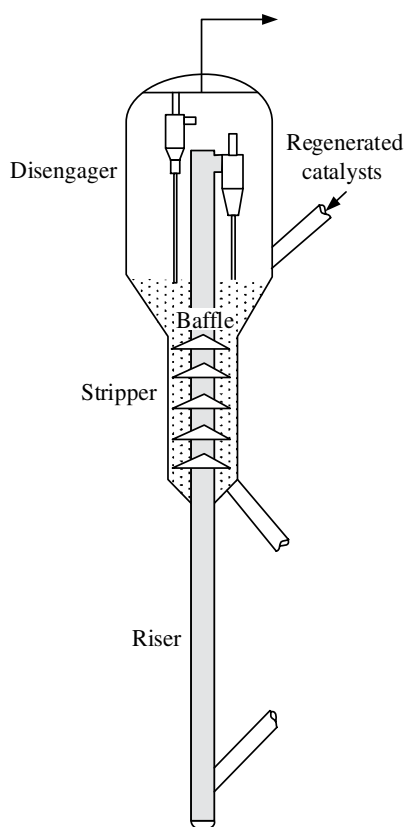


FIGURE 1.35 Schematic diagram of chemical strippers.

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 condensing 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 SINOPEC 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 $\Phi 600$ 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.

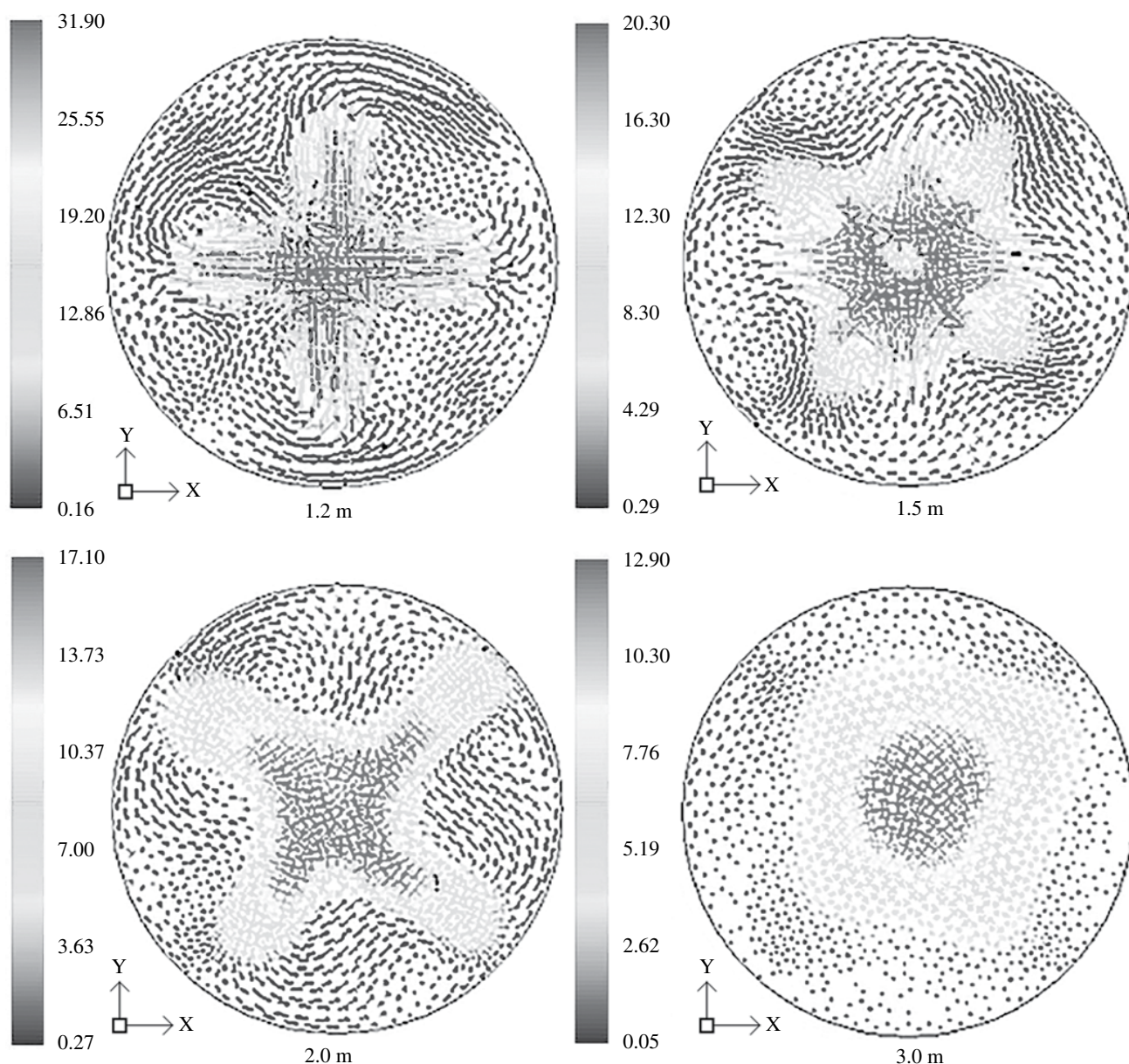


FIGURE 1.36 Numerical simulation results of gas–solid two-phase distribution within the conventional riser reactors.

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

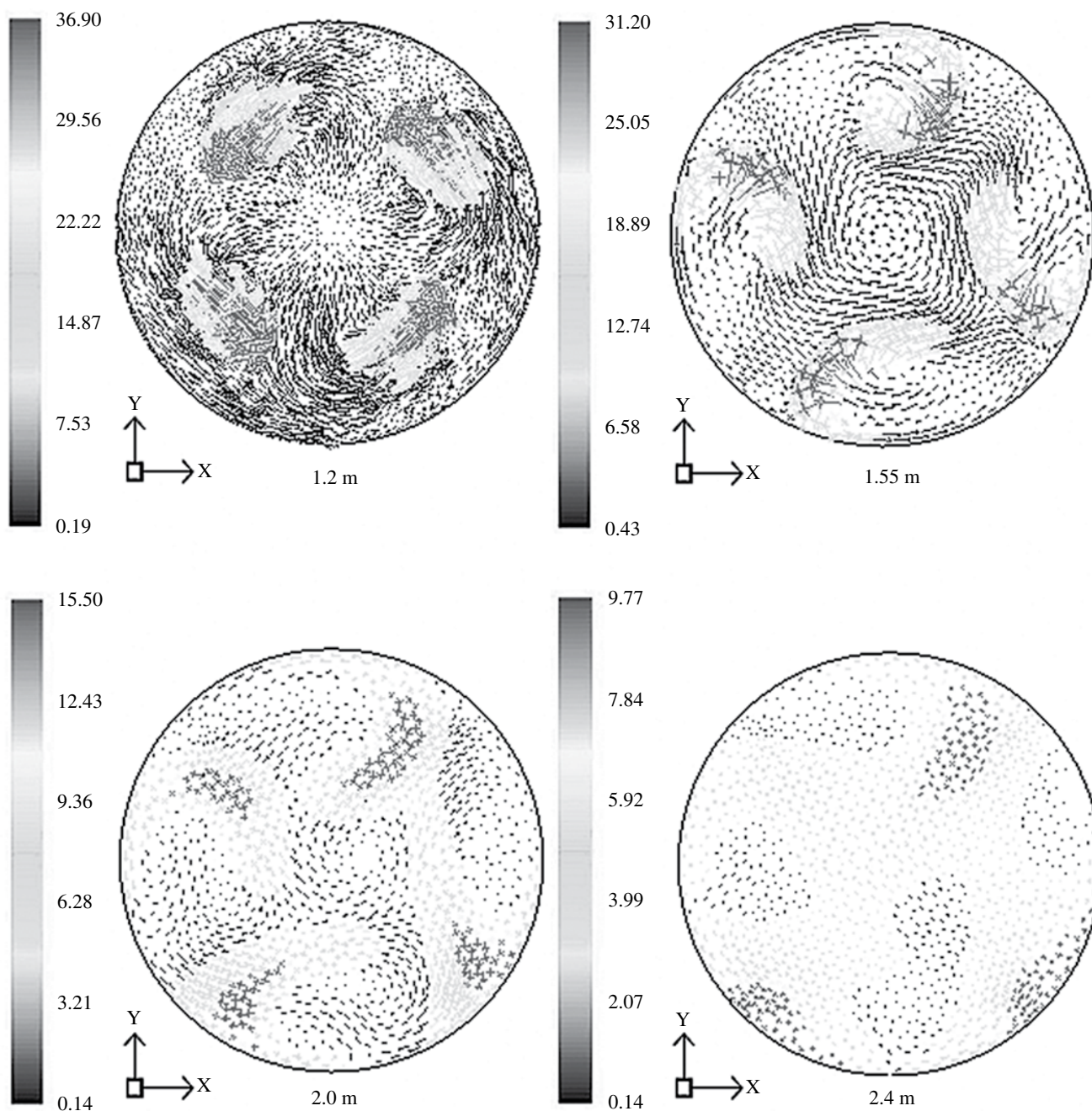


FIGURE 1.37 Numerical simulation results of gas–solid two-phase distribution within the riser reactor with new array arrangement of feed injector.

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

Ton/°C	C/O ^a	Ton ^b /s	Product Distribution, wt%						X ^c , %	Yield, wt%	
			Dry Gas	LPG	Gasoline	Diesel	Heavy Oil	Coke		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

^aCatalyst-to-oil ratio.

^bReaction time.

^cConversion.