FLUID CATALYTIC CRACKING (FCC) UNITS, REGENERATION

1. Introduction

Fluid catalytic cracking (FCC) is the central process in a modern, gasoline-oriented refinery. In U.S. refineries, the amount of feed processed by fluid catalytic cracking units (FCCU) is equivalent to 34% of the total crude oil processed in the United States (1). As of January 2003, installed FCCU capacity in the United States was $9.0 \times 10^5 \mathrm{m}^3$/day ($5.7 \times 10^6$ barrels/day calendar day basis).

The popularity of the catalytic cracker stems from its ability to produce large quantities of high octane gasoline and other valuable light products and to use a wide range of refinery process streams as feed materials. The FCCU feeds include high molecular-weight vacuum gas oils (VGO), which are traditional feeds; atmospheric and vacuum residues; coker gas oils; gas oils from other thermal and hydrocracking operations; lube oil extracts; and deasphalted oils. A survey of U.S. refiners conducted in the mid-1990s indicated that 39% of the U.S. gasoline pool was produced by the FCCU (2).

Although the FCCU has long been an important refinery processing tool in the United States, refinery gasoline demands outside the United States have been satisfied largely from the gasoline naturally present in crude oil (3). This situation is changing, and the need for catalytic cracking is now growing steadily everywhere. As of January 2003, the installed worldwide FCCU capacity stood at 22.6×10^5 m^3/day (14.2×10^6 barrels/day). Worldwide, excluding North America, and also excluding the Former Soviet Union and mainland China, for which data did not exist 10 years ago, the installed FCC capacity increased nearly 60% in the 10-year period from 1981 to 1991, and another 22% in the period from 1992 to 2002 (4,5).

The FCC process is highly complex but self-contained. A typical UOP FCC unit of 2002 design is shown in Figure 1**a**. Figure 1**a** was originally prepared by UOP for inclusion in the 3rd edition of Meyer's *Handbook of Petroleum Refining Processes*, currently in press. The 2002 design is contrasted to a mid-1970s FCC unit in Figure 1**b** (6). In the 2002 design, hot catalyst from the regenerator enters the base of the riser and is carried up the lower portion of the riser with an accelerating media, typically steam. The accelerating media conditions the catalyst flow pattern so that catalyst is uniformly dispersed across the riser cross-section. At the end of the acceleration zone, feed is injected into the riser through a series of feed distributors positioned around the riser circumference. Sufficient pressure drop is taken across the distributors to produce an atomized spray that covers the riser cross section and provides intimate contact with the upflowing catalyst. This careful orchestration of feed and catalyst contacting contrasts with the less elegant procedure used in the 1970s design. At that time feed, and catalyst mixed at the base of the riser, with no attempt at catalyst dispersion and little effort made toward feed dispersion. The improved contacting in the 2002 design has resulted in decreased coke deposition on the catalyst, which

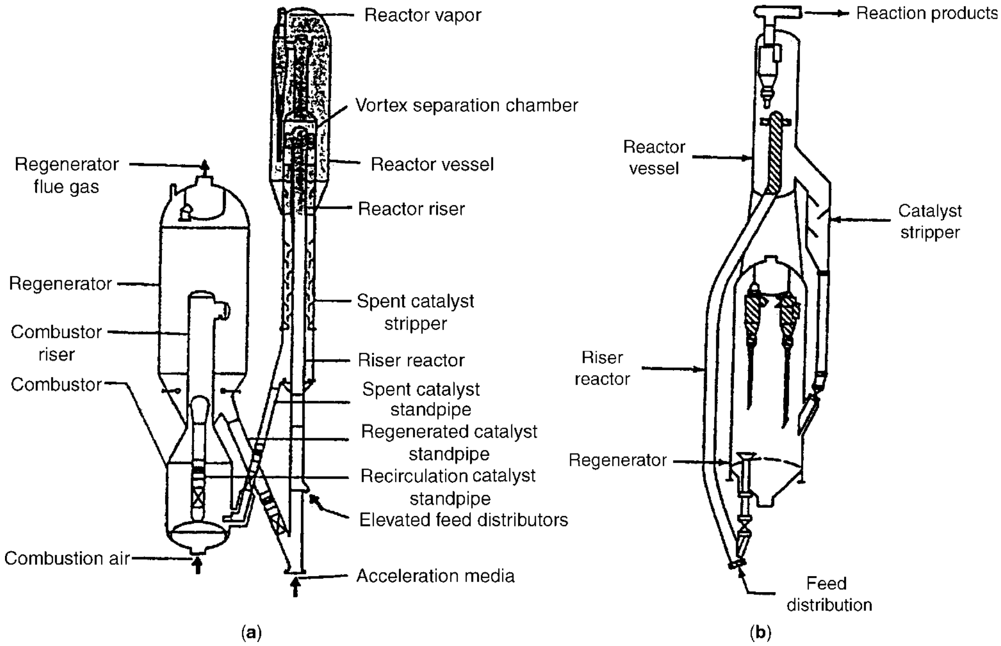

Fig. 1. (**a**) Modern UOP FCC unit with: Short contact time riser VSS disengager combustor-style regenerator. (**b**) Mid-1970s UOP FCC unit with: Riser cracking Stacked reactor bubbling-bed regenerator.

leads to lower regenerator temperatures, higher catalyst circulation rates, and higher and more selective conversion of the feed (7).

Catalyst and hydrocarbon vapors pass up the riser in a dilute-phase, plug flow. In the 2002 design, catalyst and hydrocarbon vapors are rapidly separated. Rapid separation is desired to minimize back mixed, nonselective reactions that can occur when catalyst and hydrocarbon leave the plug flow riser environment. These nonselective reactions also result in further unwanted increases in coke on catalyst. Rapid separation is achieved by discharging the riser components directly into a form of a vortex (cyclone) separator. A hydrocarbon residence time in this style separator of ~2 s have been reported, compared to a typical residence time of 20–30 s for the 1970 separator designs (8).

When in contact with the catalyst, the hydrocarbon feed cracks to form gasoline, middle distillates, liquefied petroleum gas (LPG), and fuel gas. Coke, which is also formed, deposits on the catalyst surface and reduces the catalyst activity. To restore its activity, the catalyst passes into the regenerator section where the coke is burned off. The temperature of the catalyst is increased 150–200°C as a result of the coke burn. Care must be taken on the reactor side to control coke production, so that the heat released in the regenerator does not raise the regenerator temperature beyond the metallurgical limitations of the regenerator. The 2002 UOP design utilises a high efficiency, combustor-style regenerator, which typically operates in the fast-fluidized, catalyst transport regime. By contrast, the typical 1970s style regenerator utilized a bubbling fluidized bed for air/catalyst contacting.

The heat released from coke burning is used to provide the heat requirements on the reactor side: to vaporize the feed, to compensate for the endothermic heat of cracking, to bring the reactor to the desired reactor temperature, and to compensate for heat losses to the atmosphere. Thus the FCCU always operates in complete heat balance at any desired hydrocarbon feed rate and reactor temperature. In FCC units, such as the ones shown in Figure 1, riser temperature control adjusts the catalyst circulation rate to achieve the heat balance. Catalyst flow is controlled by a slide valve located in the catalyst transfer line from the regenerator to the reactor and in the catalyst return line from the reactor to the regenerator. In some older style units, where catalyst flow is controlled by pressure balance between the reactor and regenerator, the heat-balance control is more often achieved by changing the temperature of the hydrocarbon feed entering the riser.

Prior to entering the regenerator, the spent catalyst from the reactor passes through a steam stripper where the hydrocarbon vapors that are entrained by the flowing catalyst particles are displaced by steam. The steam also acts to desorb some of the lighter hydrocarbons that are adsorbed during the reaction step. These stripped materials, which represent valuable reaction products, are carried back into the reactor by the upflowing steam from the stripper and go to the product-recovery section with the other reaction products. The removal of these materials from the catalyst stream flowing to the regenerator also reduces the amount of burnable hydrocarbon going to the regenerator, which helps to decrease the regenerator temperature.

2. FCCU Heat Balance

Because of the thermal coupling of reactor and regenerator, any change on the reactor side creates a rapid change on the regenerator side, which, in turn, influences the reactor side, and vice versa. This dynamic interaction rapidly comes to equilibrium, and the catalytic cracker adjusts to a new steady-state, heat-balanced condition. The first law of FCCU catalytic cracking is that the FCCU will always adjust itself to stay in heat balance (9). If an FCCU is not in heat balance, it is out of control. The operating characteristics of an FCCU regenerator are thus dictated by the constraints of the heat balance (Fig. 2).

Considering the overall balance, the burning of coke in the regenerator provides all of the energy required to raise the temperature of the reactor hydrocarbon feed and products to the reactor vessel temperature; raise the temperature of the combustion air from the temperature of the air blower discharge to the temperature of the regenerator flue gas; provide the endothermic heat of reaction; provide the heat that is removed from the system, including natural heat loss from the reactor and regenerator to the atmosphere as well as intentional heat removal from catalyst coolers.

$$\Delta H_{\text{Coke combustion}} = \Delta H_{\text{Products-feed}} + \Delta H_{\text{Air}} + \Delta H_{\text{Steam}} + \Delta H_{\text{Cracking}} + \Delta H_{\text{Loss}} \quad (1)$$

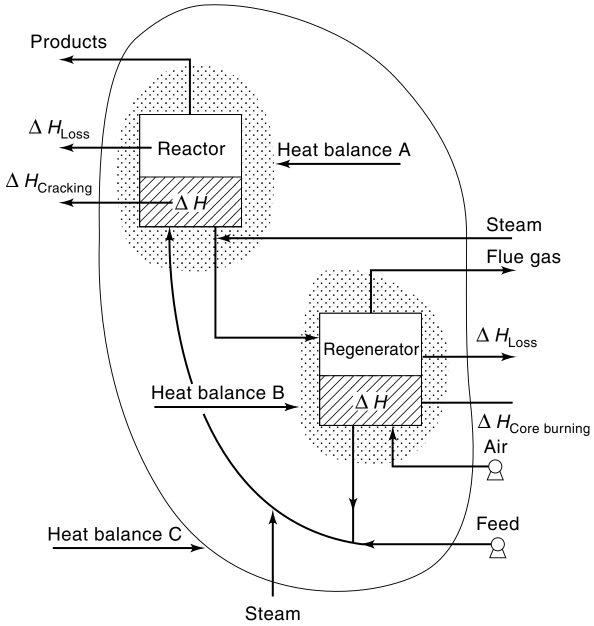

Fig. 2. Heat balances of the FCCU. Heat balance around the reactor A, heat balance around the regenerator B, and the overall heat balance around the entire catalytic cracker C must be considered.

Thus the amount of heat that must be produced by burning coke in the regenerator is set by the heat balance requirements and not directly set by the coke-making tendencies of the catalyst used in the catalytic cracker or by the coking tendencies of the feed. Indirectly, these tendencies may cause the cracker operator to change some of the heat-balance elements, such as the amount of heat removed by a catalyst cooler or the amount put into the system with the feed, which would then change the amount of heat needed from coke burning.

If FCCU operations are not changed to accommodate changes in feed or catalyst quality, then the amount of heat required to satisfy the heat balance essentially does not change. Thus the amount of coke burned in the regenerator expressed as a percent of feed does not change. The consistency of the coke yield, arising from its dependence on the FCCU heat balance, has been classified as the second law of catalytic cracking (9).

3. Coke Formation

The coke burned in an FCCU regenerator is a poorly defined, hydrocarbonaceous material that has either not been desorbed from the catalyst surface or has not been purged from between catalyst particles during the passage of the catalyst through the steam stripper. This coke originates from four different sources (10): (*1*) catalytic coke is produced directly from the acid catalyzed cracking reaction; (*2*) contaminant coke arises from the dehydrogenation activity of contaminating

Table 1. **FCCU Coke Distributions,**[a] % **of Total Coke**

Feed type	Catalytic	Contaminent	Additive	Cat/oil
VGO	65	15	5	15
resid	29	29	35	7

[a] Ref. 8 and 10.

metals (principally nickel and vanadium) in the feed to the FCCU; (*3*) additive coke is directly related to the high boiling, refractory components in the feed to the FCCU. This coke correlates with the basic nitrogen and molecular weight of the feed (11) and with the carbon residue content of the feed (10); and (*4*) cat-to-oil coke is related to the catalyst circulation rate and derives from the hydrocarbons leaving the stripper. These hydrocarbons are potentially strippable but because of incomplete stripping are entrained by the flowing catalyst into the regenerator. FCCU coke distributions for operations with zeolitic catalysts are given in Table 1 (10,12).

The amount of catalytic coke that is formed depends on the type of catalyst used in the FCCU, the coking tendency of the feed, the degree of conversion of the feed, and the length of time the catalyst is exposed to the feed (eq. 2) (13).

$$\text{Coke on catalyst} = k_c t^{1/2} \tag{2}$$

Coke deposition is essentially independent of space velocity. These observations, which were developed from the study of amorphous catalysts during the early days of catalytic cracking (13), still characterize the coking of modern day zeolite FCC catalysts over a wide range of hydrogen-transfer (H-transfer) capabilities.

Coke on the catalyst is often referred to as delta coke ($\Delta\, C$), the coke content of the spent catalyst minus the coke content of the regenerated catalyst. Delta coke directly influences the regenerator temperature and controls the catalyst circulation rate in the FCCU, thereby controlling the ratio of catalyst: hydrocarbon feed (cat/oil ratio, or C/O). The coke yield as a fraction of feed C_F is related to delta coke through the C/O ratio (eq. 3).

$$C_F = \left(\frac{C}{O}\right) \Delta C \tag{3}$$

The catalytic conversion of gas oil is well approximated by a second-order reaction, where, sv = space velocity (14).

$$\text{conversion}_{\text{2nd order}} = \frac{\text{conv}}{100 - \text{conv}} = \frac{k}{\text{sv}} \tag{4}$$

Space velocity is related to the C/O ratio through the catalyst residence time as

$$\frac{C}{O} = \frac{1}{(\text{sv})t} \tag{5}$$

Combining equations 3–5 yields

$$C_F = \frac{\Delta C}{kt}\ \mathrm{conv}_{\mathrm{2nd\ Order}} \tag{6}$$

Equation 6 relates the catalytic coke yield (as a fraction of the feed) to the delta coke, to the conversion, and to the catalyst residence time.

It has been shown that coke yield as a fraction of feed does give a linear relationship with second-order conversion (15) indicating a positive coke yield at zero conversion. This coke yield at zero conversion is the additive coke contribution to the total coke yield and is related to feed properties, particularly Conradson carbon content. The amount of this additive coke is significantly less than the Conradson carbon value of the feed (16), probably in the range of 50% of the Conradson carbon.

Catalytic coke is also a function of the type of feed being processed. The more aromatic the feed, the higher the coke (on feed) yield at a given conversion (15). The type of cracking catalyst also influences the coke yield. Increasing the H-transfer characteristics of a Y-type zeolite, by increasing the amount of rare earth exchanged on the zeolite, results in an increase in the catalytic coke yield (17). Modern catalysts for FCC applications frequently contain two distinctly different, active components; an active zeolite component for producing high yields of gasoline while yielding minimum catalytic coke and an active, nonzeolitic component, typically a catalytically active alumina located in the so-called matrix portion of the catalyst surrounding the zeolite. The active alumina matrix provides improved conversion of the heavy portion of the feed but typically increases catalytic coke yield at constant conversion (18).

Contaminant coke can vary substantially because of large variations in the metals content of the feed being processed and from variations in the manner that cracking catalysts respond to these metals. Nickel is considered the most active dehydrogenation agent, and hence the most troublesome of the contaminant metals. Copper is equally active as a dehydrogenation catalyst, but the amount of copper present is usually too small to have an effect. Typically, copper in the feed to the FCCU is only 2–5% of the nickel content. Vanadium is a less active dehydrogenation agent than nickel, about one-fourth as effective as nickel (10). The metals content of the equilibrium catalyst in the FCCU is frequently referred to as the equivalent nickel content, which is defined as

$$\text{equivalent nickel} = \mathrm{Ni} + \frac{\mathrm{V}}{4} \tag{7}$$

The equivalent nickel content of the feed to the FCCU can vary from <0.05 ppm for a well-hydrotreated VGO to >20 ppm for a feed containing a high resid content. The nickel and vanadium deposit essentially quantitatively on the cracking catalyst and, depending on catalyst addition rates to the FCCU, result in total metals concentrations on the equilibrium catalyst from 100 to 10,000 ppm.

The coking characteristics of a cracking catalyst increase as the equivalent nickel level on the catalyst increases. At high equivalent nickel levels, contaminant coke can be the major coke component on the catalyst. The effect of the contaminant nickel on the catalyst coke content can be mitigated through the use of a metal passivator added to the feed or through the incorporation of an effective metals traps into the cracking catalyst. Coking problems due to contaminant vanadium still remain a problem.

Feed additives were frequently used in the 1980s and early 1990s to reduce the contaminant coke produced through nickel-catalyzed reactions. These inhibitors were injected into the feed stream going to the catalytic cracker. The additive forms a nickel complex that deposits the nickel on the catalyst in a less catalytically active state. The first such additive was an antimony compound developed and first used in 1976 by Phillips Petroleum. During the 1980s, antimony was widely used in FCCUs that had a problem with contaminant nickel. The use of the antimony additive reportedly reduced coke yields by 15% in a commercial trial (19). In the late 1980s, other additives were introduced to combat contaminant nickel, eg, Chevron introduced a bismuth-based additive, which is claimed to provide performance similar to antimony (20).

In the late 1980s, cracking catalysts were developed with metals traps that appear to be so effective in containing the adverse effects of contaminant nickel that additive-type inhibitors are no longer needed (21). These traps consisted of reactive alumina. It has been reported that these aluminas promote a chemical reaction with the nickel to form $NiAl_2O_4$ which then diffuses into the bulk alumina phase, thereby minimizing any contact between nickel and the potential coke-forming hydrocarbons (22). By the late 1990s, all FCC catalyst manufacturers incorporated such a trap into their metals resistant catalysts.

4. Coke Burning

The burning of coke in the regenerator provides the heat to satisfy the FCCU heat balance requirements as shown in equation 1. The heat released from the burning of coke comes from the reaction of carbon and hydrogen to form carbon monoxide, carbon dioxide, and water. The heat generated from burning coke thus depends on the hydrogen content of the coke and the relative amounts of carbon that burn to CO and CO_2, respectively.

Reaction	ΔH_{comb} kJ/kg of C or H_2
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ (g)	121,000
$C + O_2 \rightarrow CO_2$ (g)	32,700
$C + \frac{1}{2}O_2 \rightarrow CO$ (g)	9,200

The impact that variations in coke content and burning conditions can have on the overall heat of coke combustion is shown in Table 2.

Because the heat balance dictates the amount of heat that is required from burning coke, the heat of combustion then determines the amount of coke that must be burned.

$$\text{coke required, kg/h} = \frac{\text{combustion heat required, kJ/h}}{\text{specific heat of combustion, kJ/kg}} \tag{8}$$

Table 2. **Specific Heat of Coke Combustion**

H_2, wt% in coke	Flue gas, CO_2/ CO	Specific heat kJ/ kg coke[a]
12	∞	43,300
7	∞	38,900
7	1.0	28,000

[a] To convert kJ to kcal, divide by 4.184.

Decreasing the specific heat of combustion increases the amount of the coke that must be burned; the coke component that increases is essentially the cat-to-oil coke, which is increased by increasing the catalyst circulation rate. Cat-to-oil coke can be expressed as (23):

$$\text{coke} = f[(\text{catalyst circulation rate})^{0.65}] \tag{9}$$

Thus decreasing the specific heat of combustion results in an increase in catalyst circulation rate. Because of this relationship to coke yield (eq. 9), the increase in the catalyst circulation rate results in a decrease in regenerator temperature.

The hydrogen content of the coke can vary considerably, depending on the efficiency of the stripping operation to remove the lighter hydrocarbons from the catalyst flowing into the regenerator. Hydrogen content in the coke can vary from 4 to 5 wt% for a highly efficient stripping operation, up to 13–15 wt% for poor stripping. The hydrogen content in a well run FCCU is in the range of 6–8 wt%.

The oxidation of carbon on the catalyst surface (coke burning) is believed to proceed through the formation of solid surface oxides, which decompose to give both CO and CO_2 as primary products (24). In an early study on the burning of graphite, it was shown that the CO_2/CO ratio is constant throughout the burning cycle, independent of oxygen partial pressure, and dependent only on the combustion temperature (25). The burning of carbonaceous deposits from porous oxides produced CO_2/CO ratios at the burning site in exact agreement with the ratios of the earlier study (25) over the temperature range 450–600°C (26). Diffusion effects in the pores of large catalyst particles influence the CO_2/CO ratio in the bulk vapor phase (26). However, for particle sizes typical of FCC operations (60–70-µm average particle size), diffusion is not a factor, and thus particle size would not influence the CO_2/CO ratio. Consequently, this molar ratio remains relatively constant at a value of ~1.0 for many regenerators operating in the region below 700°C and in the absence of a CO combustion promoter.

The rate of coke burning for coke deposited on a zeolite-containing catalyst has been reported to be first order with respect both to coke concentration c_C and oxygen partial pressure (26):

$$\frac{dc_C}{dt} = -kc_C P_{O_2} \tag{10}$$

This equation is in agreement with coke-burning studies on amorphous silica–alumina catalysts (27,28). Other investigators have found that carbon burning was second order (29) or mixed order (30) with respect to carbon. It has been

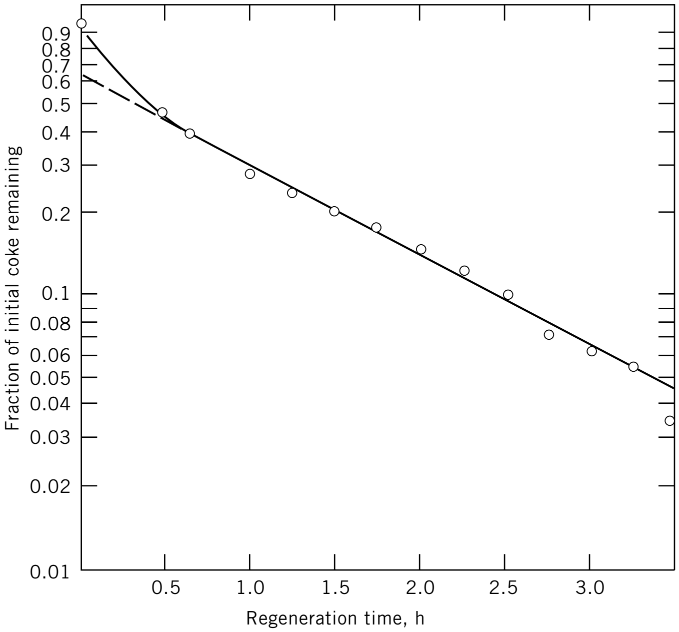

Fig. 3. Burning at 500°C in flowing air of coke from H-Y FCC catalyst.

argued that coke burning follows first-order kinetics, but only after an initial period of several minutes, when burning is not first order with carbon content (31). The data in Figure 3 on coked FCC catalyst of the H-Y type agree with this argument.

The activation energy for burning from a coked zeolite has been reported as 109 kJ/mol (32) and 125 kJ/mol (30 kcal/mol) has been found for coke burning from a H-Y FCC catalyst. Activation energies of 167 kJ/mol (40 kcal/mol) (27) and 159 kJ/mol (28) have been reported for the burning of carbon from a coked amorphous silica–alumina catalyst.

The coke-burning rate in the regenerator is thus a function of the oxygen partial pressure, the carbon content on the catalyst leaving the reactor, the temperature in the regenerator, and the residence time in the regenerator. The last three variables are all coupled together through the FCCU heat-balance requirements. For example, an increase in regenerator temperature normally results in a decrease in catalyst circulation rate to maintain a constant temperature on the reactor side. The decrease in catalyst circulation rate increases the residence time in the regenerator and is accompanied by a change in the carbon content of the catalyst coming into the regenerator. A typical interrelationship between the O_2 content in the regenerator flue gas, the regenerator temperature, and the carbon content of the regenerated catalyst (CRC) is shown in Figure 4. At a constant flue gas O_2 content, a decrease in regenerator temperature of 20°C results in a CRC increase of 0.15–0.20 wt%.

The hydrocarbon feed rate to the reactor also affects the burning kinetics in the regenerator. Increasing the reactor feed rate increases the coke production rate, which in turn requires that the air rate to the regenerator increase.

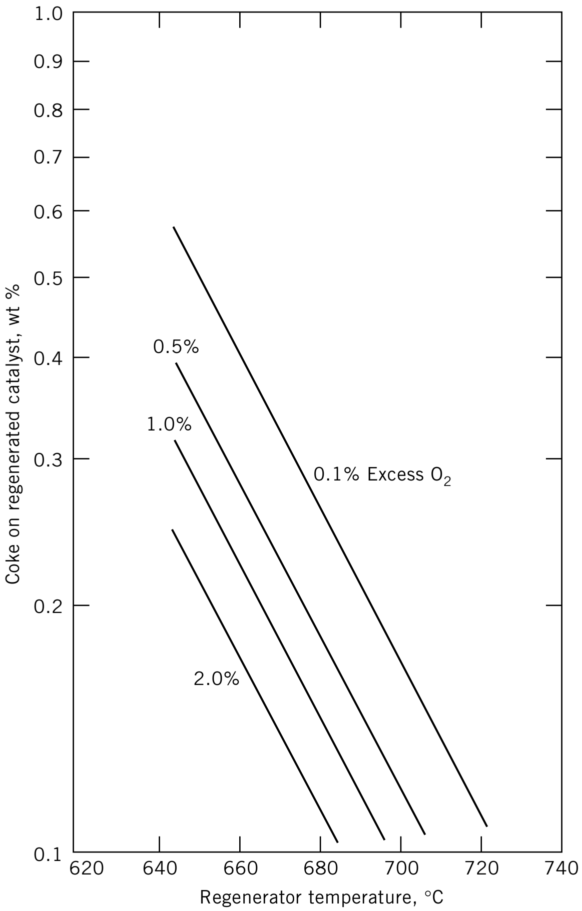

Fig. 4. Coke on regenerated catalyst (CRC) versus regenerator temperature at varying O_2 content (33).

Because the regenerator bed level is generally held constant, the air residence time in the dense phase decreases. This decrease increases O_2 content and consequently CO combustion in the dilute phase, frequently referred to as after burn (Fig. 5).

The coke-burning rates on silica–alumina catalysts have been found to increase several orders of magnitude when transition-metal oxides are present (28). The addition of 0.15 wt % chromium (as Cr_2O_3) to a silica–alumina catalyst produces a nearly fivefold increase in carbon-burning rate. The cation exchanged into a zeolite-containing catalyst affects the burning rate (32). A zeolite exchanged with copper was found to have a burning-rate constant that was 18 times greater than a zeolite exchanged with chromium.

The hydrogen contained in coke burns at a higher rate than carbon. Hydrogen-burning rates are four to five times greater than carbon-burning rates (27,29).

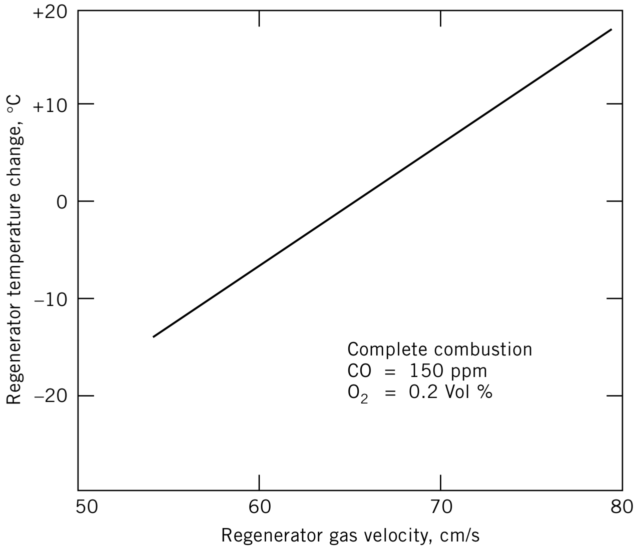

Fig. 5. Effect of gas residence time on afterburning. The temperature change ΔT is the difference in temperature between flue and dense phase (33).

4.1. CO Combustion. The combustion products leaving the coke-burning site consist of both CO_2 and CO, typically at a CO_2/CO mole ratio of 1.0. The CO formed can then be further oxidized. When a CO combustion promoter is present, the reaction of CO and O_2 to form CO_2 occurs readily in the regenerator dense phase. In the absence of such a promoter, the oxidation of CO occurs slowly in the dense phase below 700°C. This reaction occurs much more rapidly in the regenerator dilute (vapor) phase where it is believed to be catalyzed by the combined presence of fine, decoked metals containing catalyst particles and water vapor (34).

The oxidation of $CO \rightarrow CO_2$ releases twice as much heat as does the burning of $C \rightarrow CO$. The large heat release coupled with the relatively small amount of mass in the dilute-phase produces a large ΔT between the dilute and dense phases in the regenerator. For FCC operations in which a CO combustion promoter is not used, the dilute-phase temperature is frequently 15–40°C higher than the dense phase. In such operations, the dilute-phase temperature, hence the dilute-dense ΔT, becomes the limiting factor in regenerator control. The control of the regenerator temperature, in such cases, is normally achieved by adjusting the air rate to the regenerator, to control the oxidation of CO to CO_2 in the dilute phase, and thereby maintaining an acceptable dilute-dense ΔT.

With a sufficent excess of O_2 in the regenerator flue gas (1–2%), complete CO combustion can be achieved without a CO combustion promoter, if dense-phase temperatures $>720°C$ are maintained.

4.2. Promoted CO Combustion. In the early 1970s, researchers discovered that certain Groups 8–10 (VIII) metals, particularly platinum, can be incorporated into an FCC catalyst system at low concentrations (1–3 wppm) to catalyze the combustion of CO to CO_2 effectively (35,36). Of even greater importance was their discovery that at this low incorporation, the Groups 8–10 (VIII) metals did not catalyze undesirable dehydrogenation reactions during the cracking reaction. The cracking-selectivity characteristics achieved by the cracking catalyst in use in the FCCU are thus not altered when such a CO combustion promoter is added to the catalyst inventory.

The use of 1–2 ppm platinum in FCCU circulating catalyst inventories is now widely practiced throughout the world to catalyze the combustion of CO to CO_2 in the FCCU regenerator. The promoter is added to the FCC catalyst inventory either as an integral part of the fresh FCC catalyst, where it is included in the fresh catalyst at 1–2 wppm, or as a separate additive. The additive, which typically contains 500–1000 wt ppm of platinum, is added to the FCCU by a small metering system that is independent of the fresh cracking-catalyst addition system. In the United States, the separate additive approach is generally used; in Europe, the additive is most commonly incorporated with the fresh cracking catalyst.

Through the use of a combustion promoter, CO combustion occurs readily in the dense phase at temperatures well $<700°C$. Guegan reported that promoted CO combustion occurred as low as 650°C in a commercial FCCU operation (37).

Promoted combustion has a number of important benefits. First, the afterburn problem, ie, burning in the dilute phase, is greatly reduced. By consuming CO in the dense phase, the potential heat release from burning in the dilute phase is significantly decreased. A commercial example of a 50°C reduction in regenerator afterburn by using a CO combustion promoter is as follows (38):

	Without promoter	With promoter
typical flue gas temperature, °C	699	660
typical dense phase temperature, °C	663	674
afterburn ΔT, °C	+36	−14

The increased flexibility of FCCU operations resulting from using a CO combustion promoter is an even greater advantage. When using a promoter, the air rate to the regenerator can be varied to achieve any degree of CO combustion that is desired. By this mechanism, heat can readily be added to or removed from the regenerator to produce changes in regenerator temperature, catalyst circulation rate, coke yield, and reactor feed conversion. An example of how variations in the degree of CO combustion can effect the performance of an FCCU is seen in Figure 6 (33).

In actual practice, the regenerator temperature is normally controlled at the maximum temperature allowed by the regenerator metallurgy. Variations in feed quality in the FCCU can result in significant regenerator temperature excursions if the degree of CO combustion is unchanged (constant heat of combustion). With a CO combustion promoter present, the degree of CO combustion can be varied to hold the regenerator temperature constant at the desired maximum value even though significant changes in feed quality have occurred. This flexibility is achieved mainly through regenerator air rate control. To a lesser degree, additional flexibility is achieved by controlling the addition rate of

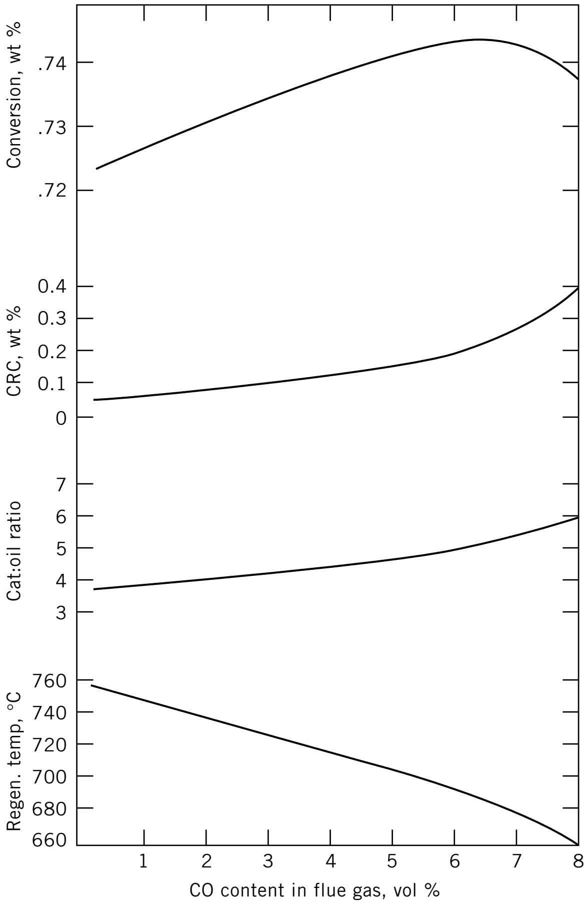

Fig. 6. Typical FCCU interdependency curves (33).

fresh CO combustion catalyst to the catalytic cracker. When a CO combustion promoter is used, changes in the air rate affect the amount of CO converted to CO_2 both in the dilute and in the dense phase. Changing the amount of CO burned in turn affects both the dense- and dilute-phase temperatures. Increasing the amount of excess O_2 in the regenerator causes an increase in CO burning in the regenerator dense phase as indicated by an increase in dense-phase temperature. Additional burning in the dilute phase also occurs, causing an increase in ΔT (afterburning) between dense and dilute phases. As a typical example, a decrease in CO content in the regenerator flue gas from 5 to 3 vol% would result in a dilute-phase temperature increase of 31°C, a dense-phase temperature increase of 16°C, and an increase in dilute-dense ΔT of 15°C.

The amount of promoter used can also be a variable in influencing the degree of CO combustion. A promoted catalyst system can be classified as fully or partially promoted. A partially promoted system is one in which an increase in promoter content results in a decrease in the dilute-dense ΔT. Conversely, a fully promoted system sees no effect on afterburn ΔT when the spromoter level is

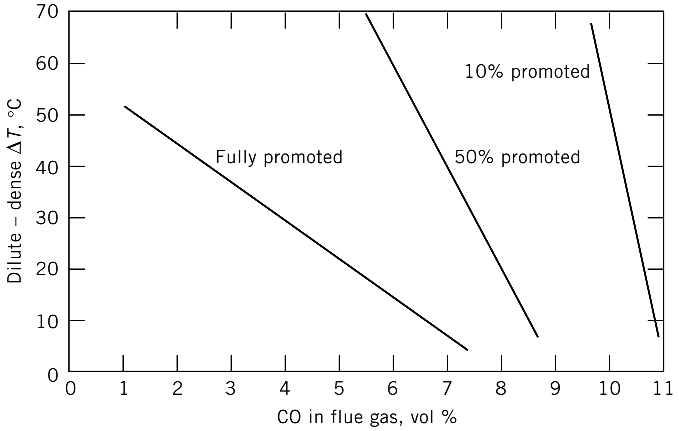

Fig. 7. Effect of promoter concentration on regenerator dilute-dense ΔT (9).

changed. An increase in the promoter content increases the proportion of CO that is burned in the regenerator dense phase. A reported response of afterburn ΔT to promoter change is shown in Figure 7 (9). The change in dilute-dense ΔT is mainly because of changes in the dilute-phase temperature. Changes in promoter concentration have only a small effect on dense-phase temperature but greatly affect dilute-phase temperatures.

The carbon-burning reaction competes with the coke-burning reaction for the available O_2 in the regenerator. When the O_2 level is low, the amount of promoter present can influence the degree that carbon is burned from the catalyst. In such situations, a high level of promoter enhances the combustion of CO and retards coke burning. A fully promoted catalyst with essentially no excess O_2 in the regenerator equilibrates at a coke content on the regenerated catalyst (CRC) of ~0.1 wt% higher than does a partially promoted system at the same degree of CO combustion (33).

Recent environmental concerns related to NO_x emissions from the FCCU regenerator have focused on the effect of platinum CO combustion promoters also promoting the formation of NO_x (39,40). Interest, consequently, has arisen in the use of non-platinum CO combustion promoters. Pladimum has been used in place of platinum with favorable results (39). Additives for the reduction of NO_x in regenerator flue gas are discussed in the next section.

5. Environmental Aspects

The FCCU regenerator is one of the principal sources of air pollutants from a refinery. In the mid-1990s, a typical 23,850 m^3/day (150,000 barrel per day), modern U.S. refinery with a 50,000 BPD FCCU processing a low sulfur, low metals content VGO feed, and operating in complete CO combustion would typically emit the following into the atmosphere from the FCCU regenerator flue gas stack: fine catalyst particles, 2–3 t/day; sulfur oxides, 3–4 t/day; nitrogen oxides, 0.5 t/day; and CO, 1.5–2 t/day. Recently, governmental regulations, particularly in the United States, have significantly reduced the allowable FCCU emissions for particulates and sulfur oxides. A new 50 MBPD unit or an existing 50 MBPD unit being significantly revamped in 2002 would be required to meet the following contaminant levels in the regenerator flue gas: catalyst particulates <0.5 t/day, sulfur oxides <0.7 t/day (41). Nitrogen oxide limits are not yet defined but are expected to be similarly constrained. Carbon monoxide emissions would be limited to <3 t/day. Much research has been done in the past and is ongoing to develop technologies to meet these emissions levels and reduce them even further.

5.1. Catalyst Emissions. High velocity air passing up through the regenerator at velocities typically around 1 m/s carries large quantities of catalyst into the vapor space above the catalyst bed. To contain these catalyst particles within the regenerator vessel, a highly efficient, generally two-stage cyclone system is installed inside the regenerator. The flue gas and the entrained catalyst particles pass through the cyclone system which is installed inside the regenerator. The flue gas and the entrained catalyst particles are typically returned by the cyclones back into the regenerator. The particles that are not retained and that leave with the exiting flue gas are small, typically <20 μm particle size.

These particles generally represent fines that have been produced as a result of catalyst attrition. Two attrition mechanisms are generally recognized: particle shattering and surface abrasion of particles. The abrasion mechanism generates fines of much smaller average size. The manufacturing techniques and chemical compositions of the various FCC catalysts influence the type and severity of the attrition mechanism. A small amount of fines (<20 μm in size) may also come from fresh catalyst additions.

Current particulate regulations vary from site to site depending on the local regulatory agency's standards. The New Source Performance Standards, NSPS, set by the U.S. federal government state that a new unit must not exceed 1lb of particulates per 1000 lbs of coke burned (1 kg/ 1000 kg). It is possible that an existing unit, that undergoes a substantial revamp, can be reclassified as a new source.

There are several ways to capture the particles remaining in the flue gas as it exits the regenerator. The most common technique is through the use of electrostatic precipitators (ESP), which can reduce particulate emissions to very low levels (41). An ESP consists of rows of collector plates and voltage discharge electrodes arranged in one or more gas tight chambers. The electrodes apply electrical charges to particles in the FCCU regenerator flue gas. The charged particles are attracted to the collector plates and are thus removed from the flue gas. While this equipment is well known and has a long record of reliable performance, it is expensive and can be dangerous. Explosions in ESPs have occured.

An alternative to the ESP is a third stage separator (TSS). The TSS is an additional cyclonic separator, external to the regenerator, which supplements the catalyst separation achieved by the two stages of cyclones typically present in an FCCU regenerator.

In the TSS, catalyst is removed from the flue gas by passing the catalyst-entrained gas stream through a set of cyclonic elements that separate out the catalyst particles. Separation efficiency depends upon the particle-size distribution of the catalyst leaving the regenerator cyclones, being most efficient on large particles, and less efficient on small particles. Essentially 100% removal of particles >5 μm in diameter have been reported (41).

Fines-depleted flue gas leaves the upper chamber of the TSS. Recovered catalyst and blow-down gas (~3% of the flue gas) exit from the bottom of the separator to an electrostatic precipitator, or to a small, conventional, fourth stage collection device for further concentration and disposal of the catalyst fines.

Recent improvements in third stage separators have put them in a class acceptable to most environmental agencies, at a fraction of the cost of an ESP. The devices are proving to be highly reliable and efficient. Current performance has been reported to yield a flue gas containing 0.3–0.6 lb of particulates per 1000 lb of coke burned, well below the NSPS standard (41,42). When a flue gas power recovery unit (described later) is present, the TSS protects the power recovery unit from erosion by catalyst fines.

Much effort has been made by catalyst manufacturers to improve catalyst attrition resistance and thus reduce the formation of fines (see CATALYSTS, SUPPORTED). In the 10-year period from 1980 to 1990, most catalyst manufacturers improved the attrition resistance of their catalyst by a factor of at least 3–4. This improvement was achieved even though the catalyst zeolite content during this period was continually increasing, a factor that makes achieving catalyst hardness more difficult. As an example of the type of attrition improvement that has been achieved, the catalyst attrition index, which is directly related to catalyst loss rate in a laboratory attrition test, decreased from 1.0 to 0.35 for one constant catalyst grade during 1989–1990 (43). This trend has continued with the recent introduction of premium catalyst technology for loss sensitive applications where power recovery equipment may be damaged by excess catalyst fines (44).

5.2. SO_x Emissions—Source and Control Options. SO_x, which refers to the combination of SO_2 and SO_3, is a major emission concern from a FCCU regenerator flue gas. A 1998 survey of 79 refineries in western Europe reveal that 13.2% of all refinery SO_x emissions originate in the FCCU (45). Of the amount of organic sulfur in the reactor feed (non-hydrotreated), ~10% (range 5–30%) goes to the regenerator with the coke, where it is converted to SO_x (39). The sulfur content of the coke is highly dependent on feed type (aromatic, paraffinic, or hydrotreated), the amount of organic sulfur in the feed, and the reactor conversion level. A general rule of thumb to estimate the regenerator flue gas SO_x content (if no attempt is made to reduce it), in parts per million:

Straight run feeds: $SO_x = 800{-}1100\ x$ wt% feed sulfur
Hydrotreated feeds: $SO_x = 2050{-}2080\ x$ wt% feed sulfur (46)

The refiner does have several options to reduce SO_x emissions, and generally will use a combination of these options to reach regulatory requirements. These include

Hydrotreating the feed
Flue gas scrubbing with NaOH, $CaCO_3$, or other basic solution.
SO_x reduction catalyst additive
Feed stock selection (low sulfur content feeds)

Hydrotreating. In hydrotreating, the FCCU feed is pretreated to convert the organic sulfur in the feed to H_2S by reacting it with hydrogen. The severity of the operation is a function of the partial pressure of hydrogen used. Mild hydrotreating at 3550–5600 kPa (500–800 psi) H_2 partial pressure, with a modern cobalt–molybdenum catalyst can reduce the sulfur content of the FCC feed by 90% or greater (47). In one published study, a FCC feed with 17,500 wppm sulfur was hydrotreated at two levels of severity. At moderate severity the sulfur in the feed was reduced to 100 wppm, a decrease of 99.4%. A resultant decrease in SO_x emission from the regenerator of 97.4% was observed. Increasing severity, by increasing H_2 partial pressure 1.4 times, resulted in a decrease in feed sulfur to 33 wppm or 99.8%. A corresponding decrease in SO_x emission of 99.2% was observed (48).

Sulfur compounds in the FCC feed can be placed into the following classifications: alkyl sulfides, aromatic sulfides, substituted benzothiophenes, and multiring benzothiophenes. Hydrotreating can effectively convert most of these sulfides, but is not very effective in converting the multi-ring benzothiophenes. These compounds are also the most difficult to crack in the FCC reactor, and usually accumulate in the heavy FCCU products (cycle oils and coke) (49). Therefore, the percent of feed sulfur on coke increases significantly with hydrotreating.

Scrubbing. Scrubbing of the flue gas is a technique commonly used among all combustion processes. In an FCC environment, however, the scrubbing technique must be such that it adds very little pressure drop to the system (on the order of several inches of H_2O). The scrubber may see large amounts of catalyst dumped to it in an upset of the FCC. It must therefore have accommodation to handle such episodes of high particulate loading without plugging or damaging circulation equipment. To maintain low pressure drop, most FCC scrubbing systems either induce flow via venturi type scrubbers or use sprays to contact the flue gas with the scrubbing liquid. The high temperature of the FCCU flue gas may require a quench section in the scrubber. Scrubbing efficiencies can vary somewhat between technologies, with reported efficiencies ranging from 85 of 99% SO_2 remova1 (41,50,51).

The most common type of scrubbing solution used is sodium hydroxide (caustic). The acid–base reaction is very fast and SO_2 removal efficiencies of 99% have been reported (50). The disadvantages to using caustic are the cost of the reagent, and the disposal of the resultant sodium sulfate solution, which requires further treatment to neutralize it.

One unique solution to the disposal of this sodium sulfate waste solution is a two-step process, which uses the THIOPAQ biological conversion technology. This technology has seen success in other scrubbing applications. It converts the SO_2 to elemental sulfur with no liquid effluent. The first step is to scrub the SO_2 from the flue gas with a buffer solution of sodium bicarbonate and caustic. This buffer solution is produced by allowing NaOH to react with CO_2 until the resultant sodium bicarbonate solution is in equilibrium with the carbon dioxide in the flue gas. The SO_2 reacts to form $NaHSO_3$ and Na_2SO_4. This buffered solution is then sent to a series of biological reactors. The first reactor operates in an anaerobic environment to convert the sodium sulfite and sodium sulfate to sodium sulfide, NaHS. The second reactor operates in an aerobic mode and oxidizes the sodium sulfide to elemental sulfur. The elemental sulfur is separated from the liquid and the sodium bicarbonate solution returned to the scrubber. The elemental sulfur is then either dried and sent to landfill as nonhazardous waste or further purified for resale (50).

Calcium carbonate (limestone) slurry is another solution that is used for scrubbing the FCCU flue gas. This material is less expensive to purchase, as it is shipped as a solid. However, it can be difficult to get into solution and plugging issues can be problematic. Its SO_2 removal efficiencies are usually 95–98% (50). The reaction chemistry produces calcium sulfite, $CaSO_3$, which for handling purposes is oxidized to calcium sulfate (gypsum), $CaSO_4$. The gypsum is dried and recycled as an additive for cement production. One drawback to this calcium carbonate scrubbing is the release of CO_2 in the reaction. Current concerns over CO_2 emissions as a greenhouse gas may make this scrubbing technique less desirable.

Sea water scrubbing to remove SO_2 is being practiced by StatOil in Mongstat, Norway. The seawater contains natural calcium and sodium buffers that absorb the SO_2. The water is returned to the sea after dilution with sea water cooling streams (52).

Although often lumped together in analysis results, SO_2 and SO_3 create there own unique emission and control issues. The SO_3 content, in FCCU flue gas, can vary from 1 to 10% of the total SO_x (53). The SO_3 emissions, are especially troublesome in that SO_3 condenses to form sulfuric acid mist that is not readily removed by wet scrubbers. The light scattering properties of sulfuric acid mist creates a visible plume that, depending on measurement technology utilized, is often measured and treated as a particulate emission. SBS Injection Technology, commercialized in the utility industry in 2002 has been proposed as a solution to FCCU SO_3 problem (53). Sodium bisulfite solution is injected into the flue gas to react the SO_3 to produce sodium sulfate and sodium bisulfate particle (solids). These then can be readily removed by an electrostatic precipitator or in an SO_2 scrubber.

SO_x Reduction Catalyst Additive. Currently, many refiners find that the use of a SO_x adsorbing additive is the most effective way to comply with the EPA regulations. With such an additive, the following steps occur

Oxidation of SO_2 to SO_3 in the regenerator:

$$2\ SO_2 + O_2 \rightarrow 2\ SO_3$$

Adsorption of SO_3 in the regenerator by the additive where MO = metal oxide and M is most commonly magnesium:

$$SO_3 + MO \rightarrow MSO_4$$

Reduction of the metal sulfate in the reactor:

$$MSO_4 + CH_4 \rightarrow MS + CO_2 + 2\ H_2O$$

Release of H_2S and regeneration of the metal oxide adsorbent in the stripper:

$$MS + H_2O \rightarrow MO + H_2S$$

The H_2S is carried out with the reactor products, goes through the product-recovery system of the FCCU, and eventually to further processing for sulfur recovery. The metal oxide adsorbent recirculates with the spent cracking catalyst back to the regenerator for the next SO_x adsorption cycle.

The first commercially effective metal oxide adsorbent consisted of a solid solution of a pure magnesium aluminate spinel ($MgAl_2O_4$) with MgO (54). Such a solid solution (Mg_2AlO_5) does not destroy the spinel framework. The adsorption activity of the dispersed MgO in the spinel is much greater than that of pure MgO itself (54).

Cerium is effective in oxidizing SO_2 to SO_3. Consequently, a cerium-impregnated $Mg_2Al_2O_5$ actively converts the SO_2 to SO_3, which is then strongly adsorbed by the dispersed MgO as $MgSO_4$. A completely cyclic SO_x removal catalyst contains, in addition to the above component, a fourth metal component such as vanadium to catalyze the conversion of $MgSO_4$ to MgO (55).

Multifunctional SO_x removal catalyst systems have been in commercial use since 1985 in the United States. Such systems have successfully reduced SO_x emissions in the FCCU regenerator by typically 20–60%, with reductions up to 90% reported (39,56,57). Additive levels in the circulating catalyst inventory range from 1 to 10%. The additive level and the amount of SO_x reduction depend on conditions, such as feed quality, the presence or absence of a CO combustion promoter, regenerator temperature, regenerator mixing efficency, and excess O_2 content (39).

Hydrotalcite, a MgO/Al_2O_3 containing compound, has also been found to have SO_x adsorbent capability and is now being used in some SO_x adsorbent additives (39). In 2003, both spinel and hydrotalcite types of SO_x reduction technology have been upgraded to higher performance standards, frequently by the addition of more magnesium oxide component (39).

Because O_2 is necessary to convert SO_2 to SO_3, decreasing O_2 in the regenerator has been found to reduce the effectiveness of the SO_x removal additive. The SO_x additives used in regenerators operating in a partial CO combustion mode, where excess O_2 is frequently limited to <0.2 vol% in the flue gas, are less successful in reducing SO_x. In such cases, SO_x removal is typically 20–30% less than for a full CO combustion (1+% excess O_2) case (56).

5.3. Nitrogen Oxide Emissions Source and Controls. The $(NO)_x$ (nitrous oxides) emissions are now recognized as a significant contributor to photochemical smog and acid rain, and therefore have come under greater regulatory scrutiny than in the past. In terms of tons emitted per year, the FCCU regenerator is one of the largest point source of NO_x emissions. Only a small portion of the NO_x present in the flue gas is produced through the oxidation of N_2 in the regenerator air stream (40,58). The main source of the NO_x comes from the combustion of organic nitrogen, originating in the FCC feed of which ~50% ultimately reaches the regenerator section in the coke. However, only 5–20% of the organic nitrogen compounds entering the regenerator end up as NO_x, predominantly NO. The remainder is converted to N_2. Since most of the organic nitrogen ends up as N_2, there is likely a secondary reaction with CO or coke to reduce NO to N_2 (59). Although feed nitrogen is the source of NO_x, researchers have found that final NO_x concentrations are due more to the type of N in the feed and to the regenerator conditions, than they are to the absolute content of N in the feed

(40). The amount of excess oxygen may have a more direct correlation with the final NO_x concentration leaving the regenerator (39,40). Increasing the O_2 in the regenerator flue gas from 0.1 to 1.6% has been reported to double NO_x emissions when no CO combustion promoter is present. Adding a platinum-based combustion promoter, which increases the available atomic O_2, can increase the NO_x content much more (60).

Hydrotreating the reactor feed can reduce feed nitrogen by 20% (low severity), 90% (moderate Hydrotreating), and up to 99% (severe Hydrotreating) (61), and thus can be a tool in reducing FCCU flue gas NO_x emissions.

An emerging picture of the complex NO_x chemistry in the FCCU regenerator includes the following reaction networks:

Pyrolysis		Oxidation
N (Coke) → HCN	→	N_2, NO, N_2O
N (Coke) → NH_3	→	N_2, NO, N_2O

NO Reduction

$$2\ NO + 2\ CO \xrightarrow{coke} N_2 + 2\ CO_2$$

$$NO + C_{FAS}^{*} \rightarrow 1/2\ N_2 + CO$$

*FAS = free active surface

Catalyst additives and regenerator design have both been found to be useful in reducing flue gas NO_x emissions. Uniform distribution of coked catalyst in the regenerator improves the probability of NO_x adsorption onto the carbon surface, necessary for NO_x reduction reactions to occur. Air grid design, spent catalyst distribution, catalyst withdrawl location, and the fluidization regime can all play major factors in the effectiveness of mixing and distribution. Poor design and/or erosion of air grids and catalyst distributors can lead to maldistribution and therefore higher NO_x values. Regenerator designs that operate in a fast fluidized regime (combustor style) rather than a turbulent regime (bubbling bed style) afford better catalyst-air mixing and therefore lower NO_x emissions.

Recent research in NO_x additives has taken two approaches: the development of CO combustion promoters that do not catalyze NO_x formation and additives that directly reduce NO_x emissions. New NO_x reduction additives have been designed to catalyze the NO reduction by CO or to block the formation of NO by oxidation of the reduced intermediates, HCN and NH_3. The major FCC catalyst vendors are now publishing the results of commercial trials of NO_x reduction additives in US FCC units. Variying degrees of successes have been reported (39,57,62). This suggests that the complex interplay between FCCU regenerator hardware, operating variables and additives for NO_x reduction requires more detailed study.

Post regenerator NO_x Reduction Technology. Two technologies have been commercialized to reduce FCCU NO_x emissions by treatment of the flue gas after it leaves the regenerator.

Selective Catalytic Reduction (SCR), which is the most proven of these processes, removes NO_x by passing it over a vanadium pentoxide/titanium dioxide catalyst bed in the presence of NH_3 and O_2. The reactions are

$$4\ NH_3 + 4\ NO + O_2 \longrightarrow 4\ N_2 + 6\ H_2O$$

$$4\ NH_3 + 2\ NO_2 + O_2 \longrightarrow 3\ N_2 + 6\ H_2O$$

Reaction is preferably carried out in the temperature range of 315–400°C , where a NO_x removal efficiency of >90% i1s claimed (41). An SCR unit installed at the Scanraff refinery, Lysekil, Sweden was reported to remove 85% of the 800 mg/nm^3 of NO_x present in the FCCU regenerator flue gas (51). For an FCCU revamp, however, considerable space in the refinery is required for the installation of the SCR reactor, which frequently makes SCR impractical or not cost effective (51). The SCR has two additional drawbacks if SO_x is not removed from the flue gas:

1. An SCR side reaction typically converts 1–5% of the SO_2 to SO_3. This significant increase in SO_3 can result in a visible plume in the flue gas leaving the regenerator stack (53).
2. Unreacted NH_3 can react with SO_3 leaving the SCR to produce $(NH_3)_2SO_4$ and NH_3HSO_4, which can increase particulate emissions and can also contribute to plume formation (41).

Another dry process utilizes activated coke to remove both SO_x and NO_x from the flue gas in a two stage, moving-bed process (51). The SO_x is removed in the first stage via adsorbtion on the activated carbon. NH_3 is injected into the flue gas, which then passes through the second bed, where the activated carbon acts to catalyze the reaction of NO_x with NH_3 to convert the NO_x to N_2 and H_2O. The activated carbon flows from the second stage to the first stage and then to a regenerator to desorb the SO_x. The desorption step releases SO_2, which must be recaptured and converted to elemental sulfur. This technology was commercialized on a resid-processing FCCU in Japan in 1987 and achieved a reported 70% removal of both NO_x and SO_x (63).

Several emerging technologies, yet to be fully commercialized also appear to have promise for reducing NO_x from the flue gas leaving the regenerator. Scrubbing of NO_x, as is done to remove SO_x , is not an effective means of removing NO_x, since NO and NO_2 are much less soluble than SO_2. A process using ozone injected into the flue gas stream converts NO_x to N_2O_5, which is highly water soluble and rapidly converts to nitric acid. Scrubbing of the flue gas with a NaOH solution is then very effective in removing NO_x and further converts the nitric acid to the neutral salt ($NaNO_3$) (53). A combination chemical–biological process utilizes an iron chelate aqueous solution to convert NO_x to a water soluble nitrosyl complex. The solution is sent to a bioreactor, where the complex is reduced to N_2, CO_2, and H_2O (50). Finally, a high temperature (870°C) noncatalytic process, suitable for use with FCCUs having a CO boiler, uses NH_3 to convert NO_x to N_2 and H_2O (59).

5.4. CO_2 Emissions Reduction.

Recently, the concern of CO_2 emissions as a contributor to green house gas levels has drawn attention to the FCCU as a point source. In a FCCU based refinery, 20% of the CO_2 emitted originates in the FCCU (64). Carbon dioxide is the natural result of complete combustion of the coke in the catalyst regeneration, the heat from which is also essential to heat balance the unit. As a result of the Kyoto Protocol, the European Union has already begun CO_2 credit trading, and therefore interest among international refiners is very strong for ways to lower FCCU based CO_2 emissions. The United States, having withdrawn from the Kyoto Protocol, has announced a separate strategy for addressing climate change, and several climate change bills have been introduced in the 108th Congress. The primary vehicle for climate change legislation is comprehensive energy legislation (65).

6. Regenerator Operating Parameters

To maximize the performance of an FCCU, most units run at one or more unit constraints. Frequently, one of these constraints is the regenerator temperature, which is set by metallurgical limits for safe operations. Process variables on both the reactor and the regenerator side are thus manipulated to keep the regenerator temperature as close as possible to this regenerator temperature limit.

Changes in feed quality, which will affect the coking tendency of the feed and the coke-making characteristics of the circulating catalyst, influence the regenerator temperature. The refiner can rapidly respond to these changes by manipulating certain independent process variables, which include reactor riser temperature, temperature of the hydrocarbon feed entering the riser, fresh catalyst addition rate, and cooling duty if a catalyst cooler exists. If the change in feed quality is of prolonged duration, the refiner can also change catalyst type.

The heavy material in the reactor feed, which remains as a residue after evaporation and pyrolysis of the oil, is designated as Conradson carbon (ASTM test method D189-76). This residue is frequently used as an indicator of the coking tendency of the feed. Incorporating heavy feedstocks such as vacuum resids into the FCCU feed greatly increases the feed's Conradson carbon content. The influence of increasing resid content on regenerator temperature has been determined and correlated against the feed Conradson carbon content (66). A 2% increase in Conradson carbon can cause a regenerator temperature increase of $\sim$28°C. Other studies indicate that an increase in the resid content of the feed that results in an increase in Conradson carbon from 1.5 to 2.9% produces a regenerator temperature increase of 37°C at constant riser temperature (13).

The presence of contaminant metals on the equilibrium catalyst can significantly increase the catalyst coking tendency, which in turn results in an increase in regenerator temperature if all other factors remain unchanged. As one example, if the metals on an FCCU equilibrium catalyst increased from an equivalent-nickel value of 2000 to 3500 wt ppm, the catalyst coking tendency would increase 30–50%. If all controllable parameters remained constant, the regenerator temperature would be expected to increase 35–50°C, resulting in a decrease in catalyst circulation rate, and a subsequent drop in conversion.

To decrease the regenerator temperature, heat must be taken out of the system either by

1. Decreasing conversion, which decreases the amount of catalytic coke produced. Decreasing conversion can be achieved by either decreasing reactor temperature or by decreasing equilibrium catalyst activity. For a given decrease in conversion, the latter is more effective in reducing regenerator temperature. Typically, decreasing reactor riser outlet temperature by 8°C decreases conversion 2–2.5% and decreases regenerator temperature by 6–8°C (8,67). Reducing equilibrium catalyst activity by four numbers, either by decreasing the fresh catalyst addition rate or by using a lower activity fresh catalyst, also reduces conversion by ~2% and decreases regenerator temperature by >42°C, depending on the initial temperature (68).
2. Through the physical removal of heat. Heat can be removed by using a catalyst-cooling heat exchanger or by cooling the feed entering the reactor. Typically, decreasing the feed temperature by 28°C decreases the regenerator temperature by 6°C (8).
3. Through a decrease in the relative amount of CO converted to CO_2 in the regenerator. Although burning coke to CO rather than to CO_2 releases 70% less heat, this method is less frequently used. It requires that more feed be converted to coke to satisfy the heat balance, thus decreasing yield profitability, and it also requires that the unconverted CO be burned to CO_2 in an external CO boiler, to prevent any CO emission to the atmosphere.

7. FCCU Regenerator Configuration and Mechanical Hardware

Since the first fluid-bed catalytic cracking unit was commissioned in 1942, the process has seen considerable improvement in mechanical construction, reliability, and process flow. A modern FCCU typically operates continuously for 3–5 years between turnarounds, during which time quantities on the order of 10^{10} kg of feedstock are processed and quantities of catalyst in the range of 7×10^{10} kg are circulated through the regenerator. Early FCCU designs (69), were complex compared with the configuration of more recent designs.

In the modern unit design, the main vessel elevations and catalyst transfer lines are typically set to achieve optimum pressure differentials because the process favors high regenerator pressure, to enhance coke-burning kinetics and power recovery from the flue gas, and low reactor pressure to enhance product yields and selectivities.

Comparing a modern design with a typically less desirable configuration of the past (70), the principal improvement factors have been aimed toward: reduced catalyst inventory and temperature limitations, enhanced coke-burning kinetics, catalyst and air contacting; and catalyst residence time distribution. New designs have eliminated horizontal transport, long standpipes, additional standpipe aeration requirements, and catalyst fines recycle.

On the regenerator side, there have been several significant design changes from the bed regenerators that were utilized in early FCC unit designs. In the 1970s, with an emphasis on more complete combustion of the coke deposits, a fast-fluidized, combustor-style regenerator design was introduced. Some of the characteristics of this new, widely applied design are described later in this section.

In the 1980s, to more effectively process high boiling, contaminated, residual feedstocks, two-stage regenerators and catalyst coolers were commercialized to allow greater unit heat balance flexibility. One version of the two-stage regenerator designs makes use of two separate regenerator vessels (71), with the first stage vessel operating in a partial combustion mode, with conventional two-stage cyclones followed by an external CO boiler. Catalyst from this first stage of regeneration is then dilute phase transported to the second stage regenerator, where the rest of the coke is burned. This second regenerator vessel has no internals in the dilute phase. The flue gas containing excess oxygen passes from the second stage regenerator to externally located, refractory lined cyclones.

An alternate two-stage regenerator design was independently developed (70,72) incorporating two distinct bed-regeneration zones within a single regenerator vessel. Coked catalyst from the catalyst stripper enters the upper regeneration zone. This first-stage is operated in partial combustion, with CO in the exiting flue gas, to produce a lower heat of combustion. Catalyst passes by gravity flow from the first stage to the second zone, located below the first stage. This second stage operates in a complete combustion mode with excess oxygen, to complete the coke burn and provides regenerated catalyst with low carbon-on-catalyst. The excess oxygen-containing flue gas from this second zone passes upward through the first stage. Additional air is also provided to the first stage through a separate air distributor. Togeteher, these two air streams provide the oxygen needed to achieve partial combustion in the first stage. A single flue gas line leaves the regenerator. Since this flue gas stream contains CO, it is sent to a CO boiler.

An external dense-phase catalyst cooler was developed specifically to remove heat from catalyst that passes from this upper regeneration zone to the lower regeneration zone. The amount of heat removed can be adjusted to provide better control of the process conditions—a key feature of the catalyst cooler.

7.1. The Effect of Fluidization on Regeneration.

Several fluidization regimes have been used in FCCU regenerators depending on the technology evolution and the objectives of the particular design. Early designs had little concern for CO emissions, but were very much concerned about catalyst loss and equipment (primarily cyclone) damage due to high temperatures of uncontrolled CO after burning. Construction materials were typically chome alloys, which limited regenerator temperatures to <700°C (1300°F).

Bubbling Bed Regime. Early FCCU regenerators operated in the bubbling–bed regime (73). The bubbling-bed regenerator design offered limited solids carryover and transport through the freeboard region. The bubbling-bed regime ranges from the minimum bubbling velocity, which typically for FCC-type particles is from 0.006 to 0.03 m/s, up to ∼0.3 m/s superficial velocity. Discrete gas bubbles flowing through the bed produce abrupt pressure fluctuations at the bed's surface. The relative fluctuations are set by the bubble frequency or superficial gas velocity. Most of the larger particles that are entrained are returned to the bed through the two-stage cyclone diplegs; the smaller fines being carried out with the flue gas (74).

The bubbling-bed design had several major problems chief among these being poor catalyst–air mixing. As a result much of catalyst returned to the reactor unregenerated or partially coked, leading to poor activity and low reactor conversion (52).

Turbulent-Bed Regime. The commercialization of high alumina catalysts in 1955 was one of the chief reasons for a shift in regenerator design to the turbulent-bed regime. The catalyst was much more active, but highly sensitive to coke deactivation, so the poor regeneration of the bubbling-bed design was no longer acceptable. The need to improve mixing of the combustion air and the catalyst, led designs to change to the turbulent fluidization regime. At the higher gas velocities of the turbulent-bed regime (0.3–1.0 m/s), the distinct bubble phase disappears, and the bulk of the gas flows in a manner described as: "In voids which continually coalesce and split tracing tortuous passages as they rise through the bed" (75). The surface of the upper bed is considerably more diffuse and has reduced pressure fluctuations and substantially higher entrainment of solids into the freeboard region. Because of the higher coke-burning capacity requirements and improved contacting efficiency, the vast majority of commercial regenerators converted to the turbulent-bed regime. In this configuration, the ultimate regeneration capacity is set by the sharp increase in solid entrainment that occurs as the linear velocity approaches 1.0 m/s and the corresponding effect this air velocity has on the cyclone separation efficiency and dipleg hydraulics (76).

Over the years, considerable efforts have been made to improve regeneration efficiency. These efforts focused on improving the radial mixing characteristics and residence-time distributions (reduce short circuiting) of the turbulent- and bubbling-bed systems. Some of these efforts include: optimizing fluidized-bed length and diameter ratios, optimizing air distribution through the proper grid pressure drop and grid plugging pattern, and optimizing catalyst distribution via cyclone dipleg discharge orientation, and proper location of the spent catalyst addition and withdrawal points into the regenerator. These addition and withdrawal devices include tangential inlets, swirl distributors, deflector plates, and baffles as well as the entry elevation into the fluidized bed (74).

Fast Fluidized Regime. In the late 1970s, the high efficiency combustor style regenerator was commercialized. This type of regenerator operates in the fast fluidized regime. The fast fluidized regime (1.0–3.0 m/s superficial velocity) extends into the transport phase (74), where a sharp increase in the rate of solids carryover occurs as the transport velocity is approached. In the absence of any solid recycle, the bed would rapidly disappear. Beyond this velocity, catalyst fed to the base of the regenerator travels upward in a fully entrained transport flow. The voidage or density of the resulting suspension is dependent not only on the velocity of the gas but also on the solid flow rate. If the solid rate is low, a dilute-phase flow will result. If solids are fed to the regenerator at a sufficiently high rate, eg, by recirculating the solid carried over back to the regenerator, then maintaining a relatively large solid concentration is possible. This condition is referred to as the fast-fluidized bed (73).

The high velocities in the combustor promote catalyst to air contact . As a result, the catalyst residence time required for catalyst regeneration is greatly reduced. The highly efficient mixing of the air and the catalyst improves the overall conversion of CO to CO_2, thus minimizing and in many cases eliminating the need for CO combustion promoter (51).

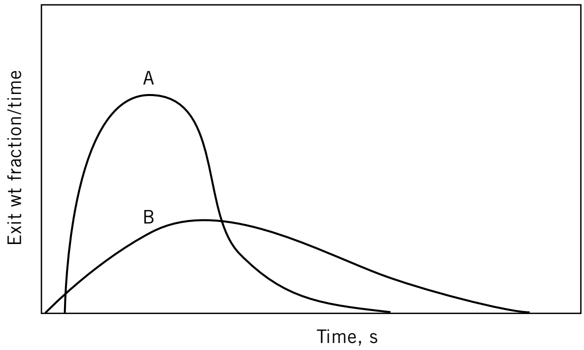

Fig. 8. Theoretical residence time distributions: A, combustor style approach to plug flow; B, turbulent bed (100% backmixed).

Figure 8 compares theoretical particle residence-time distributions of a turbulent-bed regenerator with those of a modern high efficiency combustor. The basic difference in response curves is a result of both the fluidization regime (fast fluidized) and the solids entry and exit configuration. In the combustor design, a spent catalyst particle cannot possibly leave the regenerator without passing through the dilute-phase combustion zone.

The overall benefits of this high efficiency combustor over a conventional bubbling- or turbulent-bed regenerator are enhanced and controlled carbon-burn kinetics (carbon on regenerated catalyst at <0.05 wt%); ease of start-up and routine operability; uniform radial carbon and temperature profiles; limited afterburn in the upper regenerator section and uniform cyclone temperatures; and reduced catalyst inventory and air-blower horsepower (73). As of 2003, this design was well established, with more than 45 units in commercial operation.

8. Mechanical Hardware

From a mechanical point of view, the FCCU regenerator can be divided into two main sections: the regenerator vessel and its internals, which include the air distributor, the cyclones, the plenum chamber, and catalyst coolers; and the flue gas handling section, which includes power, heat, and emission control systems (SO_x, NO_x, and particulates). Continuous advances in the mechanical design of both these areas have led to significant improvements in overall FCCU reliability, even though processing conditions, at the same time, have become more difficult (harder and denser catalysts, higher regenerator temperatures).

8.1. Regenerator Vessel and Internals.

The FCCU regenerator is one of the largest vessels in the refinery (up to 18 m in diameter) and operates at temperatures up to 775°C. The regenerator is usually a carbon steel vessel, internally lined with refractory insulation to maintain the wall temperature in the area of 340°C, which is suitable for carbon steel.

Air Distributor Grid. The function of the FCCU regenerator air distributor is to uniformly introduce O_2 into the regenerator vessel to achieve even burning of coke throughout the regenerator cross-section. Every air distributor must be

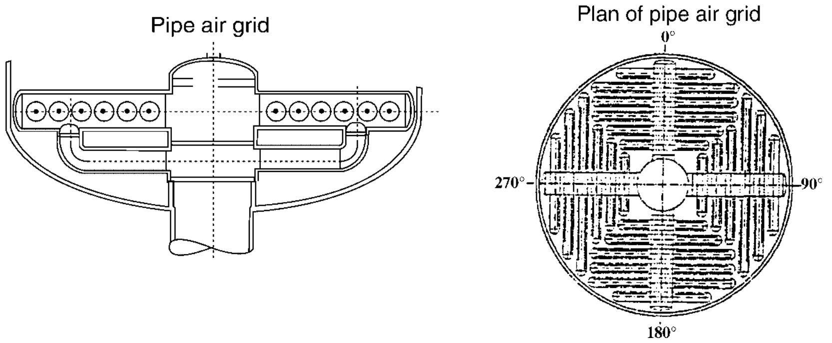

Fig. 9. Regenerator pipe grid air distributor.

designed for three conditions: start-up, normal operation, and emergency. The actual design temperatures and pressures may vary from unit to unit, depending on the process requirements and configuration. However, these three design conditions are common to all units and must be incorporated into the design. The extreme temperature of the emergency case usually dictates the selection of the distributor metallurgy.

Basically, two types of air distribution systems are used in FCCU regenerators: those that distribute air into the catalyst bed through a perforated plate and those that distribute air through a series of small pipes, known as a pipe grid (77). The pipe grid design is the most commonly used. A typical pipe grid design is shown in Figure 9. The pipe, which is typically constructed of 304 H stainless steel or $1\,\frac{1}{4}$ Cr-$\frac{1}{2}$ Mo steel, distributes the air through three or four large laterals into a number of small branches. The grid is designed for a total pressure drop in the range of 3.5–7.0 kPa (0.5–1 psi). This pressure drop is set by regulating the air leaving the branch arms through a series of nozzles that point downward. Erosion patterns at the nozzle tip are minimized with the dual-diameter jets that allow the air to develop a full-flow velocity profile across the entire nozzle cross-sectional area prior to exiting. Frequently, some of these nozzles are plugged to prevent jet impingement on adjacent pipes; increase pressure drop; and enhance carbon and air distribution within the bubbling bed. The upper operations limit of the grid is based on jet velocity limitations so as not to cause catalyst attrition. Conversely, the downturn capacity is set by low pressure drop, which can lead to aspiration of catalyst through the peripheral branches. Such aspiration results in severe and accelerated erosion.

8.2. Cyclones. The high gas velocities inside the regenerator can result in considerable catalyst entrainment into the vapor space above the catalyst bed. Cyclones are used to separate these catalyst particles from the exiting regenerator flue gas and return essentially all of these particles to the regenerator bed. In a typical regenerator, the cyclones are generally installed in sets of two (Fig. 10). In this two-stage arrangement, the gas outlet of the first cyclone is channeled directly to the inlet of the second cyclone.

The cyclones are typically designed with diameters of 100–150 cm for ease of maintenance. Cyclone inlet velocities are usually restricted to 18–22 m/s in the first stage and to 21–26 m/s in the second stage to achieve satisfactory efficiency,

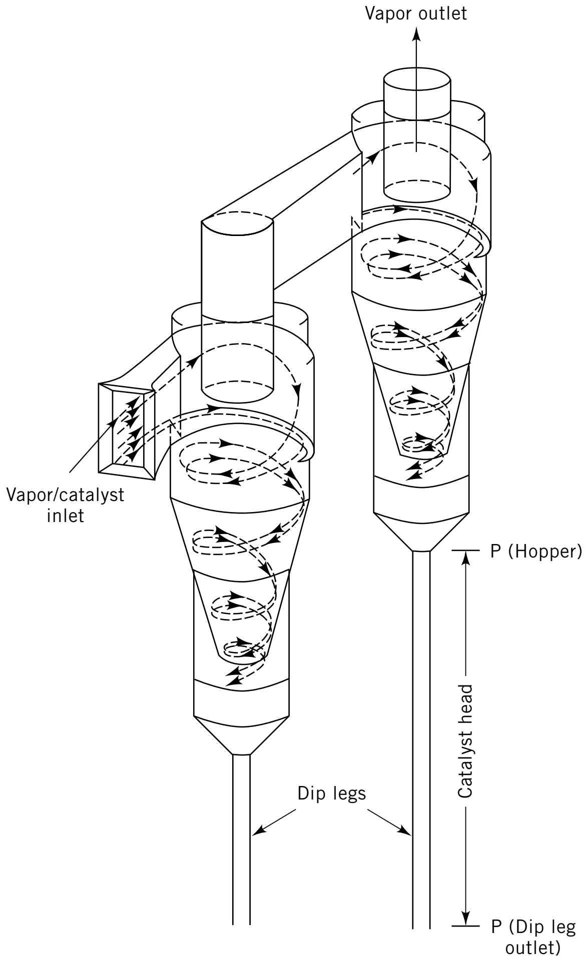

Fig. 10. Cyclone system.

pressure drop, and erosion characteristics (57). The number of sets of two-stage cyclones thus depends on the total gas flow. Finding room to house all the necessary cyclones within the regenerator frequently requires considerable ingenuity (78).

Catalyst leaving the cyclone flows down the cyclone discharge pipe, known as the dipleg, and builds a layer of catalyst at the bottom of this pipe. Sufficient catalyst head is developed in the dipleg to overcome the cyclone inlet and cyclone cone outlet pressure drop and thus allow the entrained solids to return to the regenerator bed. The second stage sets the required overall dip leg length, and the catalyst seal is maintained with either the dipleg being submerged in the bubbling bed or with a trickle-flapper valve arrangement at the catalyst discharge end. The open bottom, submerged dipleg with only a splash baffle, is used primarily on regenerator first-stage cyclones. When the diplegs are unsubmerged in a bubbling bed, a flapper valve arrangement is utilized at the catalyst discharge end of the dipleg.

The metallurgy of the cyclone equipment has in recent years focused primarily on type 304 H stainless steel. The 304 H material is durable and easy to fabricate and repair, withstands the high regenerator temperatures, and is oxidation- and corrosion-resistant. Essentially all internal surfaces of the cyclone that are subject to erosion are protected with a 2 cm layer of erosion-resistant lining. When installed and cured, most refractory linings are highly resistant to erosion.

8.3. FCC Catalyst Coolers. Heat-removal systems have been used in commercial FCCUs since the early 1940s. The earliest coolers utilized tubular cooling coils located inside the regenerator. The tube banks were normally arranged horizontally in rows of three or four, but because of their location in a continuously bubbling, or turbulent catalyst bed, they offered limited duty flexibility, with no shutdown or start-up potential.

Because of the drawbacks to the internal cooling coil, cooler design has evolved to an external exchanger type. The exchanger is either designed to have catalyst flowing dense phase down and through the exchanger to the lower portion of the regenerator, or to have catalyst flowing down into the cooler, backmixing, and returning back up into the regenerator. External cooler design improvements introduced in the middle 1980s have resulted in excellent mechanical reliability, and the same, or better, on-stream efficiency as many of the other mechanical components of the FCCU system. The design also has a wide range of easily controlled heat removal duties. This all-vertical bundle design allows either a backmixed or flow-through configuration (Fig. 11). The bayonet tube design uses forced water circulation and allows for catalyst to flow on the shellside of the bundle. Both the catalyst flux and aeration velocities are controlled at low levels and at the same time controllably produce a wide range of heat-transfer coefficients. Concerns regarding erosion or differential are minimal. The independently controlled catalyst flow produces a countercurrent

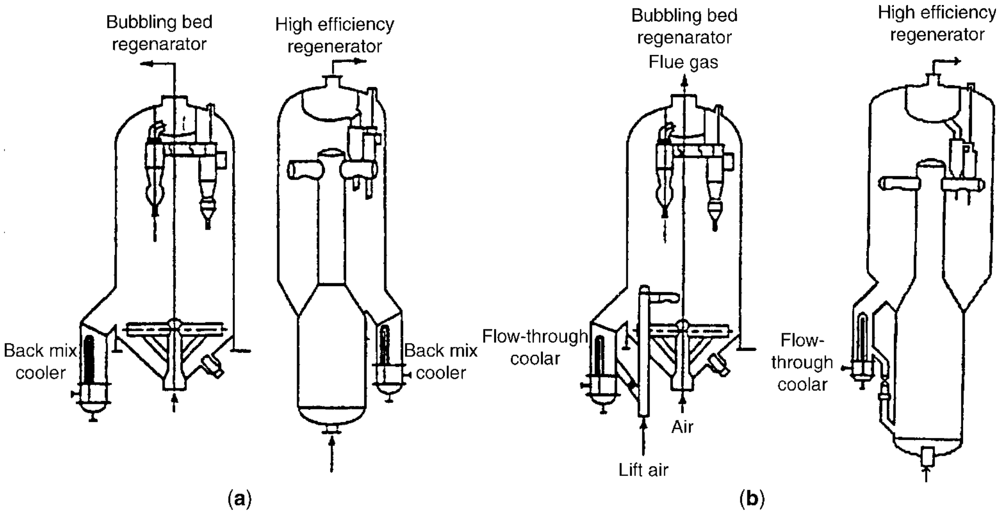

Fig. 11. Catalyst cooler configurations where (**a**) is a backmix cooler and (**b**) is a flow-through catalyst cooler (79).

gas (bubble-phase) and solid flow. Typically, a single cooler can be operated and controlled anywhere within a $6-50 \times 10^6$ watt saturated-steam production range.

8.4. Flue Gas Handling. *Waste Heat Boilers.* In a conventional FCCU flue gas system, the regenerator combustion gases generally pass through two stages of cyclonic separators, a slide valve, orifice chamber, waste heat boiler, and electrostatic precipitator or third stage separator. The slide valve and orifice chamber act in combination to reduce the flue gas to essentially atmospheric pressure.

If the CO is not completely combusted to CO_2 in the regenerator, a CO boiler is used to complete the combustion. The resulting heat of combustion and the sensible heat of the flue gas along with any heat from auxiliary fired fuel are recovered in the form of high pressure steam. When the regenerator is operated in total CO burn, the CO boiler is replaced with either a shell and tube exchanger or a box-type waste heat boiler (see HEAT EXCHANGE TECHNOLOGY).

The shell and tube exchanger, which is a single-purpose piece of equipment, has the standard parts of a normal heat exchanger, but certain parts have been modified to withstand the erosive service of the particulate-laden flue gas stream. This design has the limitation of being able to produce only saturated steam. The flue gas leaves the regenerator at temperatures up to 760°C and exits the exchanger at ~290°C. The flue gas then proceeds through the pressure-control slide valve and orifice chamber, which reduces its pressure to essentially atmospheric prior to entering the emission control system or stack.

The box cooler receives regenerator flue gas after it has been reduced to essentially atmospheric pressure. This arrangement is not limited to the production of saturated steam. Any number of coils can be installed in the box, and normally both steam-generating and superheater coils are present. The tube temperatures within the box must be maintained above the SO_3 dew point of 150–175°C to prevent sulfuric acid corrosion (80).

The principal differences between the shell and tube and the box designs may be summarized as follows:

	Shell and tube	Box
flue gas pressure	138–276 kPa	atmospheric
type of steam	saturated	saturated plus superheated
steam pressure limit	3500 kPa	none

8.5. Power Recovery. All FCC Units emit a form of “zero cost” energy as part of the flue gas discharge from the FCC regenerator. Typically, these gasses are in the 700°C range at anywhere from 240 to 380 kPa. In many cases, this hot, pressurized gas can economically be utilized by a Power Recovery System to either drive the FCC main air blower, or produce electricity for the refinery grid.

Types of Systems. There are several possible arrangements of Power Recovery Systems available for incorporation into new or existing FCC Unit operations. These systems can include 2, 3, 4, and 5 component systems (expander, main air blower, steam turbine, gear, motor/generator), specifically designed to meet a multitude of processing and economic requirements (81).

For new FCC unit applications, where plot space is generally not a primary consideration, the power recovery expander will most often be directly connected to the main air blower to drive the compressor in place of a steam turbine or motor drive. This eliminates the need for either a large electric motor, or a steam turbine to drive the main air blower requiring a surface condenser, utility support system, and condensate pumps.

For revamp applications, where plot space is most often a primary consideration, and the main air blower and driver are already in place, it is generally unlikely that a new expander can economically be positioned, and directly connected to the existing main air blower. In these situations, a stand-alone power recovery expander is typically used to drive an electrical generator to produce electricity for the refinery, rather than drive the main air blower. This installation can be a three or four component system. Generally, the three component power recovery system (expander, gear, generator), protected by a third stage separator, is the easiest configuration to add to an existing FCC unit. On many occasions, the addition of a let-down steam turbine (four body system) can be added to this train to generate additional power. In all cases, the installation of a power recovery system requires a large capital investment.

Process Flow. In a typical power recovery system, hot flue gas leaving the regenerator goes to a third stage separator, where roughly 98% of the 10 μ and larger particulate material is rermoved to protect the expander blades in the

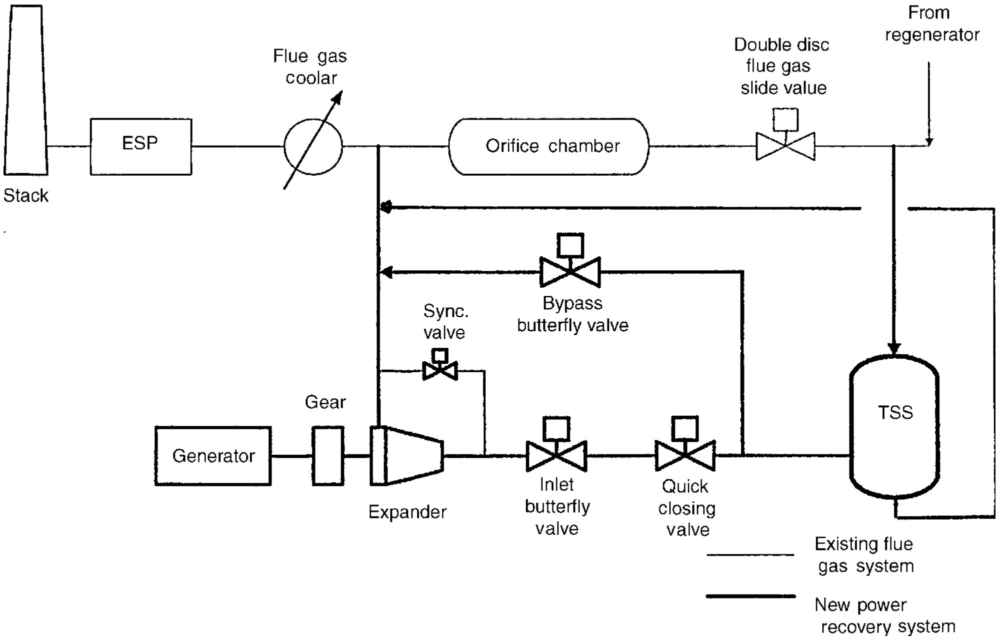

Fig. 12. Regenerator Flue Gas System, Before and After Installation of a Power Recovery System.

power recovery unit, as described earlier. Other particulate removal systems (ESP or scrubber) are not appropriate for power recovery use, since they operate at essentially atmospheric pressure.

This "clean" flue gas leaving the separator is then sent through two butterfly control valves used to direct and throttle the flue gas, etc, and through the Power Recovery Expander where the pressure in the flue gas is converted to direct mechanical energy to drive a generator and produce electricity. The expander acts as a restriction orifice and together with the inlet line butterfly valves, maintains the regenerator operating pressure. A bypass valve is provided upstream of the inlet butterfly valves to divert a portion of the flue gas around the expander during periods when the potential recoverable energy exceeds the capacity of the Power Recovery Train, or when the Power Recovery Train needs to be bypassed for maintenance. Finally, the expander exhaust gas, generally 110–120 kPa at this point, is directed back to the flue gas system (downstream of the orifice chamber) for further processing: steam production, particulate removal, and atmospheric discharge, as seen in Figure 12.

Power Production. The power recovered from the flue gas is approximately equal to the main air blower requirements. On a BPSD basis, using a 50,000 BPSD FCC (∼2.5 MM t/year) operating at 310 kPa (30 PSIG), producing approximately 200,000 kg/h (450,000 lb/h) of flue gas at 720°C (1325°F), one could expect this system to produce 11 MW of electrical power.

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