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MASTER

CONTINUOUS CHEMICAL REACTION
CHROMATOGRAPHY

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ABSTRACT

An experimental investigation of the catalytic dehydrogenation of cyclohexane over $\text{Pt/Al}_2\text{O}_3$ (60-80 mesh) in a rotating cylindrical annulus continuous chromatographic reactor was completed. A mathematical model of the reactor was developed and used for numerical simulation of reactor performance. Reaction yields in excess of the thermal "pot" equilibrium were obtained due to the chromatographic separation of the products in the reactor. An investigation of the kinetics of a candidate reaction for the continuous chromatographic reactor, the catalytic dehydration of tert-butyl alcohol over alumina, was initiated and is very nearly completed. A preliminary study of a counter-current moving bed continuous chromatographic reactor was done, and some aspects of the mathematical theory of countercurrent chromatography were considered.

A. A Rotating Cylindrical Annulus Continuous Chromatographic Reactor for Gas-Solid Reactions.

The experimental and modelling study of the performance of the rotating cylindrical annulus continuous chromatographic reactor for gas-solid reactions was completed in November, and a manuscript is being readied for publication. The chemical reaction employed in these tests was the catalytic dehydrogenation of cyclohexane by platinum supported on alumina.

The reactor is of aluminum, 18 inches in diameter by 30 inches in length, with a 1/4 inch cylindrical annulus about the circumference. The annulus is packed with 30-60 mesh alumina, serving both as a solid chromatographic stationary phase and a support for the platinum catalyst. The annulus rotates about the vertical axis, under a stationary feedport which delivers a continuous stream of cyclohexane vapor. Helium, serving as an inert carrier, is fed about the rest of the annulus. The reactor assembly is thermostatted in a resistively heated air oven. The reactor effluent is sampled at designated points about the annulus, and the samples analyzed by gas chromatography.

Tests were made to estimate the extent to which dispersion occurs as a species stream flows through the reactor. It was found that significant amounts of dispersion occur at the entrance and exit of the bed. Additionally, axial and circumferential dispersion cause further broadening of "peaks".

In experimental runs with the reaction occurring, the dispersion adversely affected the separation of the reactant and products. There was significant overlap of cyclohexane with benzene at the reactor exit. This caused the extent of reaction to be smaller than could be obtained if complete separation were obtained. Nevertheless, reaction yields which were larger than the thermal equilibrium yields based upon feed concentrations

were obtained. The above behavior contrasts strongly with the liquid phase reactor previously investigated. In the liquid phase dispersion effects were small, separations were large, and the reaction was driven to completion.

Numerical solutions of a discrete element model of the reactor were obtained. A parametric study was done to delineate how the variables of the problem affect reactor performance. Simulations of actual reactor performance were also done.

B. A Microcatalytic Reactor Study of the Dehydration of tert-Butanol Over Alumina.

As part of a continuing study supported by this grant to understand and to demonstrate continuous reaction chromatography, work has been undertaken to further developments initiated by two previous graduate students. The dispersionless model developed by B.K. Cho to model continuous reaction chromatography in a liquid/solid system was to be expanded to include dispersion and thereby be capable of predicting experimental results of a gas/solid system of the type developed by A.W. Wardwell. As input the model requires specifics concerning reactor geometry, experimental conditions, and reaction kinetics.

For investigation and experimentation, the decomposition of tert-butyl alcohol to isobutylene and water ($\text{CH}_3\text{-C}(\text{OH})\text{CH}_3 \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{-C}(\text{CH}_3)=\text{CH}_2$) using alumina as catalyst and chromatographic medium was chosen. Upon review of the literature no agreement was found concerning the reaction kinetics, and insufficient data were reported to develop the kinetics based on published results. Consequently, the task of investigating the kinetics on this catalyst was undertaken.

During the past year an appropriate column for separation of the reaction products has been selected, a microreactor has been fabricated and packed with catalyst and experimentation for determination of the kinetics of dehydration virtually completed.

To investigate the kinetics, a Barber Coleman GC which has independent temperature controllers for the injector and oven has been used. Separate temperature control is necessary in that at different carrier gas flow rates the elution times for the reaction products vary. On the one hand, to maintain approximately constant elution times the column temperature must vary inversely with flowrate. On the other hand, to run obtain isothermal kinetics the reactor must remain at constant temperature.

In order to take advantage of the separate controllers, the reactor was

made from a 5 cm length of thick walled 1/8" OD stainless steel tubing. This enabled the plumbing inside the injector box to be modified and a 5 cm length of tubing was replaced by the reactor. The flow of material is now from an injection chamber where the reactant is vaporized, through the reactor, through a swagelok union which separates the injector box from the oven, and into the analysis column.

Separation of reaction products is accomplished using a 2 m length of 1/4" OD 10 w/o carbowax 1540 on 30-60 mesh chromosorb T (teflon). The column separates the materials approximately by boiling point so that the elution order is isobutylene, tert-butyl alcohol, water, and $n\text{-C}_{11}\text{H}_{24}$. $n\text{-C}_{11}\text{H}_{24}$ is injected with the alcohol as an inert internal standard to provide a quantitative measure of the amount of alcohol injected.

It is expected that the data gathered to date will yield a rate expression, but the analysis is not yet complete. A plot of $\ln(1/1-X_A)$ vs. τ (X_A = conversion of alcohol, τ = space time) would yield a straight line if the kinetics were first order in alcohol concentration, but this was not the case. The kinetics are apparently complex. It is known that water inhibits the reaction and that at low temperatures ($T < 215^\circ\text{C}$) the reaction appears to be nearly zero order. As the temperature is raised, initial alcohol concentration has a marked effect on conversion. The data are currently being analyzed to obtain a rate expression. This should be accomplished in the very near future.

C. Preliminary Study of a Countercurrent Moving Bed Chromatographic Reactor (CCCR)

In the January, 1980 proposal, an idea for a countercurrent moving bed chromatographic reactor was outlined. It was speculated that the yield of a reversible reaction of the type $A \rightleftharpoons B$ might be caused to be greater than thermal equilibrium by the combined reaction and separation in the reactor. Briefly, the reactor operates by feeding a mixture of A and carrier gas into the center of a column containing downflowing granules of catalyst-chromato-

graphic stationary phase, and upflowing carrier gas. By proper arrangement of the countercurrent flows, if one species (say A) is strongly adsorbed, it may be carried downward on the solid, while if the other (B) is weakly adsorbed, it may be carried upward. If reaction can be made to occur solely in the section below the inlet, perhaps by heating, and not above the inlet, a reaction and separation may be achieved.

The preliminary work has been substantially completed. It is divided into three parts. (1) The equations describing the system have been determined, and first attempts at numerical solution of these partial differential equations of the model have been done. (2) Some chemical reactions that seem appropriate for experimental studies in this reactor have been identified. (3) A preliminary design of the experimental apparatus has been done.

Numerical solution of the equations describing a CCR. The reaction is described in terms of successive adsorption of reactant, reaction occurring on the surface, and desorption of product.

A^* and B^* are the adsorbed species, and k 's are first order rate constants. Let $C(x,t)$, $n(x,t)$ and $\gamma(x,t)$, $v(x,t)$ be the concentrations of A and B in the gas phase, and adsorbed on the surface, respectively. Also, if U and v are the velocities of gas and solid phase, ϵ is the bed porosity, and ρ_A

and $\mathcal{D}_B$ the diffusion coefficient for A and B, a mass balance over a control volume (assuming uniform flow profile) gives the following partial differential equations.

$$\frac{\partial c}{\partial t} + \frac{1-\epsilon}{\epsilon} \frac{\partial \gamma}{\partial t} + U \frac{\partial c}{\partial x} - \frac{1-\epsilon}{\epsilon} V \frac{\partial \gamma}{\partial x} - \mathcal{D}_A \frac{\partial^2 c}{\partial x^2} + \frac{1-\epsilon}{\epsilon} k_r \gamma - \frac{1-\epsilon}{\epsilon} k_r v = 0 \quad (1)$$

$$\frac{\partial n}{\partial t} + \frac{1-\epsilon}{\epsilon} \frac{\partial v}{\partial t} + U \frac{\partial n}{\partial x} - \frac{1-\epsilon}{\epsilon} V \frac{\partial v}{\partial x} - \mathcal{D}_B \frac{\partial^2 n}{\partial x^2} - \frac{1-\epsilon}{\epsilon} k_r \gamma + \frac{1-\epsilon}{\epsilon} k_r v = 0 \quad (2)$$

with bc: $C(0,t) = C_{A0}$, $n(0,t) = 0$

$$\frac{\partial c}{\partial x}(H,t) = 0 \quad , \quad \frac{\partial n}{\partial x}(H,t) = 0 \quad (= \text{uniform profile at the reactor exit})$$

and ic: $C(x,0) = 0$ for $C_0(x)$ $n(x,0) = 0$

This describes a slightly different situation from the above figure, one where A is fed at one end of the reactor, and A and B are both taken from the other end (where the solid enters). We can put (1) and (2) in dimensionless form using the following notation:

$$K_A = \frac{k_a^A}{k_d^A} \quad K_B = \frac{k_a^B}{k_d^B} \quad a = K_A \cdot C \quad b = K_B n$$

$$\alpha = \frac{\gamma}{\alpha^s} \quad \beta = \frac{v}{\beta^s} \quad (\alpha^s, \beta^s \text{ are the saturation concentration of } A^* \text{ and } B^*)$$

$$\theta = \frac{H}{u} \quad (= \text{residence time}) \quad \tau = \frac{t}{\theta} = \frac{tu}{H} \quad \xi = \frac{x}{H}$$

$$\mu_A = \frac{1-\epsilon}{\epsilon} K_A \alpha^s \quad , \quad \mu_B = \frac{1-\epsilon}{\epsilon} K_B \beta^s \quad , \quad \sigma_A = \frac{v}{u} \mu_A \quad , \quad \sigma_B = \frac{v}{u} \mu_B$$

$$S_A = \frac{\mathcal{D}_A}{uH} \quad , \quad S_B = \frac{\mathcal{D}_B}{uH} \quad , \quad \phi = \frac{\alpha^s}{\beta^s}$$

$$\pi_A = \mu_A \theta k_r \quad , \quad \pi_B = \mu_B \theta k_r \quad , \quad \rho_A = -\frac{\mu_A \theta \cdot k_r}{\phi} \quad , \quad \rho_B = \frac{\mu_B \theta \cdot k_r}{\phi}$$

Then equations (1) and (2) become:

$$\frac{\partial a}{\partial \tau} + \mu_A \frac{\partial \alpha}{\partial \tau} + \frac{\partial a}{\partial \xi} - \sigma_A \frac{\partial \alpha}{\partial \xi} - S_A \frac{\partial^2 a}{\partial \xi^2} + \pi_A \alpha + \rho_a = 0 \quad (1)$$

$$\frac{\partial b}{\partial \tau} + \mu_B \frac{\partial \beta}{\partial \tau} + \frac{\partial b}{\partial \xi} - \sigma_B \frac{\partial \beta}{\partial \xi} - S_B \frac{\partial^2 b}{\partial \xi^2} + \pi_B \beta + \rho_b = 0 \quad (2)$$

Now to get rid of the unknown concentrations α, β we have to assume that reaction takes place much slower than adsorption so that adsorption equilibrium (pseudo-steady state) is reached immediately at every point of the reactor. i.e.

$$k_a^A \cdot C(\alpha^S - \gamma) = k_d^A \gamma \text{ or } a = \frac{\alpha}{1-\alpha} \text{ or } \alpha = \frac{a}{1+a} \text{ and similarly } \beta = \frac{b}{1+b}$$

Substituting these two relations for α and β we get two non-linear equations.

The attempt to solve the system failed. A simpler form of the relation $\alpha = \frac{a}{1+a}$ mainly: $\alpha = a$ (and $\beta = b$) was used (this form is valid for low concentrations of A, B $a \ll 1, b \ll 1$). The final equations are:

$$(1 + \mu_A) \frac{\partial a}{\partial \tau} + (1 - \sigma_A) \frac{\partial a}{\partial \xi} - S_A \frac{\partial^2 a}{\partial \xi^2} + \pi_A a + \rho_A b = 0 \quad (3)$$

$$\text{and } (1 + \mu_B) \frac{\partial b}{\partial \tau} + (1 - \sigma_B) \frac{\partial b}{\partial \xi} - S_B \frac{\partial^2 b}{\partial \xi^2} + \pi_B b + \rho_B a = 0 \quad (4)$$

$$\text{with b.c.: } \xi=0 \quad a(0, \tau) = a_0, \quad b(0, \tau) = 0 \quad (5)$$

$$\xi=1 \quad \frac{\partial a}{\partial \xi}(1, \tau) = 0, \quad \frac{\partial b}{\partial \xi}(1, \tau) = 0 \quad (6)$$

$$\text{and i.c.: } a(\xi, 0) = 0, \quad b(\xi, 0) = 0 \quad (7)$$

The system of linear equations (3) and (4) was solved using an implicit finite-difference numerical scheme: $a(x, t)$ and $b(x, t)$ (there is a change of notation here: $\xi \rightarrow x$ and $\tau \rightarrow t$ since those are the more frequently used, also in order to keep in pace with the notation in the computer program). So $a(x, t)$ and $b(x, t)$ are approximated by $a(i\Delta x, j\Delta t)$ and $b(i\Delta x, j\Delta t)$.

The system of difference equations is:

$$(1 + \mu_A) \frac{a_{ij} - a_{ij-1}}{\Delta t} + (1 - \sigma_A) \frac{a_{i+1j} - a_{i-1j}}{2\Delta x} - S_A \frac{a_{i+1j} - 2a_{ij} + a_{i-1j}}{(\Delta x)^2} + \pi_A a_{ij} + \rho_A b_{ij} = 0 \quad (8)$$

$$(1 + \mu_B) \frac{b_{ij} - b_{ij-1}}{\Delta t} + (1 - \sigma_B) \frac{b_{i+1j} - b_{i-1j}}{2\Delta x} - S_B \frac{b_{i+1j} - 2b_{ij} + b_{i-1j}}{(\Delta x)^2} + \pi_B b_{ij} + \rho_B a_{ij} = 0 \quad (9)$$

The system of the difference equations (8), (9) was solved and some results

are given below. The values for the physical constants used were selected randomly but with care to be "reasonable".

Numerical Simulation of CCCR

$$U = 3 \text{ cm/s}; H = 250 \text{ cm}$$

$$k_r = k'_r = 0.05 \text{ s}^{-1}$$

Moving Bed			Fixed Bed		
ξ	a	b	ξ	a	b
0	1.000	0	0	1.000	0
0.05	0.789	0.023	0.05	0.81	0.023
0.10	0.627	0.041	0.10	0.667	0.042
0.15	0.502	0.055	0.15	0.549	0.056
0.20	0.406	0.065	0.20	0.456	0.067
0.25	0.331	0.072	0.25	0.381	0.076
0.30	0.274	0.078	0.30	0.322	0.082
0.35	0.229	0.082	0.35	0.274	0.087
0.40	0.195	0.085	0.40	0.236	0.091
0.45	0.168	0.087	0.45	0.206	0.094
0.50	0.147	0.088	0.50	0.181	0.096
0.55	0.131	0.089	0.55	0.162	0.097
0.60	0.118	0.089	0.60	0.146	0.098
0.65	0.108	0.089	0.65	0.133	0.098
0.70	0.100	0.088	0.70	0.122	0.098
0.75	0.093	0.088	0.75	0.113	0.097
0.80	0.088	0.087	0.80	0.106	0.097
0.85	0.083	0.086	0.85	0.100	0.096
0.90	0.079	0.085	0.90	0.094	0.095
0.95	0.075	0.083	0.95	0.088	0.093
1.00	0.071	0.082	1.00	0.082	0.092

From the results, we can see that the moving bed reactor gives better conversion than the fixed bed catalytic reactor (comparing in both cases the ratio B/A at the exit of the reactor). But the equations solved describe actually the simplest case of a chromatographic reactor. For the general case we have to include a feed point between the inlet and the outlet and force the equations to satisfy the mass balance for a control volume near the feed (there are also some problems of stability that have to be cleared first).

The second numerical method solves the system of eq. (3) and (4) at steady state (i.e. $\frac{\partial a}{\partial \tau} = \frac{\partial b}{\partial \tau} = 0$). A fourth order Runge-Kutta algorithm is used for the integration. Since the boundary conditions are given at the two different boundaries of the reactor, a shooting method is used for guessing and updating the value of a and b at $x=1$. The results obtained with this method were not comparable to those obtained from the difference equations.

We have to note that the first method, assuming that it converges as it did, is better to study the transient state and generally more accurate. The second method, since it is explicit, can lead to many solutions but it is more convenient for the study of the effect of different parameters in the steady state behavior of the reactor.

Chemical reactions that can be studied in a C.C.C.R. Any candidate rxn has to satisfy the following requirements:

- 1) It has to be a catalytic rxn of the form $A \rightleftharpoons B$ (or $A \rightleftharpoons B + C$ or $A + C \rightleftharpoons B$ where C will not affect the rate of the rxn; for example, if C is carrier gas.
- 2) Both forward and backward rxns have to take place on the solid phase only.
- 3) At some "reasonable" temperature (20°-200°C) the equilibrium of the rxn has to favor the formation of A.
- 4) Side rxns on the solid or fluid phase have to be avoided as much as possible.
- 5) The product of the rxn has to be different than the reactant w.r.t. the chromatographic properties. Namely, we expect A and B to be chromatographically separable.

6) Also, the solid phase supporting the catalyst should be one that increases the selectivity of A vs. B.

As a general conclusion for the above requirements, we can say that a possible rxn could be one in which we have:
a rearrangement of a group or bond to produce an isomer of the reactant, or disappearance of a characteristic group and formation of another of different polarity, or perhaps some selective hydrogenations. Some examples of suitable rxns are:

Disadvantage: possible side products are the cis and trans isomers of both forms.

Reaction (3), run with H_2 as carrier, looks particularly advantageous.

Design of the experimental apparatus. In order to be able to start some experiments even before a complete solution to the equations describing the C.C.C.R. was available, we designed a general purpose moving bed reactor (i.e. one which would allow experiments with different values of the physical parameters of the problem (solid and gas phase velocities, residence time, etc.)). This flexibility is desired even if we had from the beginning the rxn and all the required data since as reported by Cho in his Ph.D. thesis, for the same system for different conditions we have separation of reactant and product with the reactant feed at the top or the bottom or in between the column. The main parameter of interest for the C.C.C.R. is its length, since we assume that we have no radial gradients of the concentration. A pyrex-glass column of $D_i=1''$ with total length 10 ft. divided in 5 pieces of length 1 ft-3 ft is going to be used. Gas sample tubes are located along the column

at four inch intervals. The solid flow is calibrated using diaphragms of different diameter at the bottom of the column (free-falling bed). According to the needs of the experiment, part of the column can be heated externally with an electric coil or cooled using the cooling jacket.

D. Mathematical Theory of Countercurrent Chromatography

Last spring one of our very good undergraduate students expressed an interest in doing some work on this research project. Since he (Dimitry Altschuler) is majoring in both mathematics and chemical engineering, it was felt that he could make a contribution by investigating some aspects of the theory of countercurrent reaction chromatography.

1. Chromatography of a single solute without chemical reaction.

This case is the simplest one, and can serve as a starting point for further study. The mathematical model of this case is composed of two nonlinear differential equations (for solid and liquid phases) which can be easily reduced to a single one. The analytical study of this case is complete. All integrations have been carried out analytically. Another part of this problem is the optimal temperature profile. Two possible approaches to this problem are Pontriagin's Maximum Principle and Dynamic Programming. So far, we have obtained the integral formula via Maximum Principle.

2. Chromatography of two solutes without chemical reaction.

The mathematical analysis of this case is at the very beginning. The mathematical model reduces to two differential equations which can be studied on the phase plane. Apparently there is no way to solve this problem analytically, and it will be therefore necessary to use numerical and/or approximation methods. One fact has been proved: there exists one and only one equilibrium point, which is an unstable node.

3. Chromatography with reversible first-order reaction.

This case is perhaps the most important and the most interesting mathematically. The model includes four differential equations. It is, however,

possible to split the differential system into linear and nonlinear parts.

This permits the approximate solution via singular perturbations for the situation when the rates of adsorption of both reagent and product are much greater than the rate of forward reaction.

II. PERSONNEL

A. Co-principal Investigators

1. Rutherford Aris spent 100% of full time for one summer month in 1980 on research supported by this DOE contract. Between 1 May and 15 June, 1980, and from 15 September to present, he spent 10% of full time on the project.
2. Robert Carr spent 100% of full time for one summer month in 1980 to research supported by this DOE contract. Between 1 May and 15 June, 1980, and from 15 September to the present he spent 10% of full time upon the project.

B. Graduate Students

1. Alan Wardwell completed his investigation of the gas-solid continuous annular chromatographic reactor in November. He is currently employed by Conoco in Ponca City, Oklahoma.
2. John Bradfute. A microcatalytic reactor study of the kinetics of tert-butyl alcohol dehydration. M.S. expected March, 1981.
3. Theodore Petroulas, M.S., Purdue University. A combined experimental and modelling study of a moving bed continuous chromatographic reactor.

C. Undergraduate Student

Dimitry Altschuler. Third year student, majoring in both chemical engineering and mathematics. Spent last summer working on theoretical aspects of counter-current moving bed reactors.

III. PUBLICATIONS

A. Published

B.K. Cho, R.W. Carr, Jr., and R. Aris, A Continuous Chromatographic Reactor. Chem. Eng. Sci., 35, 74 (1980).

B.K. Cho, R.W. Carr, Jr., and R. Aris, A New Continuous Flow Reactor for Simultaneous Reaction and Separation. Separ. Sci. and Technol 15, 679 (1980).

B. Submitted

B.K. Cho, R. Aris and R.W. Carr, Jr., A Counter-Current Chromatographic Reactor.

C. In Preparation

B.K. Cho, R.W. Carr, Jr., and R. Aris, A New Performance Criterion for Chromatographic Reactions.

A.W. Wardwell, R.W. Carr, Jr., and R. Aris, An Annular Continuous Chromatographic Reactor for Gas-Solid Reactions. The Dehydrogenation of Cyclohexane.

D. Conference Paper

Dimitry Altschuler. Optimal Temperature Profile for Steady State Operation for a Counter-Current Moving Bed Chromatographic Reactor. 181st ACS National Meeting, Atlanta, GA, 2 April, 1981.