

Regeneration of Fluidized Cracking Catalysts

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An equation for correlating regeneration process variables in fluid-catalytic cracking has been developed from pilot plant data. This equation takes into account not only the chemical-reaction rate for burning coke deposited on the catalyst but also the diffusional resistance to oxygen transfer. The resistance presumably occurs between the bubbles within the fluidized bed and the void spaces in the relatively denser mass of particles. The coefficient of mass transfer was found to be inversely proportional to the 1.5 power of the average particle diameter and directly proportional to the square of the gas mass velocity. The specific reaction-velocity constant was found to be a function of temperature and catalyst activity as well as the nature of the feed from which the coke was deposited. Comparison of pilot plant data with commercial data suggests that nonuniform gas distribution in larger beds makes some of the catalyst ineffective.

Regeneration of coked or spent catalyst by burning the coke with air is an essential part of the catalytic-cracking process; indeed, the capacity of the regenerator for burning the formed coke often limits the rate at which a unit can crack feed. To understand the performance of the regenerator, the process variables involved in regeneration must be recognized and a knowledge of the relations among them obtained.

The kinetics of regeneration have been established from fixed-bed studies (2, 14). Other studies have shown how the mechanics of fluidization might influence the reaction rate in a fluidized bed (3, 4). Combination of these two types of information should lead to a useful relationship between the important variables. Such a correlation has been developed from theoretical considerations. Pilot plant studies have been used to evaluate the constants.

THEORY

During burning of coke, oxygen must be transferred from the air stream to the surface of the catalyst. Burning rate may as well be limited by diffusion from the air stream to the surface as by reaction on the surface. In a fixed bed, the resistance to diffusion occurs in a stagnant film surrounding the individual catalyst particles. In a fluidized bed, however, much of the gas passes through the catalyst in the form of pseudobubbles or pockets and relatively little flows through the interstices between the more densely packed particles (3). Much of the catalyst can receive oxygen only by diffusion or mass transfer of gas from the bubbles. Resistance to mass transfer can be combined with reaction kinetics to develop an equation for the over-all rate of reaction. A material balance can be combined with this equation to give an

equation interrelating the process variables (7), provided certain assumptions are made.

The concentration of carbon on the catalyst can be considered uniform throughout a fluidized bed, because the rate of catalyst mixing is rapid (3). The gas flow can be assumed unidirectional, because by-passing or short-circuiting of gas in a fluidized bed is far more pronounced than back mixing (3, 4). Gas by-passing causes the oxygen concentration to vary across the horizontal cross section of the regenerator, but an average oxygen concentration can be assumed to exist at a given vertical level. Although coke contains 5 to 15% hydrogen, the carbon on the catalyst can be taken as a measure of the coke.

Resistance to mass transfer can be combined with reaction kinetics in a manner similar to that proposed by Hurt (8). The rate of reaction of carbon is known to be first order with respect to the concentration of carbon on the catalyst (14) and the partial pressure of oxygen (2). However, carbon and oxygen must react in some stoichiometric ratio. Hence the rate of reaction of oxygen r , in moles/hr./lb. of catalyst can be expressed as

$$r = k_r C_c p_i \quad (1)$$

where the proportionality constant relating the rates of carbon and oxygen reactions is contained in k_r , the specific reaction-velocity constant in moles/hr./atm./lb. The term C_c is the fraction of carbon on regenerated catalyst, and p_i is the partial pressure of oxygen in interstices of catalyst in atm. The rate of oxygen transfer depends upon the pressure gradient of the oxygen from the interior of the bubbles to the interstices of the catalyst. Thus r_d , the rate of oxygen diffusion from bubbles to catalyst

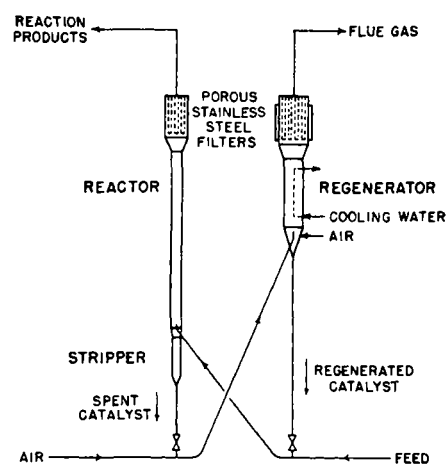


Fig. 1. Pilot plant.

in moles/hr./lb. of catalyst, can be expressed as

$$r_d = k_d(p - p_i) \quad (2)$$

where k_d is the coefficient of mass transfer in moles/hr./atm./lb. and p is the partial pressure of oxygen in bubbles in atm. At steady state conditions, the over-all rate of reaction must equal the rate of oxygen transfer or rate of surface reaction. Thus, after equating Equations (1) and (2), solving for p_i , and substituting this expression in Equation (1) one can express the over-all rate of reaction r , in moles/hr./lb. of catalyst, as

$$r = \frac{p}{\frac{1}{k_d} + \frac{1}{k_r C_c}} \quad (3)$$

A material balance on oxygen across a differential length of regenerator may be written

$$F dN = -r dW \quad (4)$$

where F is the feed rate of gas in lb./hr., N is the oxygen concentration in the gas in lb. moles/lb. feed, and W is the weight of catalyst in lb. If Equation (3) is substituted in Equation (4) and the total moles of reactants and products is considered constant, the resulting equation may be integrated from the inlet to the outlet oxygen concentration to give

$$-\frac{W}{F} = \frac{N_i}{P} \left(\frac{1}{k_d} + \frac{1}{k_r C_c} \right) \ln \frac{N}{N_0} \quad (5)$$

where N_t is the total moles gas/lb. of feed to the regenerator, P is the total pressure in atm., and N_0 is the inlet oxygen concentration in lb. moles/lb. feed. The quantity FN_t/W is defined as the space velocity S and equals the moles of gas fed to the regenerator/hr./lb. of catalyst. The quantity N/N_0 is the fraction of inlet oxygen unconverted in the regenerator and is defined as f . If these terms are introduced in Equation (5), it may be rearranged to give

$$-\frac{PC_r}{S \ln f} = \frac{C_r}{k_d} + \frac{1}{k_r} \quad (6)$$

Significant variables are thus related in terms of a specific reaction-velocity constant and coefficient of mass transfer.

Equation (6) could be used to evaluate the specific reaction-velocity constant k_r from regeneration data if values of k_d were available. Although some data on mass transfer in fluidized beds exist (11), there are no data on particles in the 0- to 100- μ range. Hence the coefficient of mass transfer can be assumed to be a function of some powers of the mass velocity of the gas and the average particle diameter. Higher gas velocities or finer catalysts will increase the distance between particles and so the resistance to diffusion will be less. Thus the coefficient of mass transfer k_d may be expressed as

$$k_d = \frac{1}{\alpha} \frac{G^m}{D_p^n} \quad (7)$$

where α is a proportionality constant, m and n are unknown exponents, G is the gas mass velocity in the regenerator in lb./hr./sq. ft., and D_p is the average particle diameter in μ . Equation (7) can be substituted in Equation (6) to give

$$-\frac{PC_r}{S \ln f} = \alpha \frac{CD_p^n}{G^m} + \frac{1}{k_r} \quad (8)$$

which represents a straight line of slope α and intercept $1/k_r$ when $-PC_r/(S \ln f)$ is plotted against $C_r D_p^n/G^m$. Both k_r and α can be evaluated from regeneration data if suitable values of m and n can be obtained.

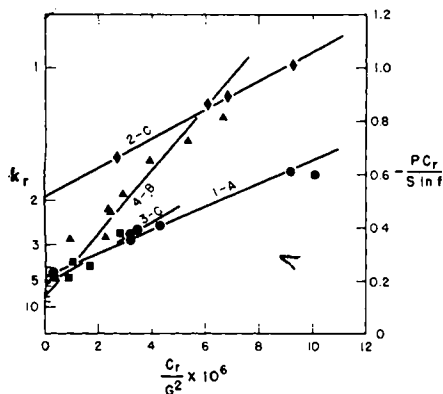


Fig. 2. Determination of correlation constants. Curves identified by catalyst number and feed letter.

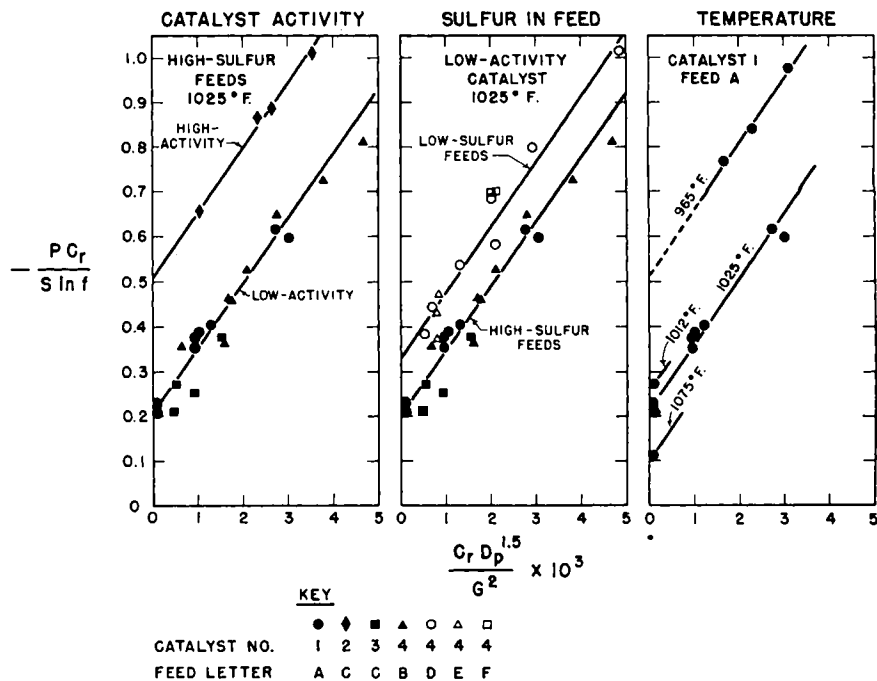


Fig. 3. Correlation of regeneration variables.

EVALUATION OF CONSTANTS

Forty-two pilot plant tests were made to evaluate the constants α , m , and n in Equation (8) and to determine k_r for catalysts of different activities and with carbon deposited by various feeds.* For each catalyst and feed, a series of tests was made at a constant temperature but with differing superficial gas velocities, carbon-on-catalyst levels, pressures, catalyst inventories, and oxygen conversions.

The capacity of the pilot plant was 2 bbl./day. A simplified diagram of the unit is shown in Figure 1. The regenerator, excluding the filter section, was constructed of 10-in. extraheavy steel pipe 5 ft. long.

*Data on these tests have been filed as document 4792 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for \$1.25 for photoprints or 35-mm. microfilm.

Synthetic silica-alumina catalysts were used. Three of them were removed from commercial units to obtain samples with representative equilibrium activities. The fourth was a fresh catalyst which was deactivated in the pilot plant. Table 1 gives the properties. Activity was measured by the Indiana relative activity method (13) and particle-size distribution was determined by a modified Roller analysis (9, 12). The average particle diameter was defined as that diameter representing the specific surface of the catalyst (5, 6).

Properties of the gas-oil feeds are shown in Table 2. Feeds A, B, and C were derived from high-sulfur West Texas crude; E and F from low-sulfur Midcontinent crude; feed D was a West Texas gas oil that had been extracted to remove sulfur and aromatic compounds. Concentration of oxygen in the flue gas was

TABLE 1. PROPERTIES OF CATALYSTS

Catalyst	Roller analysis, μ					Average particle diam. μ	Indiana relative activity
	0-10	10-20	20-40	40-80	80+		
1	1.5	4.4	16.4	34.1	43.6	44.5	35
2	4.0	3.0	6.7	21.2	65.1	52.7	90
3	0.0	0.1	16.3	35.3	48.3	67.1	32
4	0.0	0.0	3.2	40.1	56.7	79.0	20

TABLE 2. PROPERTIES OF FEEDS

Feed No.	Gravity, °A.P.I.	A.S.T.M. distillation				Sulfur, wt. %	Aniline Point, °F.
		Initial	50%	90%	Max.		
A	26.7	378	640	764	—	1.62	158
B	26.7	420	650	744	750	1.61	157
C	28.2	268	619	741	—	1.65	150
D	30.0	408	658	768	—	0.64	172
E	31.1	496	640	752	—	0.40	177
F	31.6	410	612	738	744	0.36	175

continuously measured by a Beckman analyzer (10).

The carbon on the catalyst was determined by igniting a catalyst sample in a boat placed in a furnace with a stream of oxygen. The carbon dioxide and traces of sulfur dioxide formed were absorbed in soda lime and weighed. No correction was made for the sulfur dioxide. The hydrogen in the coke was estimated from the difference between the oxygen actually consumed in the regenerator and that required to burn the carbon.

A trial-and-error procedure was used to determine the value of m , exponent of mass velocity. Data obtained at a constant temperature, with a given catalyst, and with superficial velocities of 0.1 to 0.6 ft./sec. were plotted as $-PC_r/(S \ln f)$ vs. C_r/G^m . The value of m was adjusted to produce the best straight line. A value of $m = 2$ provided the best correlation, as shown in Figure 2.

According to Equation (8), the slopes of the straight lines in Figure 2 for catalysts of different particle sizes should equal αD_p^n . Thus a plot of the log of the slope against the log of the average particle size should give a straight line of slope n . Such a plot gave the value of n as 1.5.

Finally plots of $-PC_r/(S \ln f)$ vs. $C_r D_p^{1.5}/G^2$, as shown in Figure 3, established the slope α as 146. The final equation relating the fundamental process variables to the specific reaction-velocity constant of the catalyst is

$$-\frac{PC_r}{S \ln f} = 146 \frac{C_r D_p^{1.5}}{G^2} + \frac{1}{k_r} \quad (9)$$

DISCUSSION

The effects of catalyst activity, type of feed, and temperature of regeneration are shown in Figure 3. The low-activity catalysts show a higher reaction-velocity constant than does the high-activity catalyst. This effect was observed in laboratory fixed-bed and commercial fluidized-bed units in which fresh or high-activity catalysts regenerated more slowly than low-activity or used catalysts. Metals deposited from the feed lower the catalyst activity for cracking but apparently act as catalysts to promote burning of carbon.

At a constant temperature and catalyst activity, the reaction-velocity constant for carbon deposited from high-sulfur feeds is higher than from low-sulfur feeds. It is not known whether a fundamental difference exists in the nature of the coke or whether sulfur or some other compound promotes the burning of coke.

The effect of temperature on the reaction-velocity constant is pronounced. A plot of the constants from Figure 3, according to the Arrhenius equation, is shown in Figure 4. The slope of the plot gives an activation energy of 63,000

B.t.u./lb. mole (35 kcal./g. mole). Fixed-bed data have given a value of 36 kcal./g. mole (14). These values agree only because mass transfer resistances have been separated from the reaction-velocity constants; otherwise the activation energy in the fluidized bed would have been much lower.

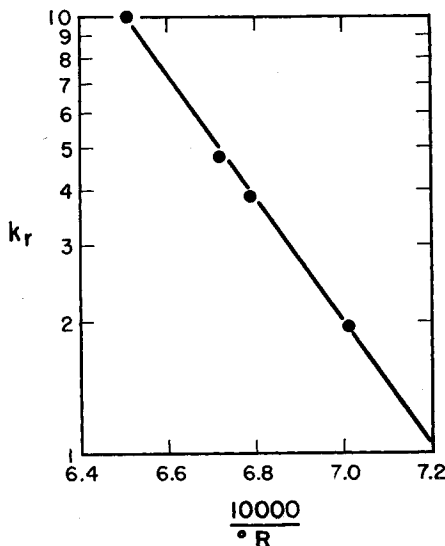


Fig. 4. Arrhenius plot for catalyst 1, feed A.

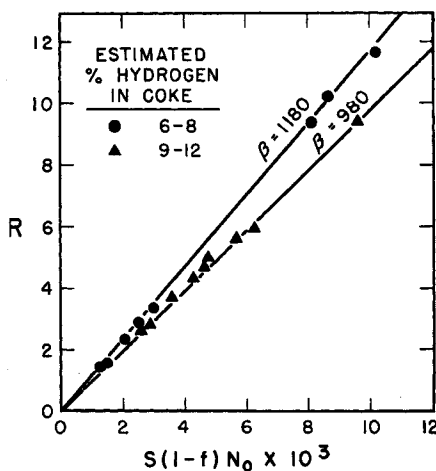


Fig. 5. Relation between rate of carbon burning and oxygen consumption.

APPLICATION OF CORRELATION

To aid in the application of Equation (9) for predicting regenerator performance, an auxiliary equation relating the total coke-burning capacity of the unit to the regeneration variables may be developed. Thus, from the stoichiometry of the regeneration process, the weight of carbon burned must be proportional to

the moles of oxygen consumed. R , the lb. of carbon burned/hr./100 lb. of catalyst, can be expressed as

$$R = \beta N_0(1 - f)S \quad (10)$$

where β is a proportionality constant. By definition

$$R = (C_r - C_s) \frac{U}{W} \quad (11)$$

where C_s is the fraction of carbon on spent catalyst and U is the catalyst-circulation rate in lb./hr.

A plot of Equation (10) with data for seventeen tests is shown in Figure 5. The slope of the line β is a function of the percentage of hydrogen in coke, because R was calculated in terms of carbon and neglects the hydrogen in the coke.

The application of Equations (9), (10), and (11) for analyzing pilot plant regenerator performance may be shown by an example. A regenerator may be required to burn a certain quantity of coke with a given catalyst inventory and air rate. From Equation (10), the value of f may then be calculated. If catalyst-circulation rate and concentration of carbon on spent catalyst are also fixed by reactor conditions, the concentration of carbon on regenerated catalyst may be calculated from Equation (11). If the regenerator operates at constant pressure, the reaction-velocity constant may be calculated from Equation (9). The regeneration temperature may then be estimated from Figure 4.

The correlation has proved less useful when applied to commercial units, where such interfering factors as afterburning and partial combustion in large transfer lines are more difficult to control. Equation (9) usually gives lower reaction-velocity constants than are observed in the pilot plant. Reaction-velocity constants developed from pilot plant data contain a factor that represents the extent of participation of the catalyst in the reaction. In commercial units, where the regenerator may be 30 ft. in diam., part of the catalyst may be ineffective because of nonuniform gas distribution in the fluidized bed. The observed better regenerator performance with finer catalysts (1) may be the result of more uniform fluidization and greater participation of the catalyst. Higher superficial velocities would also be expected to increase the effectiveness of the catalyst.

Two additional types of investigations might increase the usefulness of the correlation for commercial units. Pilot plant studies at the higher velocities used in commercial units might lead to constants more applicable in the correlation. A study of the effect of superficial velocity in a commercial unit should increase understanding of the differences in fluidization in small and large regenerators.

NOTATION

C_r = fraction of carbon on regenerated catalyst
 C_s = fraction of carbon on spent catalyst
 D_p = average particle diameter representing specific surface of catalyst, μ
 f = fraction of inlet oxygen unconverted in regenerator (N/N_0)
 F = rate of gas feed to regenerator, lb./hr.
 G = gas mass velocity in regenerator, lb./(hr.)(sq. ft.)
 k_d = coefficient of mass transfer, lb. mole/(hr.)(atm.)(lb.)
 k_r = specific reaction velocity constant, lb. mole/(hr.)(atm.)(lb.)
 m = exponent on G
 n = exponent on D_p
 N = oxygen concentration in gas, lb. mole/lb. feed
 N_0 = inlet oxygen concentration in gas, lb. mole/lb. feed
 N_T = total moles gas/lb. feed to regenerator
 p = partial pressure of oxygen in bubbles, atm.

p_i = partial pressure of oxygen in interstices of catalyst, atm.
 P = total pressure, atm.
 r = over-all rate of reaction of oxygen, lb. mole/(hr.)(lb.)
 r_d = rate of diffusion of oxygen from bubbles to catalyst, lb. mole/(hr.)(lb.)
 r_r = rate of reaction of oxygen at surface of catalyst, lb. mole/(hr.)(lb.)
 R = carbon burning rate, lb./(hr.)(100 lb. catalyst)
 S = space velocity, moles/(hr.)(lb.)
 T = catalyst temperature, °F.
 U = catalyst circulation rate, lb./hr.
 W = catalyst inventory, lb.

Greek Letters

α = a proportionality constant, slope of Equation (8)
 β = a proportionality constant in Equation (10)

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Performance of an Internally Baffled Multistage Extraction Column

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Internally agitated extraction columns generally require increasing heights for a theoretical stage for the larger column diameters. The present work describes a design developed to minimize this objection and presents the performance data on a system considered easy to extract and on systems considered difficult to extract. H.E.T.S. values as low as 3 in. on the first system and 4 in. on the second type of system were obtained in an 11½ in. I.D. glass column. The stage efficiencies were correlated as a function of power input per unit volume of solvent throughput and the ratio of the flow rate of the dispersed phase to that of the continuous phases. The supplementary effect of packing was studied and found to be most beneficial in the system which has a low interfacial tension and is considered easy to extract. By the use of this particular arrangement of internal baffles, it is believed possible, in the larger diameter columns, to reduce the height to a ratio of H.E.T.S. to diameter below the value of ¼ obtained in the present column.

The performance studies on mechanically agitated liquid-liquid extraction columns generally indicate that the height required for a theoretical stage increases as the diameter of the column becomes

greater although not necessarily in a direct proportionality. In the design of extraction columns consisting of alternate mixing sections and packed calming sections, it was found that the optimum packing height which gives the minimum H.E.T.S. values was approximately proportional to the square root of the column

diameter for the 1- and 12-in. sizes. Early studies on the use of vertical baffles in the mixing sections of such a column indicated that although these baffles eliminated the rotational motion of the fluids and probably improved the mixing, they transformed this motion into vertical motion and required an even greater

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