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UTILIZATION OF THE RECYCLE REACTOR IN DETERMINING KINETICS OF GAS-SOLID CATALYTIC REACTIONS

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CATALYSIS AND REACTION modeling comprise a substantial portion of many reaction engineering courses, as well as being subjects of considerable industrial interest. Classroom lectures in this area of instruction are, with greater frequency, being supplemented by laboratory experiments. Several experiments, suitable for an undergraduate laboratory course, have previously been described. These have included both homogeneous reactions (typical examples being saponification reactions [16, 17], and the popular reaction of $Na_2S_2O_3$ with H_2O_2 for demonstration of reactor stability described by Schmitz [13]) and heterogeneous reactions (of which hydrocarbon or methanol oxidation on Pt wire [1, 6], alcohol dehydration on alumina in a batch [9] or fixed bed reactor [11], and ethylene hydrogenation on a Pt coated tube wall [2] are typical examples.)

The conservatively clad **Arvind Varma** (left), received his PhD at Minnesota under the direction of Neal Amundson. Varma also immersed himself in experimental work at the University of Minnesota under Aris McPherson Rutherford, noted distillation expert. The chap dozing on the right is **J. J. Carberry** (PhD, Yale), who is no doubt contemplating his co-authorship with Aris McPherson Rutherford of the monograph "Aquinas, Boethius and their Indebtedness to the Gill Report" to be published by the University of Houston Athletic Department. The fellow in the middle who did all the work reported here is **Steve Paspek** (PhD, Notre Dame 1979). This paper is based upon Steve's undergraduate senior year project. Steve is now with SOHIO where it is hoped that their equipment and instrument budget is commensurate with his Ambrosian tastes which nearly bankrupted Notre Dame.

While experiments involving homogeneous liquid phase reactions are relatively routine, formidable difficulties exist in the accurate modeling of solid catalyzed gas phase reactions. The majority of these problems can be attributed to gradients of temperature and concentration within the catalyst pellet and the reactor; such gradients frequently mask kinetic data to the point of rendering it useless. While it is difficult to design a perfect laboratory scale reactor to determine the kinetics of a gas-solid catalytic reaction, this paper indicates that an external recycle reactor will economically eliminate gradients for a number of gas-solid heterogeneous systems.

COMMON BENCH SCALE REACTORS

REACTORS IN LABORATORY use fall into four general categories: fixed bed reactors (including integral and differential types), pulsed reactors, agitated reactors, and recycle reactors. Excellent reviews of the various reactor types and their merits are given by Weekman [15] and by Doraiswamy and Tajbl [8]. Some serious difficulties inherent to the first three categories of reactors are presented below.

The integral packed bed reactor can rarely be operated in an isothermal fashion. At even moderate enthalpies of reaction, substantial amounts of heat are generated, creating both radial and axial temperature gradients. Zoned heat control, as illustrated by Viselov et al. [14] can minimize axial temperature profiles, but cannot mitigate radial gradients. Furthermore, the change of gas com-

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position with bed depth leads to severe concentrational gradients, making the acquisition of meaningful kinetic data very difficult.

Use of the differential packed bed reactor is an attempt to minimize gradients by operating at extremely low conversion levels. This effectively limits the amount of heat generated, allowing near-isothermal operation. However, as noted by Weekman [15], extremely precise analytical techniques are required to measure the minute differences between the feed and effluent streams. For multicomponent systems this problem is intensified.

The pulse reactor yields differential results at relatively large conversion levels. However, the results are characteristic of only the initial catalytic response; the reactor cannot be operated in steady state. Furthermore, Makar and Merrill [10] note that the concentration of reactant species upon the catalyst surface changes as the pulse is forced through the reactor by the inert carrier, thus masking the true rate-concentration functionality.

Agitated reactors include the spinning-basket configurations developed by Carberry [12] and Doraiswamy [7], as well as internal recycle configurations popularized by Berty [3] and Bennett [4]. By virtue of severe agitation within the reaction vessel, the gas phase is mixed to a uniform composition and temperature. In the internal recycle reactors, the stationary catalyst bed allows direct measurement of the catalyst temperature. However, in the spinning basket design, the actual catalyst temperature cannot be measured; it must be inferred from the rate of reaction, the heat of reaction, and the rates of heat and mass transfer within the reactor. Unfortunately, the actual gas velocity relative to the catalyst pellet cannot be determined, and the standard correlations for heat and mass transfer rates cannot be applied to the system. Furthermore, both the spinning basket and internal recycle configurations involve a rather elaborately machined (and hence expensive) reactor vessel, as well as high temperature rotating seals.

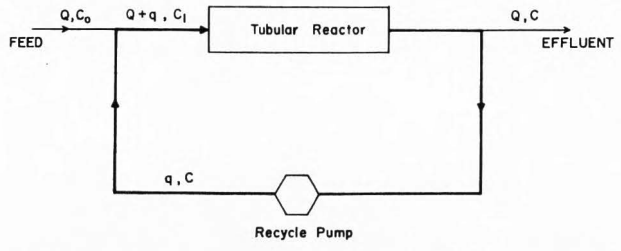

FIGURE 1: Schematic of external recycle reactor system.

EXTERNAL RECYCLE REACTOR

THE EXTERNAL RECYCLE REACTOR (Fig. 1) consists of a small isothermal tubular reactor coupled with a bellows-type recycle pump. The per pass conversion in the tubular reactor is quite low, approaching that of a differential reactor, and minimizing the amount of heat generated. However, by recycling a large portion of the effluent through the fixed catalyst bed many times, the overall conversion level is raised to that of an integral reactor. The reactor construction, detailed below, involves only readily available stainless steel tubing and Swagelock fittings; no machining is required.

The gas velocity relative to the catalyst particles can be easily determined, allowing the use of standard heat and mass transfer correlations for fixed beds. In addition, above a certain minimum rate, the gas velocity can be varied to suit the reaction system without effecting kinetic measurements. The recycle ratio R is defined as the ratio of the volumetric flow rate of recycled effluent/feed; as R increases, the reactor behavior approaches that of a CSTR.

A material balance around a recycle reactor for a first order reaction yields the expression

$$\text{Rate} = \frac{C_o}{\theta}\left[1 - \frac{\exp(-k\theta/R + 1)}{(1 + R) - R\exp(-k\theta/R + 1)}\right] \quad (1)$$

where C_o is the reactant concentration in the feed, k is the rate constant, and θ is the holding time (i.e., catalyst bed volume/volumetric feed rate). In the limit of $R \to \infty$, this expression reduces to

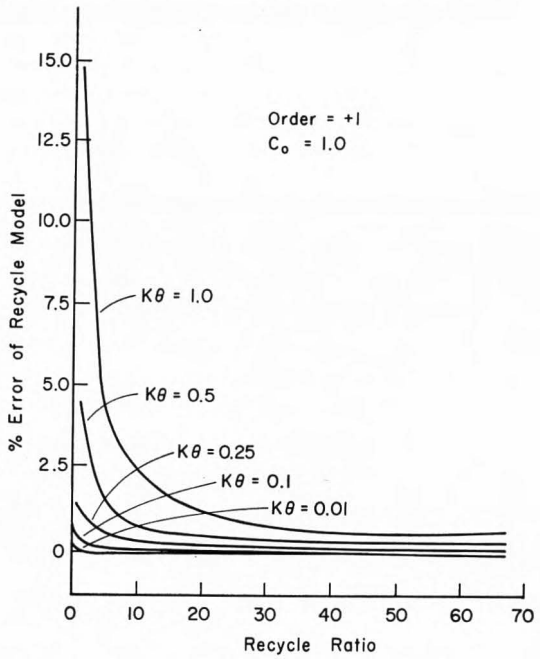

FIGURE 2: Plot of relative error between CSTR model and recycle reactor model for finite recycle ratios.

the CSTR rate expression

$$\text{Rate} = (C_o - C)/\theta \qquad (2)$$

The error between these two rate expressions is plotted in Fig. 2 for finite values of R. In general, the error is less than 1% for values of R greater than 25.

The instructional merit of the recycle reactor is that by operating with recycle ratios from 0 to over 25, plug flow to CSTR behavior becomes manifest, although complete isothermality is not guaranteed at recycle ratios less than 25.

EXPERIMENTAL DETAILS

THE REACTION VESSEL AND the preheater are 1.25 x 35 cm. SS tubes. The reactor tube is packed with active catalyst, while the preheater tube is filled with inert alumina pellets to promote mixing. Both tubes are held at constant temperature in individually controlled electric tube furnaces. Thermocouples are inserted into the gas stream at the exit of the preheater and the reactor through standard Swagelock fittings.

The recycle pump* is a metal bellows pump designed for high temperature operation, with a nominal capacity of 600 scc/sec. A standard arrangement of valves, rotameters, etc. is employed to control the reactor feed, admitted to the preheater at room temperature and atmospheric pressure.

Cooling coils quench the reactor effluent to reduce pump wear. Both the reactor feed and effluent compositions are determined via gas chromatography. The effluent sample is taken from the discharge side of the recycle pump; due to the pump's high suction, the inlet pressure is too low to allow flow through the chromatograph sample valve. Volumetric flow rates are determined by a mass flow meter or a soap film meter.

The recycle reactor can be easily automated by the addition of several cam timers, solenoid valves, and automatic needle valves. To determine isothermal kinetics, one must measure the reaction rate at a number of different reactant concentrations. This involves setting a feed rate and concentration, allowing the system to stabilize and equilibrate, and then sampling the feed and effluent streams to accurately determine their compositions. The reaction rate is calculated as the difference in composition divided by the holding time. A new feed composition or net flow rate is then selected, and the process is repeated.

Automatic operation was achieved by installing timer controlled solenoid valves on the feed and effluent lines, which periodically admitted samples to a gas chromatograph. The feed concentration was varied by coupling a small 1 RPM motor to a standard 10 turn needle valve. A cam timer activated the motor for a fixed period of time (i.e., 10 seconds) resulting in a fractional opening or closing of the valve, with the subsequent change in feed composition. The net reactor flow rate was continuously monitored by an electronic mass flow meter. However, the flow rate could also be measured with a soap film meter, and assumed constant for small changes in the

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*Recycle pump available from Metal Bellows Corporation, 1075 Providence Highway, Sharon, Mass. 01067. Model MB-158HT was used in the apparatus.

minor reactant flow rate.

A schematic of the apparatus appears in Fig. 3.

APPLICATION OF THE RECYCLE REACTOR TO CO OXIDATION KINETICS

THE CATALYTIC OXIDATION of CO to CO_2 over noble metals is an interesting reaction because of the curious dependence of rate upon CO concentration (in excess O_2) :

$$\text{Rate} = \frac{kC}{(1 + KC)^2} \qquad (3)$$

The kinetics, then, are of positive order for low CO concentrations, and change to negative order at CO concentrations greater than approximately 1%. Typical data for supported platinum are shown in Fig. 4.

Rate constants are easily determined by a least-squares fit of the rearranged rate expression:

The recycle reactor can be easily automated by the addition of several cam timers, solenoid valves, and automatic needle valves.

$$\sqrt{\frac{C}{\text{Rate}}} = \frac{KC}{\sqrt{k}} + \frac{1}{\sqrt{k}} \qquad (4)$$

By assuming the Arrhenius form of the rate constants, and determining their values at several temperatures, the activation energies can be deduced. Results for platinum, shown in Fig. 5, are in excellent agreement with current literature data.

INTERPHASE GRADIENTS

Concentration and temperature gradients between the catalytic surface and the bulk gas phase depend upon two parameters as defined by

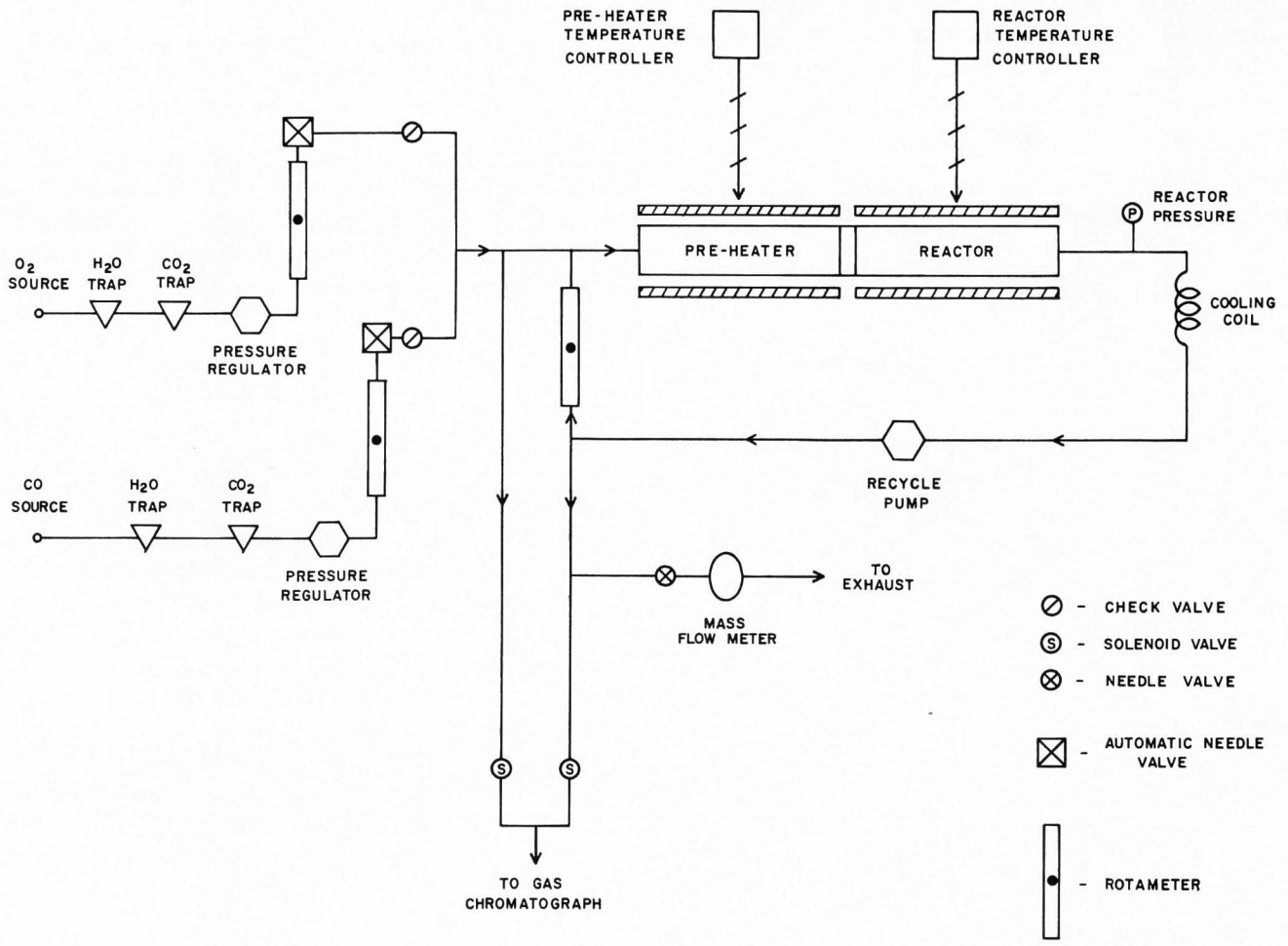

FIGURE 3: Details of Notre Dame automated recycle reactor system.

Carberry (5):

$$\eta Da = \frac{\text{Rate}}{k_g a C}$$

$$\overline{\beta} = \frac{-\Delta\ HC}{\rho C_p T Le^{2/3}}$$

where k_g is the external mass transfer coefficient, a is the surface to volume ratio of the catalyst pellet, ΔH is the enthalpy of reaction, T is the reaction temperature, Le is the Lewis number (usually one for gases), ρ is the gas density, C_p is the gas heat capacity, and C is the reactant concentration in the reactor (which is equal to the effluent reactant concentration at high values of R). Then, the dimensionless ratios of surface to bulk values are defined as:

$$\frac{C_s}{C} = 1 - \eta\ Da$$

$$\frac{T_s}{T} = 1 + \overline{\beta}\eta\ Da$$

Gradients of less than 1% will not significantly effect kinetic data. In this investigation, gradients were less than 0.2% for all operating conditions.

INTRAPHASE GRADIENTS

THE RIGOROUS EVALUATION of concentration and temperature profiles within a single catalyst particle involves the simultaneous solution of two coupled second order differential equations describing the heat and mass transport within the pellet. However, the maximum temperature difference between the center and surface of the pellet can be readily calculated (5):

$$\frac{\Delta T}{T} = \beta(1 - \eta\ Da)$$

where

$$\beta = \frac{-\Delta H\ DC}{\lambda T}$$

and D is the diffusivity of the reactant in the pellet, while λ is the pellet thermal conductivity.

This assumes that the reactant concentration is equal to zero at the pellet center, and is equal to $(1 - \eta\ Da)$ at the pellet surface. While the recycle reactor does nothing to eliminate this gradient, for small pellets, the internal temperature gradients are minimal. The gradients can be further limited, as in this investigation, by depositing active metal only on the external geometric surface of the pellet. The pellet center is then inert, and in the absence of reaction, remains near the surface temperature.

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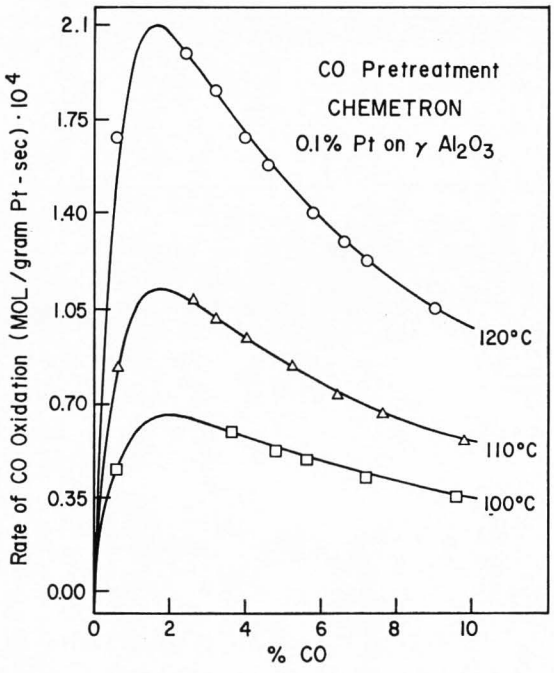

FIGURE 4: Plot of reaction rate vs. % CO for supported platinum catalyst.

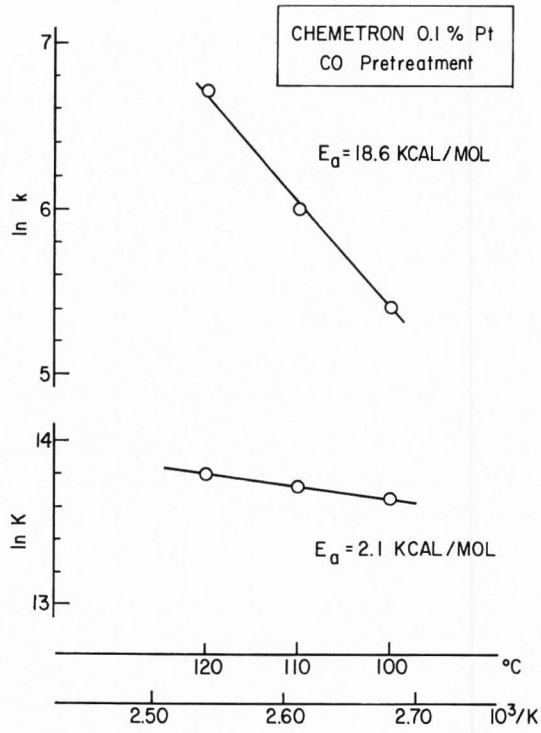

FIGURE 5: Plot of log k and log K vs. inverse temperature for supported platinum catalyst.

conditions for an optimum, one-dimensional optimization, unconstrained optimization, linear programming, nonlinear (constrained) optimization, staged system optimization, and optimization under uncertainty and risk. The last topic is the only unconventional chapter in the book. The chapter on linear programming takes a reasonably fresh, although rigorous, viewpoint. The LP presentation is not based on a cookbook manipulation but on vector-matrix manipulations. It is precisely this pedagogy, however, which makes the book non-introductory in nature.

The book will not help bridge the gap between theory and practice; very few complicated or real-world examples are worked out and presented. Another deficiency is that very few numerical details are provided, which would help the reader understand the computer "behavior" of various algorithms. Very few direct comparisons of comparable algorithms via common problems are drawn. At the end of several chapters, the authors give their recommendations on which methods to use for different types of problems, but their comments tend to be superficial and to ignore the many studies on optimization algorithms that have been undertaken. For example, the authors state that it is not possible to generalize upon the performance of existing nonlinear programming algorithms, a point with which I disagree. The authors devote only one paragraph to Powell's non-derivative method; it certainly deserves more. They also fail to point out some obvious deficiencies of some algorithms; e.g., the fact that the Davidson-Fletcher-Powell method becomes disadvantageous for large problems.

This book, like several others published recently, also includes a chapter on optimization of functionals. I have mixed feelings about including such a topic, since a single course on optimization must by necessity devote 95% or more of the lectures to static optimization. Therefore, such a topic is of dubious value in a book like this, except for limited self-study. In order to gain the proper perspective and background for optimization of functionals, the interested student or professional should take a course or read a book devoted exclusively to optimal control.

In summary, *Introduction to Optimization Theory* is a noble effort to use a rigorous, interdisciplinary approach for developing various optimization techniques. Its notation is clear, but to most chemical engineers the material and examples presented will seem a little sterile. □

RECYCLE REACTOR

Continued from page 82.

APPLICATIONS

EQUILIBRATION TIMES WERE determined by continuously monitoring the effluent composition with an infrared CO_2 analyzer. Steady state was generally realized in 30-60 minutes. Consequently, a large amount of data can be obtained in a relatively short time, making this system ideal for both undergraduate catalyst characterization experiments and graduate level research. Furthermore, catalyst beds can be easily changed, allowing the ready investigation of many different types of catalyst.

CONCLUSIONS

No laboratory reactor is truly ideal; nevertheless, the recycle reactor appears to offer a practical and educational solution to many of the problems which plague heterogeneous catalytic investigations, insofar as it offers isothermal operation at easily measured conversion levels. □

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