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The Use of a Gradientless Reactor in Petroleum Reaction Engineering Studies

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A laboratory-scale gradientless reactor based on internal recycling of reactants has been modified to provide reliable kinetic data for the mathematical modeling of petroleum processes. Ultraforming kinetic studies have shown that the reactor minimizes problems of heat and mass transfer, permits evaluation of a wide range of catalyst particle sizes without contacting and pressure-drop problems, and gives accurate data on deactivation rates which are not obscured by the coke gradients normally encountered in fixed bed or other types of reactors.

INTRODUCTION

Kinetic data, free from mass and heat transfer effects, are essential to the development of rate equations needed in the design of chemical reactors. Heterogeneous catalytic reactions, in particular, are difficult to study due to the possibility of film concentration and temperature gradients between solid catalyst and the fluid stream. Consequently, kinetic data from many laboratory and pilot plant reactors are obscured by purely physical processes occurring simultaneously with the catalytic reaction. For example, the batch reactor and the conventional stirred tank reactor are not well suited for vapor-phase catalytic studies, in which rates are typically very high. This leads to extreme difficulty in obtaining samples without affecting the relative concentrations of the reactants. Additionally, it is difficult to circulate catalyst pellets homogeneously in such configurations.

Consequently, most catalysis studies are conducted in flow systems that more closely resemble commercial processes, such as fixed bed, fluid bed, and recycle reactors (*1*, *2*). However, the fixed bed has substantial concentration and temperature gradients that are caused by integral conversion, and its operation is often restricted by excessive pressure drop. The fluid bed suffers from imperfect mixing of reactants, it can use only small catalyst particles, and its residence time distribution is frequently undefined. Recycle reactor systems, with either external or internal circulation, are probably the most useful for obtaining catalytic kinetic data. Nevertheless, external circulation is plagued by mechanical pumps, which require cooling and subsequent reheating of the recycle stream; also, perfect mixing, which depends on the recycle rate, is hard to achieve. CSTR behavior (perfect mixing) can be achieved in a recycle reactor if the recycle ratio is greater than 25 (*3*).

Reactors employing internal recycling are mainly of two types: the so-called "spinning basket" (*4*, *5*), in which the catalyst moves through the reactants; and the type originally designed by Berty and co-workers at Union Carbide Corp. (*6*), in which the reactant mixture moves through a stationary catalyst. Both types are referred to as gradientless because they suppress all gas-phase internal gradients.

The spinning basket reactor was developed by Professor J. J. Carberry and his co-workers at the University of Notre

Dame. This reactor is made so that the catalyst basket itself is rotated, thereby reducing film diffusion effects. The catalyst is contained in four baskets of approximately one particle thickness at right angles to each other. Propellers and baffles are added to increase mixing. The gas phase is well mixed, but there is some doubt as to how fast the gas actually moves past the catalyst particle. Also, the motion of the particles makes it difficult to measure temperature in the vicinity of the catalyst.

By using a *stationary* catalyst with turbine-driven circulation of the gas, the Union Carbide reactor system eliminates the temperature and velocity restrictions inherent in the spinning basket system. However, as originally designed, it could not be used above 600°F, which is far below the temperatures normally required for many petroleum processes.

With the cooperation of Autoclave Engineers, Inc., the original design has been modified to permit operation at higher temperatures. Thus, the modified gradientless reactor system can now be used up to 1100°F if the pressure is no more than 1000 psig, or up to 1000°F at 2000 psig. These conditions cover most current vapor-phase commercial catalytic processing in the petroleum industry.

The versatility of the modified system has been demonstrated in the evaluation of kinetic experiments on Ultraforming, a proprietary catalytic naptha reforming process of Amoco Oil Co.

Amoco Oil Gradientless Reactor System

Our aim was to design a bench-scale catalytic reactor to operate at commercial petroleum processing conditions and also eliminate the effect of external heat and mass transfer on the reaction rates. To satisfy this requirement each catalyst particle inside the reactor must be surrounded by a vapor at the same temperature and composition with film gradients around the pellet eliminated. Also, the physical environment around the catalyst particle must approach that in a full-scale commercial reactor.

The Union Carbide reactor met all of the above criteria with the single exception of being able to operate at petroleum processing temperatures, viz, in the range 700–1100°F. The Teflon bearing used in their standard Magne-drive assembly could withstand a maximum reactor temperature of about 600°F, which could not be exceeded merely by substituting a graphite bearing for Teflon. Graphite is not a suitable bearing material in a dry, high temperature, hydrogen-rich atmosphere. The problem was solved by adding an additional bearing made of Rulon, a ceramic material impregnated with Teflon, farther from the reactor body and surrounding it with a water cooling jacket (see Fig. 1). Without the jacket, any bearing in this position or closer to the reactor (as in the Union Carbide reactor) would be destroyed at 1100°F. Rulon was also used as the bearing material throughout the drive shaft and Magne-drive assembly. (Additional details are available from Autoclave Engineers, Inc.)

Details of the reactor flow are shown in Fig. 2. The reactant mixture enters the vessel through the inlet connection and is driven up the draft tube by the motion of the impeller. The vapor passes through the catalyst bed, moves outside the draft tube, and is then recycled through the catalyst bed. After some 20 to 100 passes, the mixture is expelled through the outlet connection by pressure difference. The high re-

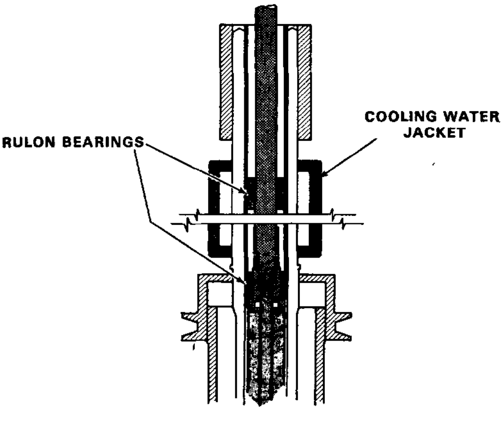

Fig. 1. Modified drive shaft assembly.

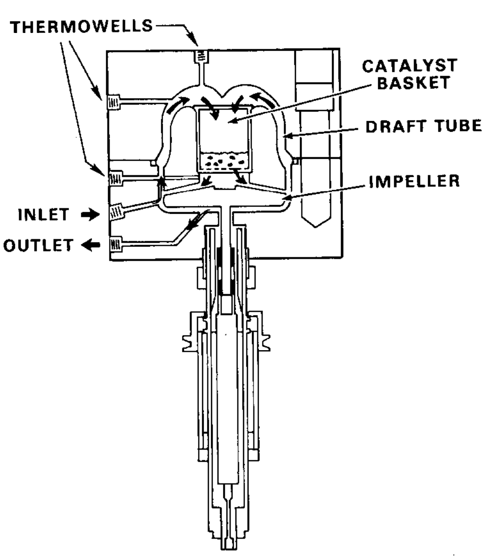

FIG. 2. Internally recycled catalytic reactor.

cycle rate insures that the vapor-phase mixture inside the reactor is completely backmixed, i.e., at a uniform temperature and composition.

The degree of mixing is a function of the impeller speed and the gas-phase density, and perfect mixing is easily achieved under most operating conditions. However, at high temperature and low pressure, some difficulty does arise. The criterion for complete mixing is the insensitivity of conversion to turbine speed at constant process conditions.

Recycle rates and hence linear velocity can be determined by measuring either the small pressure or temperature drop across the catalyst bed. The pressure drop is measured by sensitive manometers and then correlated with linear velocity by means of Leva's correlation (7). The temperature difference across the catalyst bed is determined by strategically placed thermocouples. The recycle rate can then be determined by thermodynamics based on the ratio of the adiabatic temperature change and the measured temperature difference.

$$\frac{\text{mass flow through the catalyst bed}}{\text{mass flow out of the reactor}} = \frac{\Delta T \text{ adiabatic}}{\Delta T \text{ measured}}.$$

The total adiabatic temperature change is calculated from heat and material balances. A typical value of the recycle rate in our experiments is 60, based on a thermodynamic calculation.

Because the gradientless reactor permits reaction studies at isothermal conditions with uniform concentrations, it eliminates the need for integral or partial-differential equations, whose solution often requires complex and lengthy computer programming and processing. Instead, each steady-state experiment with integral conversion yields a reaction rate that is simply calculated from the ordinary difference equation:

$$\frac{W}{F} = \frac{(X_o - X_i)}{r_p}, \tag{1}$$

instead of the integral equation:

$$\frac{W}{F} = \int \frac{dX}{r_p}, \tag{2}$$

where r_p is the global rate of reaction per unit mass of catalyst, F is the feed rate of reactant, W is the mass of catalyst, X is the concentration of reactant, and subscripts o and i refer to outlet and inlet concentration. Transient experiments can be analyzed with the simple differential expression:

$$\frac{W}{F} = \frac{(X_o - X_i)}{(dX/dt)\rho_{\text{cat}}^{-1} + r_p} \tag{3}$$

rather than with a partial-differential equation:

$$\delta\left(\frac{W}{F}\right) = \frac{\delta X}{(\delta X/\delta t)\rho_{\text{cat}}^{-1} + r_p}. \tag{4}$$

ρ is the density of the catalyst.

Since we were only concerned with steady-state experiments, all of our data were analyzed by the first equation. For fixed bed reactors, k, the rate constant, is calculated from the equation:

$$d\left(\frac{W}{F}\right) = \frac{dX}{r_p} = -\frac{dC}{Ckf(C)}, \tag{5}$$

where C is the concentration at a catalyst site. Simplifying assumptions are usually made so that the expression can be integrated analytically. This introduces some error. A precise value of k can normally only be determined by digital computation of a numerical solution. Such a solution would take axial as well as a radial concentration and temperature gradients into account. With the gradientless reactor, a more exact value of k is arrived at by means of a desk top calculation, namely Eq. (1).

Deactivation of catalysts by "coke," an important design parameter, has largely been evaluated in fixed-bed flow experiments with either steep coke gradients or low coke levels throughout the catalyst bed, neither of which lends itself well to mathematical precision. The coke level determined at the end of a run is an average value for the entire bed. It is difficult to dump a catalytic bed in order to determine an approximation of coke gradient. The mathematical relationship between deactivation rate, process conditions, and coke level suffers from such averaging. In the gradientless reactor, a precise deactivation rate can be determined for an actual coke level because in order to determine a point rather than an average value for deactivation, the system must be free of gradients in both coke and hydrocarbon composition.

In Fig. 3 we have illustrated the gradient present in a fixed bed catalytic reformer operating at integral conversion levels. The temperature varies due to the different heat effects of the complex reaction network. The reactant concentration decreases while passing through the bed as the reactant is converted to products. The undesirable side reaction is the production of coke, which, in this illustration, the concentration increases as the reactant passes down the bed. A precise mathematical design relationship between all these *nonlinear* interrelated parameters is difficult to obtain. In the gradientless reactor, the elimination of gradients at all coke levels gives a more exact relationship between deactivation and coke.

ULTRAFORMING KINETIC STUDIES

Ultraforming, which is a high-severity catalytic naphtha reforming process, operates at high conversions, and the catalyst deactivates rapidly between regenerations. Thus, kinetic studies are essential in order to model this process. These studies have been divided into three main areas:

1. Reaction mechanism.
2. Catalyst deactivation.
3. Mass transfer limitations.

Dehydrocyclization of paraffins, the slowest of the major types of reforming reactions, requires effective promoters to accelerate the reaction rate and decrease its decline with time.

Our studies were concerned with the reactions of n-heptane catalyzed by a commercial platinum-on-alumina catalyst which had been activated by a halide promoter. A bimetallic promoter, that reduces

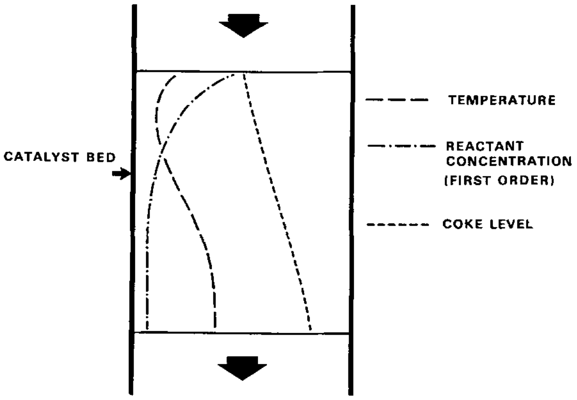

FIG. 3. Gradients in fixed bed tubular reactors with plug flow conditions.

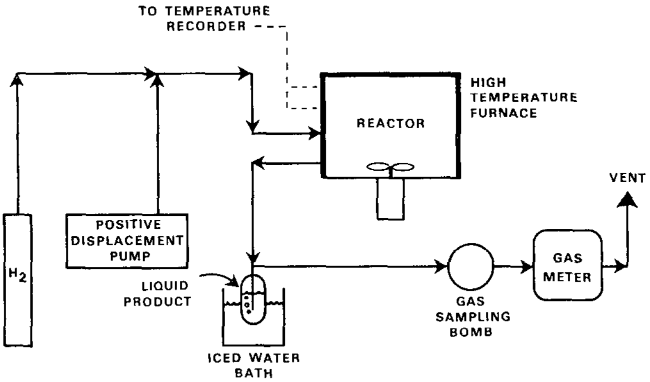

Fig. 4. Flow diagram of gradientless reactor.

deactivation rates, was present in some of the catalyst compositions. The n-heptane was dried with 3 Å molecular sieves. No impurities could be detected on a Hewlett-Packard 5750 gas chromatograph.

In a typical run, prepurified hydrogen was mixed with the hydrocarbon in the prescribed mole ratio (see Fig. 4). The reformate product was collected in an iced liquid–gas separator which was at reactor pressure. The overhead gas passed through a gas sampling bomb and a wet test meter. The liquid and gas samples were analyzed by gas chromatography and the results were combined to give the final values of the rate constants. A typical run lasted from a few hours to a few days. Process conditions were constant so that the catalyst deactivated at a constant temperature and pressure.

The basic kinetic scheme and mass balances are shown in Figs. 5 and 6. Because the precise determination of small methylcyclohexane (MCH) concentrations is difficult in samples containing large amounts of n-heptane, the dehydrogenation of MCH to form toluene is omitted from our mechanism. Also, because the kinetic rate constants depend on the platinum and halide present in the catalyst, the final values of the rate constants were corrected to a base case with known platinum, halide, and hydrogen concentrations.

In the next series of figures are presented some experimental results from our n-heptane catalytic reforming experiments. The data are presented on a semilog plot of the rate constant versus the square root of time on stream, the familiar Voorhies relationship. The rate constant is in units of g-moles per hour per gram of catalyst. The abscissa is in units of the square root of time. In Fig. 7, the dehydrocyclization deactivation is seen to take place in two distinct regimes, a rapid, initial step followed by a slower, more gradual decline. It should be pointed out that Arrhenius activation energies are normally based on initial values of the rate constant, which are determined by extrapolation back to zero time. Thus, both the initial, extrapolated value of the rate constant and the value of ΔE depend on which deactivation regime is chosen for extrapolation. Considerable confusion in the literature could have been avoided if the precise means of determining the value of the rate constants and ΔE had been disclosed.

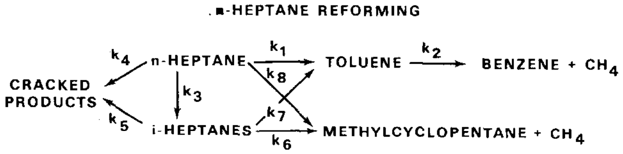

Fig. 5. Basic reaction mechanism.

$$Y = \text{MOLE FRACTION}$$

$$\theta = (\text{MOLAR SPACE VELOCITY})^{-1} = \frac{W}{F}$$

$$Y_{TOLUENE} = \theta\left[k_1(Y_{nC_{7o}} + Y_{iC_7}) - k_2\, Y_{TOLUENE}\right]$$

$$Y_{BENZENE} = \theta\, k_2\, Y_{TOLUENE}$$

$$Y_{nC_{7i}} - Y_{nC_{7o}} = \theta\, Y_{nC_{7o}}(k_1 + k_3 + k_4)$$

$$Y_{iC_7} = \theta\left[k_3\, Y_{nC_{7o}} - (k_1 + k_4 + k_6)\, Y_{iC_7}\right]$$

$$Y_{MCP} = 2\,\theta\, k_6\left[Y_{iC_7} + Y_{nC_{7o}}\right]$$

FIG. 6. Mass balances.

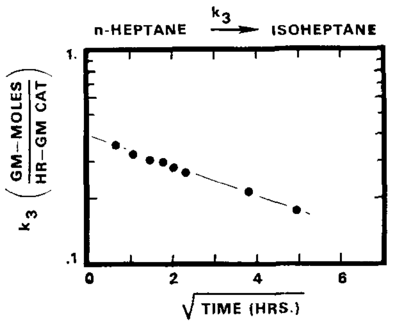

FIG. 8. Paraffin isomerization deactivation.

Rates of the other reactions in the *n*-heptane reaction mechanism decline more slowly than does that of the dehydrocyclization reaction. This difference is readily apparent from Figs. 8 and 9 where the paraffin isomerization rate constant declines at a fairly slow and constant rate and the hydrocracking rate constant not at all. Figures 7, 8, and 9 were obtained from a single experiment at commercial reforming conditions from which a point value of the end of run coke level of 3.35% was precisely measured.

The gradientless reactor is ideally suited to study the kinetic reactions of a wide range of catalyst particle sizes. Experiments have been conducted using particles which range from 1/12-in. extrudates to small 40-mesh particles. By varying particle size, one is able to ascertain the magnitude of intraparticle pore diffusion effects on reaction rate constants. Reducing the particle size and hence the diffusion length reduces the effect of this type of mass transfer resistance on reaction rate. Most bench-scale and pilot plant tubular reactor systems are limited to a fairly narrow range of particle size because of either contacting problems or pressure drop considerations. Both problems are eliminated in the gradientless reactor, which can use a wide range of catalyst sizes, and thus several differences in diffusion resistances.

For example, in Fig. 10, the dehydrocyclization rate constant is shown to increase when smaller size catalysts are used. In this case, the ratio of diffusion lengths is about 3 to 1. This mass transfer effect is purely intraparticle and not external because the linear velocity was varied over a wide range and found to have no influence on conversion.

One of the most significant advances in catalytic reforming technology occurred in 1968 with the introduction of platinum reforming catalysts promoted with a second metal. It was demonstrated that bimetallics reduced deactivation rates thereby increasing the time before the catalyst had to be

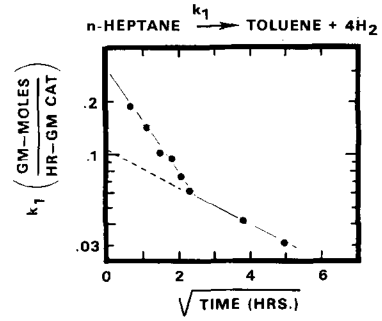

FIG. 7. Dehydrocyclization deactivation.

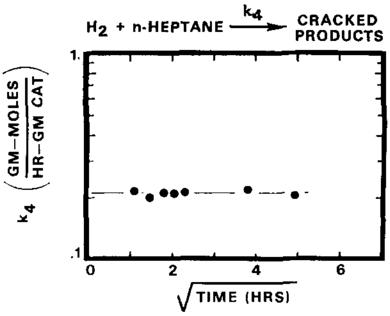

FIG. 9. Paraffin hydrocracking deactivation.

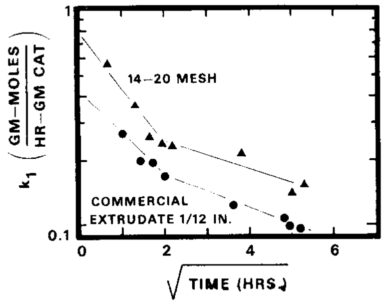

Fig. 10. Effect of pore diffusion on dehydrocyclization rate constant.

regenerated. Figure 11 shows the dehydrocyclization rate constant plotted as a function of $(t)^{1/2}$ for both the conventional and bimetallic reforming catalyst, which were evaluated in the gradientless reactor at the same process conditions. Both the initial and lined-out deactivation rates are significantly less when the promoter is added to the catalyst composition. Few hypotheses have appeared in the published literature to explain this novel effect. This is due, in part, to the difficulty in determining small differences in kinetic mechanisms and deactivation rates when fixed bed reactor systems are used. The hypotheses that the metallic promoter affects only the dehydrocyclization deactivation rate and not initial activity is substantiated in this particular experiment.

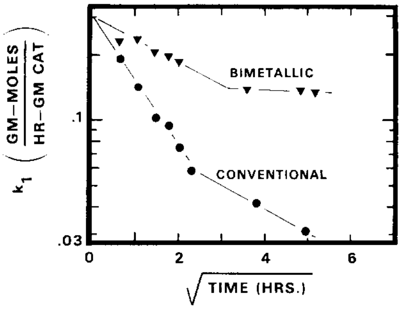

Fig. 11. Effect of bimetallic promoter on deactivation rate.

Summary

The Union Carbide internally recycled reactor was modified to permit kinetic studies and catalyst development work under gradientless conditions at temperatures up to 1100°F. Because external heat and mass transfer resistances can be eliminated, the modified reactor permits study of the true chemical kinetics of a reaction system, including deactivation mechanisms in the absence of coke gradients. Intraparticle effects can be precisely ascertained because of the large particle size range that can be used without contacting or pressure drop problems.

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References

1. Smith, J. M., "Chemical Engineering Kinetics," 2nd ed., Chap. 3, 12. McGraw-Hill, New York, 1970.
2. Levenspiel, O., "Chemical Reaction Engineering," Chap. 5. Wiley, New York, 1965.
3. Carberry, J. J., *Ind. Eng. Chem.* **56,** 39 (1964).
4. Tajbl, D. G., Simons, J. B., and Carberry, J. J., *Ind. Eng. Chem. Fundam.* **5,** 171 (1966).
5. Gillespie, B., and Carberry, J. J., *Ind. Eng. Chem. Fundam.* **5,** 164 (1966).
6. Berty, J. M., Hambrick, J. O., Malone, T. R., and Ullock, D. S., *AIChE Meet.,* New Orleans, LA. *1969.* Prepr. 42E.
7. Perry, J. H., "Chemical Engineering Handbook," 4th ed. McGraw-Hill, New York, 1963.