

Catalyst Regeneration Kinetics

V. RAMASWAMY and F. J. STERMOLE
Colorado School of Mines, Golden, Colo.

The kinetics of catalyst regeneration were investigated in a differential reactor. In the presence of excess oxygen (oxygen concentration essentially constant at the lowest air flow rate investigated), the order of the over-all regeneration reaction was 1 with respect to carbon concentration. Air flow rate through the reactor was varied from 0.03 to 0.095 cubic foot per minute and the temperature ranged from 940° to 1045° F. An Arrhenius dependence of the specific rate constant on temperature was observed. A highly porous clay catalyst was used.

THIS INVESTIGATION concerns the kinetics of catalyst regeneration. Data have been obtained in a differential reactor, and it has been shown that in the presence of excess oxygen (such that oxygen concentration remained essentially constant at the lowest air flow rate investigated) the order of the over-all regeneration reaction was one with respect to carbon concentration. Air flow rate through the reactor was varied from 0.03 to 0.095 cu. foot per minute and the temperature range studied was from 945° to 1045° F. An Arrhenius dependence of the specific rate constant on temperature was observed.

The catalyst used in the present investigation was a spent clay catalyst (Filtrol clay 110) obtained from a local refinery where it was used in a commercial cracking unit. The original catalyst pellets were cylindrical in shape, about 3.2 mm. in diameter, and the length varied from 4.8 to 6.4 mm. The concentration of carbon in the coke deposited on the catalyst studied was approximately 1% by weight. The bulk density of the catalyst was 0.875 gram per cc. The surface area of the catalyst (N₂ adsorption, B.E.T. method) was 100 sq. meters per gram. Pore volume was 0.35 cc. per gram, and average pore diameter was 85 Å.

EXPERIMENTAL

Experimental equipment consisted primarily of a reactor made of Vycor to withstand the high temperatures used. The reactor was 35 mm. in diameter and 30 cm. long and was electrically heated with Nichrome wire wound around the reactor on an asbestos core. The reactor was insulated with 3/4-inch thick asbestos insulation. The heat input to the reactor was controlled by means of a Powerstat. A thermowell located vertically in the center of the reactor permitted measurement of the temperature inside the reactor and this was recorded on an eight-point Brown recorder. An inlet at the top of the reactor admitted regeneration gas which, for this study, was air. The inlet to the reactor was connected to a manifold which had two lines with controlling valves on them. One line was connected to the air supply and the other was connected to a nitrogen cylinder. The gases flowing through the manifold were metered with the help of a wet-test meter. Nitrogen gas was passed through the reactor during the initial heat-up to the desired regeneration temperature. Regeneration started when nitrogen flow was stopped and the air flow started.

At the reactor outlet regenerated gases flowed into a caustic absorption system where the carbon dioxide in the flue gases was absorbed. In the first stage of the absorption system a buret with sodium hydroxide was set up and the rate of formation of carbon dioxide was determined by titration using the following neutralization reaction:



To obtain the desired data a differential reactor was used. Thus, the authors assumed that all catalyst regen-

erated simultaneously. The differential reactor was constructed by packing a weighed quantity of catalyst in between glass beads. The volume of the catalyst was approximately 25 cc., and when packed between glass beads the thickness of the catalyst bed was approximately 2.6 cm.

In a typical run, the bed was preheated with Nichrome wire wrapped around the reactor. During the preheating period nitrogen was passed through the reactor to prevent oxidation of carbon. As soon as the desired temperature was reached the nitrogen was turned off and the air was turned on, which started the regeneration. The preheating with nitrogen helped serve two purposes: to remove the volatiles present in the catalyst, and to present an oxygen-free atmosphere to the catalyst until the desired temperature was attained. Volatiles were removed in the 400° to 600° F. range, which was well below all starting regeneration temperatures investigated.

As the regeneration proceeded, the temperature inside the bed started rising sharply to a peak and then slowly started falling to attain eventually the original temperature of the bed. The temperature plot for some typical runs is shown in Figure 1. The peak temperature attained depends on the air flow rate and the initial bed temperature, as is evident from Table I. Several runs were made at most conditions and the experimental data were very reproducible. Data for different runs at the same conditions fell upon the same curves with 5% error or less.

THEORY

The main reaction that governs catalyst regeneration is the oxidation of carbon,



The rate equation for the above reaction can be written as

$$r = \frac{dC_c}{dt} = -kC_cC_{\text{O}_2} \quad (3)$$

where

C_c = concentration of carbon

C_{O_2} = concentration of oxygen

k = reaction rate constant

r = rate of reaction

The concentration of carbon refers to the total amount of carbon that can be oxidized from the catalyst. The catalyst used was highly porous and the carbon was distributed both on the outside of the catalyst and inside the pores. A fractured specimen of the spent catalyst showed

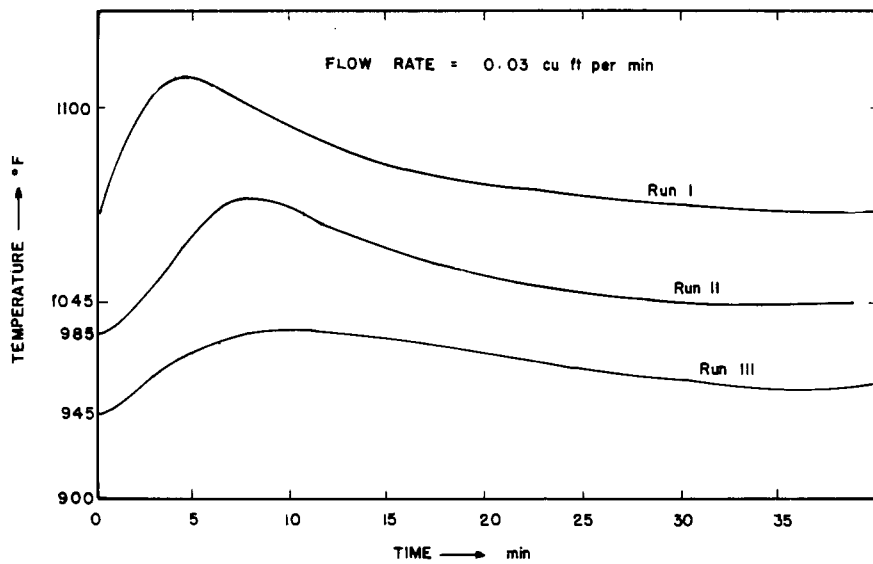


Figure 1. Differential reactor bed temperature

Table I. Summary of Results

| Run No. | Flow Rate, Cu. Ft./Minute | Activation Energy, Kcal./G.-Mole | Initial Temp., ° F. | Rate Constant K, 1.0/Minute | Peak Temp., ° F. |
|---------|---------------------------|----------------------------------|---------------------|-----------------------------|------------------|
| I | 0.030 | | 1045 | 0.179 | 1116 |
| II | 0.030 | 27.00 | 985 | 0.103 | 1055 |
| III | 0.030 | | 945 | 0.063 | 987 |
| IV | 0.065 | | 1045 | 0.186 | 1108 |
| V | 0.065 | 27.30 | 985 | 0.101 | 1050 |
| VI | 0.065 | | 945 | 0.063 | 988 |
| VII | 0.095 | | 1045 | 0.172 | 1105 |
| VIII | 0.095 | 26.40 | 985 | 0.106 | 1042 |
| IX | 0.095 | | 945 | 0.062 | 978 |

that there was uniform deposition of coke inside the pores. Initial carbon concentration was taken as the carbon content in the catalyst after preheating to 1000° F. in nitrogen atmosphere to remove volatile material.

Assuming the reaction is elementary, the reaction is overall second order and first order with respect to carbon and oxygen. Several previous workers (3, 6, 7) have assumed that the regeneration rate has a first-order dependency with respect to oxygen where oxygen is not in excess, and experimental results have verified the validity of this assumption. However, the order of regeneration with respect to carbon has not been clarified; it has been reported to be between 0.5 and 1.0. In the present study this regeneration reaction order is shown to be 1 for the catalyst studied under excess oxygen conditions. If oxygen is in excess the concentration of oxygen does not change significantly as combustion progresses, and hence, it can be assumed constant and lumped with the rate constant. Therefore, Equation 3 can be transformed to the following form

$$r = -KC_c \quad (4)$$

where $K = kC_{O_2}$

The mathematical solution of Equation 4 is

$$C_c = C_{co}e^{-Kt} \quad (5)$$

where C_{co} = initial concentration of carbon in the catalyst. Hence, a plot of $\ln(C_c/C_{co})$ vs. time should be a straight line with a negative slope equal to the rate constant K . Figure 2 shows excellent agreement between experimental data and this theoretical expression.

However, Figure 2 shows that near the end of each run the regeneration rate becomes slower, indicating that pore diffusion becomes significant during removal of carbon during the last stages of regeneration.

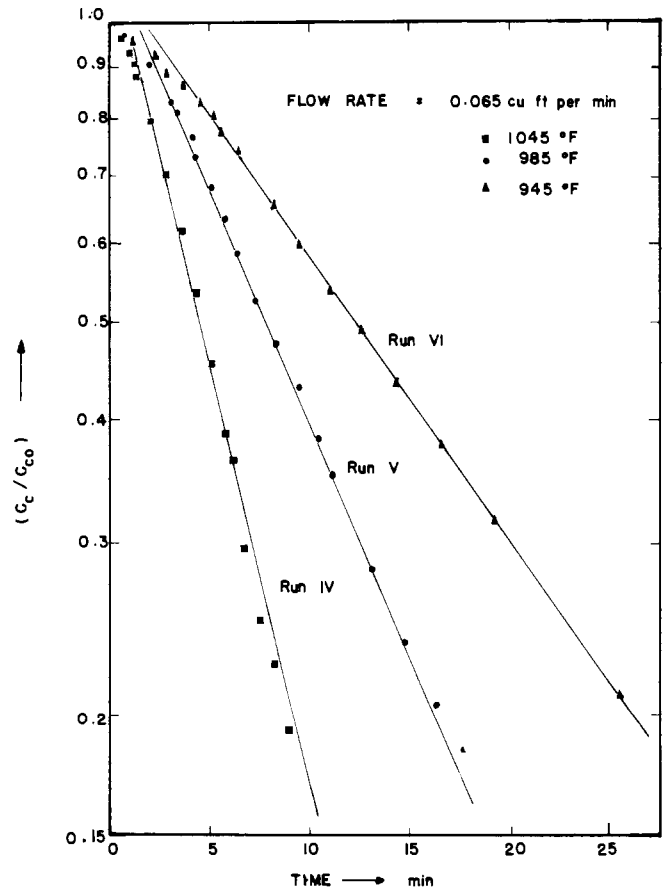


Figure 2. Reaction rate curves for 0.03 cu. ft. per minute

The reaction rate constant experimentally followed an Arrhenius function of temperature—that is,

$$K = K_0 e^{-E/RT}$$

where

K_0 = frequency factor

E = activation energy

R = universal gas constant

T = absolute temperature, ° R.

For the Arrhenius expression, a plot of experimental data for $\ln K$ vs. $1/T$ should be a straight line with a negative slope of E/R . A typical plot for a flow rate of 0.03 cu. foot per minute is given in Figure 3, which shows excellent agreement between experimental data at three different temperatures and the Arrhenius expression. The slope of the line is $E/2.303 R$ and this relation showed that the activation energy was 27 kcal. per gram mole of carbon for this flow rate.

DISCUSSION

Since oxygen was in excess and oxygen concentration remained essentially constant even at the lowest flow rate studied, the flow rate of the regeneration gas had little significant effect on the reaction rate constant within the range of experimental accuracy (Figure 4).

Table I lists the conditions of the runs, the reaction rate constants, peak temperatures attained, and the activation energy values. The results obtained show that in the presence of excess oxygen where oxygen concentration remains constant, the over-all burning rate of coke from the surface and pores of the catalyst used in this study was first order with respect to carbon concentration on the catalyst surface. Previous studies (1, 5, 6) have shown that in the presence of deficient oxygen catalyst regeneration rate depends upon oxygen concentration.

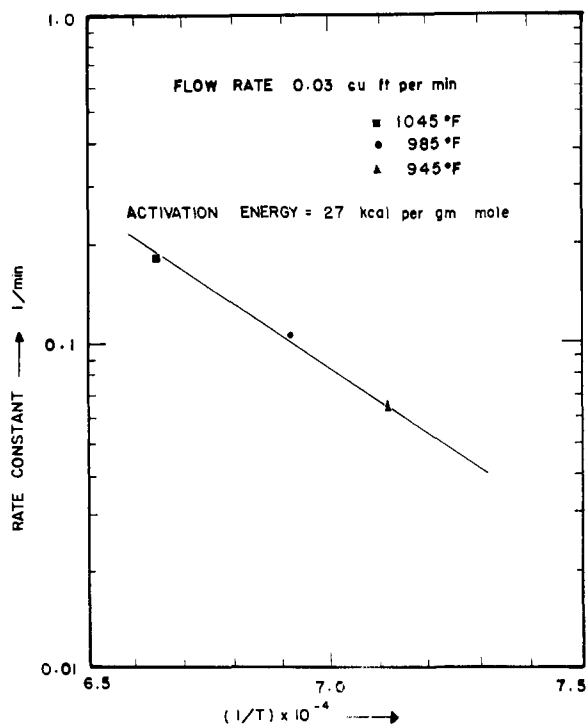


Figure 3. Effect of temperature on rate constants

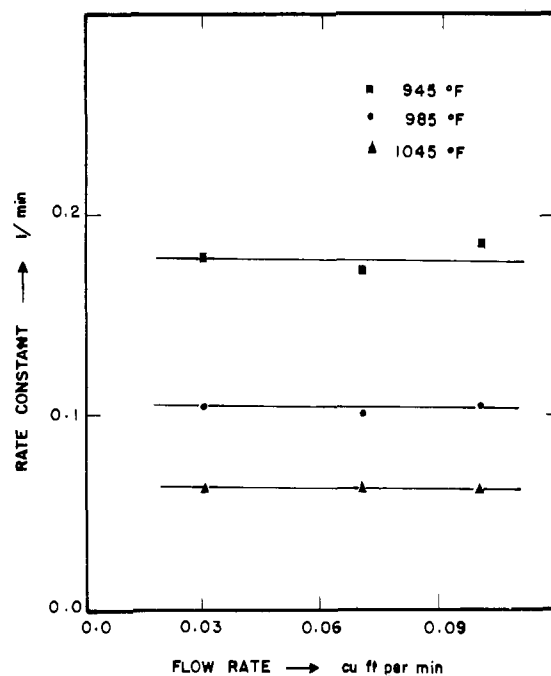


Figure 4. Effect of flow rate on rate constant

In a fully packed bed there will be a definite oxygen concentration profile. Hence, it is probable that in a fully packed bed, the reaction mechanism will change from first to second order at different positions in the bed, depending on whether the catalyst is exposed to excess or deficient oxygen. Also pore diffusion becomes significant and changes the regeneration mechanism during the latter stages of regeneration.

The specific rate constant was shown to follow the Arrhenius function for variation in temperature; it depends only on temperature and not on the air flow rate in the range studied.

The average activation energy obtained was 27 kcal. per gram-mole of carbon. This value is lower than the value reported by Effron and Hoelscher (2) for the oxidation of graphite which was 35 to 40 kcal. per gram mole of carbon. Hall and Rase (4) in their studies with carbonaceous deposits in silica-alumina catalysts report an activation energy of 30 kcal. per gram mole of carbon, which is in close agreement with the present findings.

ACKNOWLEDGMENT

The authors thank the Colorado School of Mines Foundation for the financial support of this research.

LITERATURE CITED

- (1) Dart, J.C., Savage, R.T., Kirkbride, C.G., *Chem. Eng. Progr.* 45, 102 (1949).
- (2) Effron, E., Hoelscher, H.E., *A.I.Ch.E. J.* 10, 388 (1964).
- (3) Essenhig, R.H., Froberg, R., Howard, J.B., *Ind. Eng. Chem.* 57, (9) 33 (1965).
- (4) Hall, J.W., Rase, H.F., *Ind. Eng. Chem. Process Design Develop.* 2, 25 (1963).
- (5) Johnson, B.M., Froment, G.F., Watson, C.C., *Chem. Eng. Sci.* 17, 835 (1962).
- (6) Johnson, M.F.L., Mayland, H.C., *Ind. Eng. Chem.* 47, 127 (1955).
- (7) Mickley, H.S., Nestor, Jr., J.W., Gould, L.A., *Can. J. Chem. Eng.* 43, (2) 61 (1965).

RECEIVED for review November 16, 1966. Accepted July 24, 1967