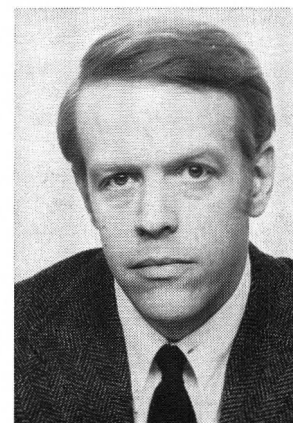


DIFFUSION AND REACTION IN CATALYST PELLETS

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The coupling of chemical reaction with mass transport by diffusion provides some of the most difficult problems in reactor design. Because of this the interaction of diffusion and reaction processes is given extensive treatment in most chemical engineering reactor textbooks. For diffusion and reaction within catalyst pellets the theory is sufficiently developed to allow computation of coupling effects for systems with known intrinsic kinetic behavior. This experiment was developed in order to provide students with first hand experience with intraparticle diffusion effects on reaction rates.

In the Thermoform catalytic cracking (TCC) process oil feed stocks are cracked in a reactor containing porous silica-alumina catalyst pellets in the form of beads which become contaminated by a carbonaceous material. Beads are circulated to a regeneration chamber for removal of the carbonaceous material by oxidation with air. A complete description of the process has been given by a group at Mobil Oil Company.¹ The coupling of diffusion and reaction rates in the oxidation of the carbonaceous deposits is examined in this experiment.

As in the investigations by Weisz and Goodwin,² oxidation of the carbonaceous deposits is carried out in small furnaces at several temperatures. Sample pellets are removed at intervals during the course of reaction. For oxidation at less than 850°F the process is reaction-rate limited and the carbon concentration decreases uniformly within the bead. The bead, initially black throughout, becomes lighter in color passing through gray and eventually becomes nearly clear. At temperatures above 1000°F the process is limited by the diffusion of oxygen into the pellet and carbon removal takes place in a shell-progressive manner. The spherical carbon-containing region shrinks in the course of reaction and disappears. Since a partially oxidized pellet has the appearance of a fish's eye, high temperature oxidation has been re-

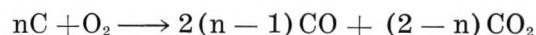
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ferred to as "fish-eye burning." At intermediate temperatures the reaction is partially rate-limited and partially diffusion-limited. Oxidation in this regime produces a diffuse boundary for the carbon-containing region.

Since the carbon-free regions of the beads are nearly clear the qualitative characteristics of operation in the three regimes are immediately observable. For quantitative analysis the beads are ground on a lapping wheel to obtain flat center sections. Measurements of the size of carbon-containing regions are made with a cathetometer. If sufficient time is available measurements of the carbon density profiles for beads oxidized at intermediate temperatures can be made with an optical densitometer. Quantitative comparison of results with theoretical predictions is made only for beads oxidized in the diffusion limited regime.

THEORETICAL BACKGROUND

The reaction may be represented as



where n is the number of atoms of carbon re-

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moved per molecule of oxygen consumed. The reaction rate is assumed to be first order in carbon concentration and in oxygen concentration. Oxygen and the reaction products are assumed to undergo equimolar counter diffusion with constant effective diffusivities. Pellet temperature is taken as constant.

For a spherical pellet of radius R_0 , the continuity equations for carbon and oxygen are as follows:

$$\frac{\partial C_c}{\partial t} = -kn C_c C_{ox}, \quad (1)$$

$$\frac{\partial C_{ox}}{\partial t} = -k \frac{1}{\epsilon} C_c C_{ox} + D \left(\frac{\partial^2 C_{ox}}{\partial r^2} + \frac{2}{r} \frac{\partial C_{ox}}{\partial r} \right), \quad (2)$$

with boundary conditions

$$\text{at } t = 0, \quad 0 \leq r \leq R_0, \quad C_c = C_c^0, \quad C_{ox} = 0$$

$$t > 0, \quad r = R_0, \quad C_{ox} = C_{ox}^0,$$

$$t \geq 0, \quad r = 0, \quad \frac{\partial C_{ox}}{\partial r} = 0$$

where

C_c = carbon concentration per unit volume

C_{ox} = oxygen concentration per unit volume of gas

ϵ = void fraction within pellet

D = effective diffusivity of oxygen

k = intrinsic rate constant

r = radial distance

t = time

R_0 = pellet radius

C_c^0 = initial carbon concentration

C_{ox}^0 = oxygen concentration at pellet surface

The equations may be made dimensionless by the following substitutions:

$$C_c' = \frac{C_c}{C_c^0}, \quad C_{ox}' = \frac{C_{ox}}{C_{ox}^0}, \quad r' = \frac{r}{R_0},$$

$$\phi = R_0 \sqrt{\frac{kn C_{ox}^0}{D}}, \quad t' = t kn C_{ox}^0, \quad \psi = \frac{C_c^0}{C_{ox}^0 \epsilon n}.$$

The resulting dimensionless equations are:

$$\frac{\partial C_c'}{\partial t'} = -C_c' C_{ox}', \quad (3)$$

$$\frac{\partial C_{ox}'}{\partial t'} = -\psi C_c' C_{ox}' + \frac{1}{\phi^2} \left(\frac{\partial^2 C_{ox}'}{\partial r'^2} + \frac{2}{r'} \frac{\partial C_{ox}'}{\partial r'} \right) \quad (4)$$

$$t'=0, \quad 0 \leq r' \leq 1, \quad C_c' = 1, \quad C_{ox}' = 0$$

$$t' > 0, \quad r' = 1, \quad C_{ox}' = 1,$$

$$t' \geq 0, \quad r' = 0, \quad \frac{\partial C_{ox}'}{\partial r'} = 0.$$

The solution for this set of equations will depend only on two parameters: the ratio of carbon and oxygen concentrations as give by ψ and the Thiele modulus ϕ . Since ψ is not varied significantly in the experiments the regime of operation depends on the Thiele modulus alone. For large

values of ϕ the reaction is diffusion limited while at small values of ϕ the reaction is rate limited. The equations may be simplified for extreme values of ϕ . In the intermediate regime, solution of the equations as written is necessary. Numerical integration may be used but requires a relatively large amount of computing time (typically 20 minutes on an IBM 7094 for a single integration). A perturbation technique shows some promise in obtaining approximate solutions.

Weisz and Goodwin² have given solutions for both the rate-limited and diffusion-limited regimes. When the reaction is rate limited, the oxygen concentration may be assumed uniform throughout the bead and equal to the external oxygen concentration. Equation (1) may then be integrated to give

$$C_c = C_c^0 \exp(-kn C_{ox}^0 t). \quad (5)$$

For the diffusion-limited regime, Weisz and Goodwin relate the rate of carbon removal (and the change in radius of the carbon-containing sphere) to the rate of diffusion of oxygen into the pellet. A steady-state assumption is made in order to simplify determination of the oxygen diffusion rate. The resulting equations give the fraction carbon remaining y as a function of burning time where

$$\frac{1}{2} (1 - y^{2/3}) - \frac{1}{3} (1 - y) = Kt, \quad \text{Where } K = \frac{nDC_{ox}^0}{R_0^2 C_c^0} \quad (6)$$

The fraction carbon remaining is related directly to the radius R_b of the carbon-containing region by

$$y = \left(\frac{R_b}{R_0} \right)^3 \quad (7)$$

MATERIALS AND APPARATUS

The silica-alumina catalyst beads used contain approximately one per cent by weight carbonaceous material. These were obtained as a sample from a commercial TCC unit. Typical pellet characteristics are as follows:

Material:	SiO ₂ , Al ₂ O ₃ -10% wt., Cr ₂ O ₃ -0.15% wt.
Diameter:	0.4 to 0.5 cm
Carbon concentration:	1.0% wt.
Density:	1.2 gm/cm ³
Pore volume:	0.4 cm ³ /gm
Thermal conductivity:	10 ⁻³ cal/sec-cm-°C
Effective diffusivity for O ₂ :	2 x 10 ⁻³ cm ² /sec (500°C)

The pellet regeneration apparatus is shown in the photograph of Figure 1. When in operation the oven is

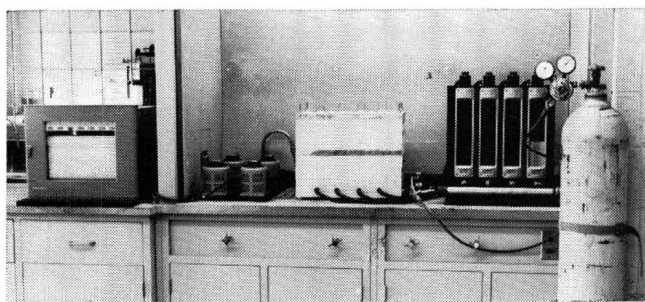


FIG. 1.—Apparatus for combustion of carbonaceous material in catalyst pellets.

located within a fume hood. Auxiliary components are located outside the hood.

Compressed air is supplied at about 50 psig to manifold with outlets to four rotameters (full scale — 1.12 SCFM air). Pressure is reduced to about one atmosphere and flow is controlled by $\frac{1}{8}$ -inch needle valves at the manifold outlets. The air from each rotameter passes to the oven through $\frac{1}{4}$ -inch ID rubber tubing.

Details of the construction of the oven are shown in Figure 2. The oven is made by stacking sections of Marinite 15, an asbestos material, drilled to provide four separate chambers together with necessary gas inlet, electrical lead and thermocouple ports. Each chamber is 1.5 inches ID and 13 inches high. The air supplied at the bottom of each chamber passed upward across a 2000-watt electrical heating coil (a heat gun replacement element), through a stainless steel safety screen past a thermocouple to stainless steel mesh baskets in which 10 to 20 pellets are placed. The baskets are cylindrical, 1- $\frac{1}{2}$ inches in diameter, $\frac{1}{2}$ inch high. These are supported on wires about 5 inches from the tops of the chambers. A second thermocouple is inserted from the top and located immediately above the basket in each chamber. Gas exhausts directly from the open top of each chamber.

Power input to each oven heater is provided by a 7- $\frac{1}{2}$ -ampere variable transformer. Control of oven temperatures is manual. A multipoint temperature recorder is used to monitor all eight thermocouples.

For grinding sample pellets to expose cross-sections through their centers a 10-inch diameter, felt-covered lapping wheel is used with an alumina abrasive. Measurements of the size of carbon containing regions of the pellets are made with a cathetometer at 10x magnification. For measurements of density profiles of the carbonaceous deposits several types of optical densitometers have been used.

PROCEDURE

Several hours before the experiments are to be run the ovens are preheated to 850, 900, 950 and 1000°F with an air flow of about 20 SCFM. Fifteen to twenty pellets, selected for uniformity and spherical shape, are placed in each basket. A nitrogen flow is substituted for the air flow and the baskets are placed in the ovens and allowed to approach thermal equilibrium. At time zero the nitrogen flow is stopped and air flow begun.

At fifteen-minute intervals each basket is lifted from its oven and two sample pellets are removed. The remain-

ing pellets are mixed to aid in uniform oxidation. The combustion is continued for a period of 2 to 2 $\frac{1}{2}$ hours.

After practice with unburned pellets, students grind the sample pellets on the lapping wheel to obtain flat center sections. A wet alumina powder is used as the abrasive. Pellets are held by hand. The pellets are then placed in water in a shallow dish and measurements of the diameter of the carbon-containing core (for fish-eye burning) and pellet diameter are made. Qualitative observations of pellets burned under rate-controlled conditions are made.

The grinding operation can be avoided with some sacrifice in accuracy by making measurements of the carbon core in whole pellets. The measuring errors due to refraction of light are reduced by placing the pellets under water for the measurements. If the pellets are placed in water about 1 mm deep capillary action causes the water to fill the pellet without trapping air in the pores. The water level is then raised and measurements are made with the cathetometer.

Measurements of carbon concentration with an optical densitometer require at least a second three-hour period. One half of each pellet is removed by grinding and the remaining half is cemented to a glass microscope slide with a drop of rosin placed on the heated slide. The pellet is lapped further to obtain a thin center section. It is rinsed, saturated with water and placed in the optical densitometer. Blank measurements are made at the center and edges of the pellet where either all or none of the carbon remains. Light transmission is then measured as a function of position within the pellet. The readings are converted to fraction carbon remaining with the assumption of Beer's law. The success of the measurements depends almost entirely on obtaining a section as thin as 0.1 mm so that light transmission in the sample is adequate.

STUDENT PERFORMANCE

Because this experiment requires several hours to conduct, students are given a complete set of specified operating conditions and the procedure

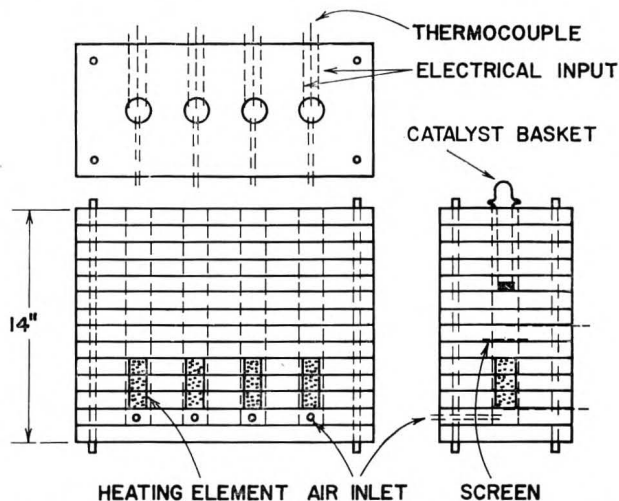
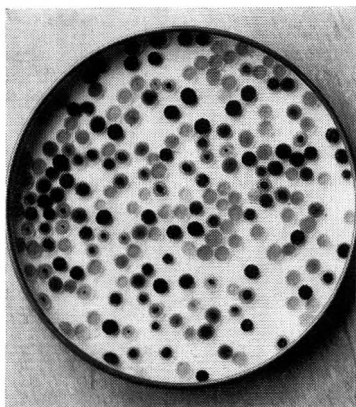


FIG. 2.—Drawing of oven for TCC catalyst regeneration at four temperatures.

FIG. 3.—Collection of partially regenerated pellets.



is outlined to them. Unfortunately there is no time available for students to determine procedures in a single laboratory session.

Students have no difficulty with the carbon burning operation if the laboratory air pressure and electrical voltage are reasonably constant. Otherwise temperature control of the ovens may present difficulties. Initially, there were occasional burned fingers in removing pellets from the baskets but an assortment of pliers and tweezers eliminated this hazard. Some practice is required for the pellet lapping to be successful but most students have little difficulty in grinding away half the pellet without losing the pellet or damaging their fingers. The measurements with the

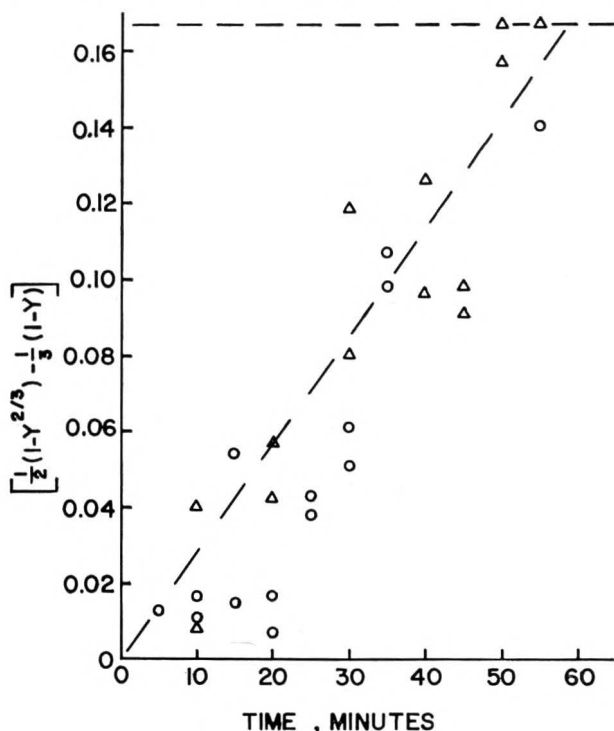


FIG. 4.—Student correlation of results for oxidation under diffusion-limiting conditions.

cathetometer are straightforward.

Measurements with the optical densitometer were attempted with several student groups. The techniques required for obtaining thin center sections are difficult and most students were unsuccessful. Reliable results were obtained only when the instructor took charge in what approached a "demonstration" experiment.

A collection of pellets from students' experiments is shown in Figure 3. These pellets were oxidized under the various oven conditions and show the effects of rate-limited, intermediate and diffusion-limited oxidation. The results obtained by one group of students using the cathetometer for measurements are shown in Figure 4 in which a function of the fraction carbon remaining is plotted against time as suggested by Eqn. (6). A part of the scatter in the data is due to variations in pellet diameter. This could be eliminated by using t/R_0^2 as a modified time parameter. The value of K determined from the experiment was within a factor of 2 of that calculated from the pellet characteristics.

DEVELOPMENT OF THE EXPERIMENT

The experiment follows from the original investigations by Weisz and Goodwin. In the first version of the oven, a tubular combustion furnace was used. Two baskets were placed one above the other in the vertically-mounted chamber. Temperature control proved difficult and only two regions of operations could be examined at one time. The specially-designed oven allows four baskets to be used and improves temperature control. The installation of a pressure regulator on the air supply and use of packed beds of metal below the baskets to damp fluctuations would improve control still further.

It is doubtful whether the measurement of carbon density profiles could be improved to the extent that students could obtain satisfactory results in a few hours. As a more lengthy project in conjunction with numerical solutions of the transient equations profile measurements might be valuable.

REFERENCES

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2. P. B. Weisz and R. D. Goodwin, *J. Catalysis* 2, 397 (1963).