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Effect of Fouling in a Fixed-Bed Reactor for a Complex Reaction: Test of Proposed Model and Formulation of an Optimal Policy*

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The model proposed earlier by Sadana and Doraiswamy [*J. Catal.* 23, 147 (1971)] has been experimentally verified using the consecutive reaction system: tetrachloroethane → pentachloroethane → hexachloroethane; the reaction was carried out on activated silica gel using a mixture of tetrachloroethane and chlorine as feed. The dependence of the rate constant on time was observed to be linear and the selectivity for the intermediate product was independent of the decay parameter, as postulated in the model. It was found necessary, however, to rewrite the linear decay function used by Sadana and Doraiswamy in a slightly different form to enable the testing of the model.

The reaction and decay parameters can be manipulated in such a manner as to give the maximum yield of the intermediate at all times during the reaction. For this purpose an optimal feed policy has been formulated which necessitates the variation of feed in a predetermined manner.

NOMENCLATURE

A	Reactant
B'	Reaction parameter, $Wk_{1.0}/F$ (dimensionless)
C	Plant capacity (g-moles/hr)
f	Void fraction of the bed
F	Feed rate of A across the bed, F'/f (g-moles/hr)
F'	Feed rate of A (g moles/hr)
F_0	Initial feed rate of A corresponding to $y_{R,\max}$ (g-moles/hr)
F_{Cl}	Feed rate of chlorine (g-moles/hr)
$\bar{F}$	Feed rate of A at any decay time (g-moles/hr)
$k_{1.0}$, $k_{2.0}$	Rate constants for steps 1 and 2 at no decay (g-moles/hr)
$k_{1.i}$, $k_{2.i}$	Rate constants for steps 1 and 2 at any decay time (g-moles/g hr)
r	Rate of reaction (g-moles/g hr)
R	Intermediate desired product
s	Selectivity, $k_{1.0}/k_{2.0}$
S	Undesired product
t	Clock time (hr)
t_m	Catalyst decay time (hr)
T	Temperature of bed (°C)
W	Weight of the catalyst (g)
x	Fractional conversion of A
y_A, y_R, y_S	Instantaneous mole fractions of A, R, S in the product
$y_{R,\max}$	Maximum yield of intermediate
α_1, α_2	Decay velocity constants for steps 1 and 2 (1/hr)
θ	Normalized time, t/t_m (dimensionless)
λ	Decay parameter, αt_m (dimensionless)

INTRODUCTION

It is a matter of common experience in the chemical industry that the cost of replacement or regeneration of a decaying catalyst plays a dominant role in deter-

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mining the cost structure. The frequency of catalyst replacement or regeneration is dependent not only on the type of catalyst, feedstock and operating conditions (such as reactor temperature), but also on the reactor type—a fact not often appreciated.

Although considerable literature (*1–15*) has accumulated on the subject of catalyst fouling during the last decade, the first significant attempt to relate the performance of a reactor charged with a time-decaying catalyst to the properties of the reactor itself was made by Weekman (*16, 17*). His method was characterized by the introduction of two dimensionless parameters, one for the extent of reaction and the other for the extent of decay, and was developed for a simple reaction of the second-order which is frequently encountered in the catalytic cracking of petroleum feedstocks. Later Weekman and Nace (*18*) applied Weekman's model to a consecutive reaction system, and showed that the time averaged yield of gasoline, the intermediate, in a fixed-bed reactor was a kind of kinetic disguise. (At the end of this paper, we have proposed and illustrated an optimal feed policy to circumvent the time-averaging of yield of intermediate in a fixed-bed reactor). Weekman and Nace also described conditions for maximum intermediate yields in fixed-, moving- and fluid-bed reactors.

Sadana and Doraiswamy (*19*) who followed up Weekman's work dealt with a similar problem and made a further theoretical analysis of the behavior of fixed-, fluid- and moving-bed reactors under conditions of catalyst decay. They studied a hypothetical two-step series reaction of the type $A \rightarrow R \rightarrow S$ with identical decay parameters for both the steps, using two different decay patterns, exponential and linear. Two interesting observations were made: (a) the yield of intermediate y_R showed a maximum [Fig. 4 of Ref. (*19*)] with increase of the decay parameter λ; (b) the optimum space velocity was broader at higher levels of fouling (unpublished data). However these points were not experimentally verified. The object of the present paper is to verify the validity of these findings and to formulate an optimal feed policy for a fixed-bed reactor operating with a decaying catalyst such that the yield of intermediate is maximum at every instant during the on-stream time.

EXPERIMENTAL METHODS

Choice of System

Considerable preliminary screening had to be done in the choice of a suitable reaction system. The reaction selected was chlorination of tetrachloroethane (TCE) to hexachloroethane (HCE) via pentachloroethane (PCE),

$$C_2H_2Cl_4 \rightarrow C_2HCl_5 \rightarrow C_2Cl_6,$$

on activated silica gel ($-30 + 40$ mesh). Preliminary runs, shown in Table 1, revealed the following: (a) at higher temperatures thermal chlorination took place and side reactions were also present, viz,

TABLE 1
PRELIMINARY RUNS

				Product distribution (mole %)				
No.	Mole ratio Cl_2:TCE	Catalyst	Temp (°C)	Trichloroethylene	Tetrachloroethylene	TCE	PCE	HCE
1	4:1	None	300	4.6	1.2	84.2	9.8	0.20
2	4:1	None	250	3.4	0.8	87.5	8.1	0.15
3	4:1	Silica gel	300	10.5	8.0	36.0	40.5	5.00
4	10:1	Silica gel	300	1.3	0.1	46.2	48.9	4.90
5	10:1	Silica gel	200	—	—	65.3	32.3	2.40
6	10:1	None	200	—	—	99.6	0.4	—

dehydrochlorination of TCE to trichloroethylene and PCE to tetrachloroethylene; and (b) at lower temperatures ($\leq$200°C) and high chlorine to TCE ratios (10:1) homogeneous conversion to PCE was less than 0.5% while that to HCE was not detectable, and the dehydrochlorination reactions were eliminated. All the runs were therefore carried out at 200°C. No experimental verification of the irreversible nature of the reactions was attempted as it is known from thermodynamic considerations that hydrochlorination of PCE or HCE with liberation of chlorine is not significant at the temperatures considered.

Experimental Assembly and Organization of Runs

The experimental assembly consisted mainly of four units: constant rate feeding system for TCE and chlorine; reactor, preheater and thermostat assembly; product separator and collector system; and analytical equipment for determining product composition.

TCE was fed at a constant rate from a stainless steel metering pump with a Teflon shaft seal (minimum rate, 7 ml/hr). The flow of chlorine was controlled by a titanium seated needle valve and indicated by a calibrated capillary flow meter. A close control on the flow could be maintained by the introduction of a high resistance strainer in the chlorine line. The reactor (2 cm diam with an axial thermowell) and preheater were made of glass and were surrounded by an electrically heated inert fluidized bed acting as a thermostat. The temperature of the bed was maintained at 200 ± 1°C by careful control of the rate of fluidizing air and power input. There was no detectable axial temperature gradient in the bed.

Product collection was done by a pair of coiled condensers, the coolant used was refrigerated water at 5°C. Material balance on TCE indicated no TCE in the vent gases. Acetone was used to wash down the condenser sides and also to react away the excess chlorine contained in the product mixture.

The analytical equipment used was an NCL designed gas chromatographic unit with hydrogen flame ionization detector. Several types of columns have been used (*20–25*) for the chromatographic analysis of TCE, PCE and HCE. In the present investigation the product mixture was separated over silicone SE 30 (methyl) 15% over Chromosorb P column, 10 ft long and kept at 125°C, with nitrogen at 10 lb/in.^{2} as the carrier gas. The percentage composition was then obtained by standard methods.

TCE and PCE were twice fractionated at a pressure of 100 mm Hg; TCE was col-

TABLE 2
DETAILS OF THE RUNS

No.	Feed rate of reactant F' (g-moles/hr)	Voidage f	$F = F'/f$ (g-moles/hr)	Wt of catalyst W (g)	W/F (g hr/g mole)	Feed rate of Cl_2 F_{Cl} (g-moles/hr)	Temp T (°C)	Normalized time $\theta = t/t_m$	Catalyst decay time t_m (hr)
1	0.447	0.581	0.769	15	19.5	4.470	200	1	0–10
2	0.342	0.581	0.588	20	34.0	3.420	200	1	0–10
3	0.207	0.581	0.357	25	70.0	2.075	200	1	0–10
4	0.197	0.581	0.339	30	88.5	1.970	200	1	0–10
5	0.173	0.581	0.298	35	117.5	1.730	200	1	0–10
6	0.097	0.581	0.166	40	240.6	0.966	200	1	0–10
7	0.087	0.581	0.149	45	300.8	0.869	200	1	0–10
8	0.081	0.581	0.139	50	361.0	0.805	200	1	0–20
9	0.084	0.581	0.145	55	379.0	0.843	200	1	0–20
10	0.074	0.581	0.127	60	474.2	0.735	200	1	0–20

lected at 82.9°C and PCE at 93°C directly into amber colored bottles. Nitrogen was bubbled through them before they were stored in the refrigerator for future use. HCE used was of analytical grade supplied by the BDH.

The entire experimental assembly was shielded from sunlight such that no photochlorination took place. The catalyst was charged into the reactor and chlorine was passed at 300°C for 1 hr. Then the temperature was brought down to 200°C and TCE was passed. The first sample after about 2 min (i.e., at $t_m \doteq 0$) was collected for a small fraction of time and thereafter at 1 hr intervals for 10 hr (20 hr in the case of runs 8, 9 and 10); the details are given in Table 2. The samples were freed of HCl, one of the products of reaction, by passing nitrogen for 15 min before analysis, and the results are shown in Table 3.

TEST OF THE MODEL

The Model

The details of the model for a reaction of the general type,

$$\underset{\alpha_1}{\overset{k_{1.i}}{\mathrm{A} \rightarrow}} \mathrm{R} \underset{\alpha_2}{\overset{k_{2.i}}{\rightarrow}} \mathrm{S},$$

have been described by Sadana and Doraiswamy (*19*). The second suffix of the rate constant refers to the clock time t in hours; thus $\mathrm{k}_{1.0}$ is the rate constant of the first step at no decay. Two different decay forms were employed, exponential and linear, the expressions for $k_{1.0}$ and the yield y_{R} for the two cases being:

Exponental:

$$k_{1.i} = k_{1.0}e^{-\alpha t}, \tag{1}$$

$$y_{\mathrm{R}} = \frac{s}{1-s} \times \left[\exp(-B'e^{-\lambda\theta}) - \exp\left(-\frac{B'}{s}e^{-\lambda\theta}\right)\right]. \tag{2}$$

Linear [first-order]:

$$k_{1.i} = k_{1.0} - \alpha t, \tag{3}$$

$$y_{\mathrm{R}} = \frac{s[1 - \lambda\theta/k_{1.0}]}{1-s} \times \left\{\exp\left[-B'\left(1 - \frac{\lambda\theta}{k_{1.0}}\right)\right] - \exp\left[-\frac{B'}{s}\left(1 - \frac{s\lambda\theta}{k_{1.0}}\right)\right]\right\}. \tag{4}$$

It may be noted that when instantaneous values are involved t becomes equal to t_m (i.e., $\theta = 1$) and is replaced by t_m

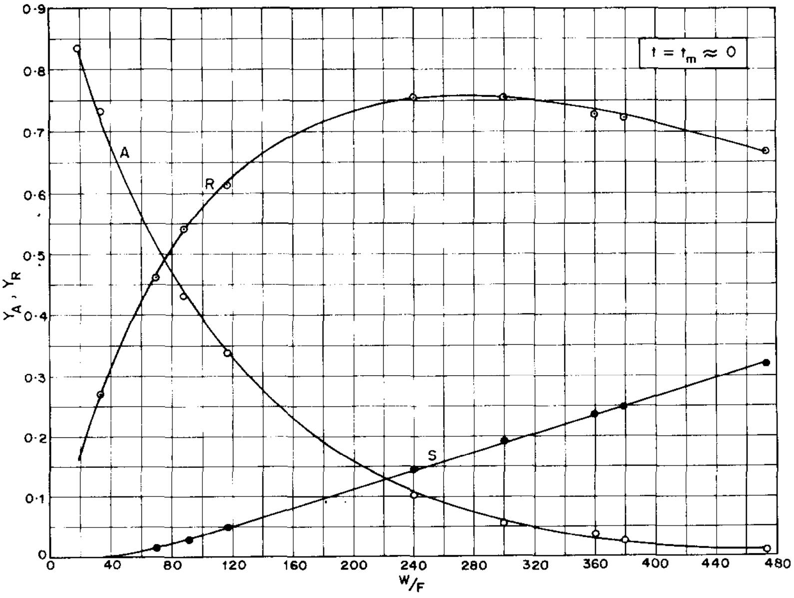

FIG. 1. Experimental product distribution curves at $t_m \simeq 0$.

TABLE 3

Product Distribution at Different Values of Decay Time (t_m) and W/F

W/F		Catalyst decay time t_m										
		0	1	2	3	4	5	6	7	8	9	10
19.5	y_A	0.835	0.839	0.840	0.848	0.853	0.859	0.863	0.869	0.874	0.880	0.885
	y_R	0.163	0.160	0.155	0.150	0.145	0.140	0.128	0.121	0.110	0.120	0.110
	y_S	0.002	0.001	0.005	0.002	0.002	0.001	0.009	0.010	0.016	0.000	0.005
34.0	y_A	0.730	0.740	0.743	0.760	0.768	0.766	0.780	0.787	0.800	0.800	0.812
	y_R	0.270	0.255	0.255	0.240	0.230	0.225	0.218	0.206	0.198	0.192	0.185
	y_S	0.000	0.005	0.002	0.000	0.002	0.009	0.002	0.007	0.002	0.008	0.003
70.0	y_A	0.525	0.540	0.545	0.544	0.556	0.578	0.585	0.595	0.607	0.625	0.642
	y_R	0.460	0.455	0.450	0.425	0.430	0.405	0.395	0.400	0.380	0.365	0.348
	y_S	0.015	0.005	0.005	0.031	0.014	0.013	0.020	0.005	0.013	0.010	0.010
88.5	y_A	0.432	0.450	0.447	0.475	0.480	0.485	0.524	0.520	0.546	0.556	0.563
	y_R	0.540	0.516	0.507	0.501	0.500	0.490	0.465	0.455	0.435	0.415	0.424
	y_S	0.028	0.034	0.046	0.024	0.020	0.025	0.011	0.025	0.019	0.029	0.013
117.5	y_A	0.340	0.339	0.0363	0.378	0.399	0.410	0.418	0.435	0.440	0.464	0.483
	y_R	0.612	0.610	0.610	0.582	0.566	0.585	0.540	0.540	0.529	0.520	0.494
	y_S	0.048	0.051	0.027	0.040	0.035	0.005	0.042	0.025	0.031	0.016	0.023

TABLE 3 (*continued*)

		Catalyst decay time t_m															
W/F		0	1	2	3	4	5	6	7	8	9	10	12	14	16	18	20
240.6	y_A	0.101	0.120	0.122	0.125	0.137	0.141	0.155	0.175	0.189	0.196	0.218					
	y_R	0.755	0.753	0.747	0.741	0.750	0.735	0.735	0.735	0.721	0.713	0.703					
	y_S	0.144	0.127	0.131	0.134	0.113	0.124	0.110	0.090	0.090	0.091	0.079					
300.8	y_A	0.055	0.060	0.075	0.075	0.095	0.105	0.102	0.114	0.127	0.135	0.148					
	y_R	0.755	0.758	0.760	0.763	0.758	0.757	0.765	0.755	0.750	0.752	0.746					
	y_S	0.190	0.182	0.165	0.162	0.147	0.138	0.133	0.131	0.123	0.113	0.106					
361.0	y_A	0.038	0.042	0.037	0.052	0.053	0.060	0.074	0.073	0.077	0.097	0.095	0.126	0.156	0.190	0.241	0.310
	y_R	0.727	0.708	0.740	0.745	0.744	0.752	0.755	0.756	0.757	0.752	0.750	0.740	0.732	0.727	0.688	0.643
	y_S	0.235	0.250	0.223	0.203	0.202	0.188	0.171	0.171	0.166	0.151	0.155	0.134	0.112	0.083	0.071	0.047
379.0	y_A	0.029	0.033	0.040	0.041	0.045	0.052	0.057	0.075	0.071	0.075	0.100	0.114	0.143	0.179	0.224	0.281
	y_R	0.722	0.705	0.733	0.737	0.748	0.748	0.750	0.744	0.750	0.756	0.757	0.753	0.735	0.715	0.709	0.650
	y_S	0.249	0.262	0.227	0.222	0.207	0.200	0.193	0.181	0.179	0.169	0.143	0.133	0.122	0.106	0.067	0.069
474.2	y_A	0.010	0.014	0.015	0.018	0.020	0.024	0.029	0.032	0.037	0.042	0.050	0.066	0.087	0.116	0.154	0.205
	y_R	0.670	0.675	0.690	0.695	0.705	0.717	0.725	0.728	0.735	0.745	0.746	0.759	0.747	0.753	0.730	0.708
	y_S	0.320	0.309	0.298	0.287	0.275	0.263	0.250	0.240	0.228	0.217	0.204	0.175	0.166	0.121	0.116	0.087

in the above equations; and when average values are involved Eq. (2) and (4) are integrated along the variable θ between the limits 0 and 1.

Data Required for Testing

As can be seen from the above equations, the data required for testing the model are the rate constants $k_{1.i}$ and $k_{2.i}$ at various levels of decay, from which the intrinsic rate constants can be extracted and the decay constants α_1 and α_2 also determined. (As it turned out in the present case, $\alpha_1 \doteq \alpha_2$.) To obtain these constants, product distribution as a function of time ($t = t_m$) with space velocity as parameter is required, and experiments were accordingly planned and executed. The results are presented in Table 3.

Estimation of Reaction Rate and Decay Constants

a. Rate constants. Typical plots of y_A, y_R and y_S versus W/F are shown in Figs. 1 and 2. Based on the reported work of Kim (*26*) first-order kinetics was assumed for step 1, and plots were made according to the equation

$$\frac{W}{F} = \frac{1}{k_{1.i}} \ln \frac{1}{1 - x}. \qquad (5)$$

It was observed from these plots (not shown in the paper) that first-order kinetics is valid for all t_m; the corresponding $k_{1.i}$ values are presented in Table 4. Figure 3 shows that the dependence of $k_{1.i}$ on time is linear.

To evaluate the rate constants ($k_{2.i}$) for step 2, first-order kinetics was again assumed and the following equations were employed:

$$k_1 y_A - k_2 y_R = 0 \quad \text{at} \quad r_R = 0, \qquad (6)$$

or

$$\frac{k_1}{k_2} = \frac{y_R}{y_A} (= s) \quad \text{at} \quad \frac{dy_R}{d(W/F)} = 0 \cdot \qquad (7)$$

From a knowledge of $k_{1.i}$, and of s determined from product distribution curves (e.g., Figs. 1 and 2) at $dy_R/d(W/F) = 0$, $k_{2.i}$ was estimated at various values of t_m, and the results are included in Table 4. From the selectivity values recorded in Table 4, it can be seen that there is no particular trend and that an average value of 8.71 is obtained (with a maximum deviation of 9%). Again, from a least squares

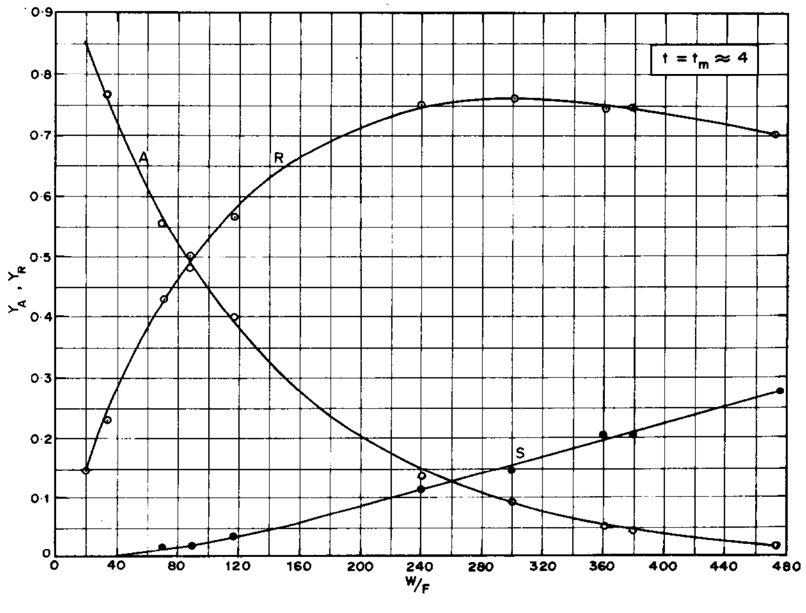

FIG. 2. Experimental product distribution curves at $t_m = 4$.

TABLE 4
RATE CONSTANTS AND SELECTIVITIES AT VARIOUS VALUES OF t_m

t_m:	0	1	2	3	4	5	6	7	8	9	10	s_{av}
$k_{1.i} \times 10^2$	0.932	0.902	0.875	0.844	0.815	0.783	0.749	0.722	0.699	0.663	0.632	
s	8.86	8.93	8.93	8.65	8.63	7.98	9.49	8.64	8.92	8.70	8.14	8.71
$k_{2.i} \times 10^3$	1.052	1.010	0.980	0.976	0.944	0.981	0.789	0.836	0.784	0.761	0.776	

fit of the $k_{2.i}$ values obtained into a straight line (Fig. 4), $k_{2.0}$ was determined and the selectivity was estimated to be 8.66, which is nearly the same as the average value recorded in Table 4. It is this value (8.66) that has been used in model testing.

To establish the correctness of the parameter values determined above, a comparison of the calculated and experimental product distributions for all values of t_m using the average selectivity and individual $k_{1.i}$ values was made. The following equations were used in the calculations:

$$y_A = e^{-k_{1.i}(W/F)}, \tag{8}$$

$$y_R = \frac{s}{1-s}\left\{e^{-k_{1.i}(W/F)} - \exp\left[\frac{-k_{1.i}}{s}(W/F)\right]\right\}. \tag{9}$$

The fact that the agreement is good is evident from an examination of Table 5.

b. Decay constants. The observation that selectivity was invariant with time, whereas the rate constants varied linearly, led us to modify the model derived by Sadana and Doraiswamy to the extent that the selectivity had to be isolated from the decay function, resulting in the following equation which satisfies the requirement:

$$k_{1.i} = k_{1.0}[1 - \alpha t]. \tag{10}$$

The decay constants α_1 and α_2 were then obtained from Figs. 3 and 4, respectively:

$$\alpha_1 = 0.0322,$$
$$\alpha_2 = 0.0320.$$

The fact that $\alpha_1 \doteq \alpha_2$ provides evidence in support of the assumption of constancy of decay parameters for all reaction steps in a complex reaction, an assumption first made by Weekman (*17*). Incidentally, it may be further argued that the main criterion for the decay of a catalyst is the irreversible adsorption of carbonaceous material or an independent poison in the feed, resulting in the progressive decrease in the surface area available for the useful reactions, whether the chemical reaction is simple or complex; and hence an identical effect should be felt by each reaction step. This argument is valid even if one step of the reaction is favored by one kind of surface and another by another kind, as long as there is only one kind of decay, viz, the irreversible adsorption of nonvolatile matter.

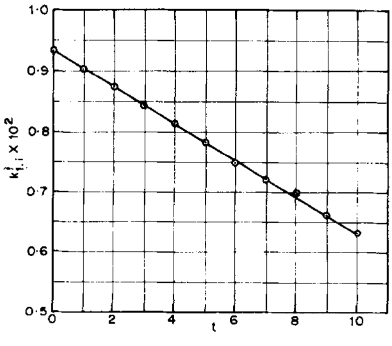

FIG. 3. Variation of the overall first-order constant $k_{1.i}$ with time.

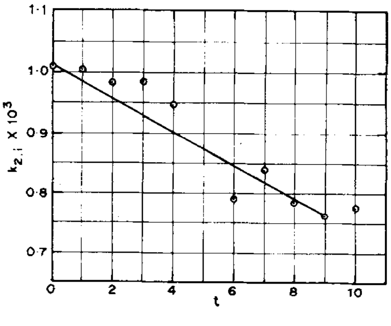

FIG. 4. Variation of the overall first-order constant $k_{2.i}$ with time.

TABLE 5

Comparison of Experimental and Calculated [Eqs. (8) and (9)] Values of Product Distribution at $t_m = 0$ and $t_m = 4$

	$t_m = 0$						$t_m = 4$					
	y_A		y_R		y_S		y_A		y_R		y_S	
W/F	Expt	Calcd	Expt	Calcd	Expt	Calcd	Expt	Calcd	Expt	Calcd	Expt	Calcd
19.5	0.835	0.8339	0.163	0.1654	0.002	0.0007	0.853	0.8531	0.145	0.1455	0.002	0.0014
34.0	0.730	0.7284	0.270	0.2665	0.000	0.0051	0.768	0.7580	0.230	0.2380	0.002	0.0040
70.0	0.525	0.5208	0.460	0.4644	0.015	0.0148	0.556	0.5652	0.430	0.4196	0.014	0.0152
88.5	0.432	0.4383	0.540	0.5324	0.028	0.0293	0.480	0.4861	0.500	0.4907	0.020	0.0232
117.5	0.340	0.3345	0.612	0.6184	0.048	0.0471	0.399	0.3838	0.566	0.5784	0.035	0.0378
240.6	0.101	0.1062	0.755	0.7534	0.144	0.1404	0.137	0.1407	0.750	0.7430	0.113	0.1163
300.8	0.055	0.0606	0.755	0.7503	0.190	0.1891	0.095	0.0861	0.758	0.7552	0.147	0.1587
361.0	0.038	0.0346	0.727	0.7286	0.235	0.2368	0.053	0.0528	0.744	0.7462	0.202	0.2010
379.0	0.029	0.0292	0.722	0.7201	0.249	0.2507	0.045	0.0456	0.748	0.7408	0.207	0.2136
474.2	0.010	0.0121	0.670	0.6665	0.320	0.3214	0.020	0.0210	0.705	0.7011	0.275	0.2779

Test of the Model

With the introduction of the new linear relationship given by Eq. (10), the expression for the instantaneous yield of intermediate y_R becomes

$$y_R = \frac{s}{1-s}\left[e^{-B'(1-\lambda\theta)} - e^{(-B'/s)(1-\lambda\theta)}\right]. \quad (11)$$

It is now required to be shown that the experimental results can be described by the above equation and that an experimental optimum λ that corresponds to the null-derivative with respect to λ of Eq. (11) exists. Figure 5 shows that the model represented by Eq. (11) (with θ replaced by unity) represents the observed values of y_R remarkably well and that there do exist maxima at lower space velocities which can be reasonably well predicted by

$$\lambda = 1 - \left(\frac{s}{[s-1]B'}\right)(\ln s), \quad (12)$$

which is obtained by equating the derivative of Eq. (11) with respect to λ to zero.

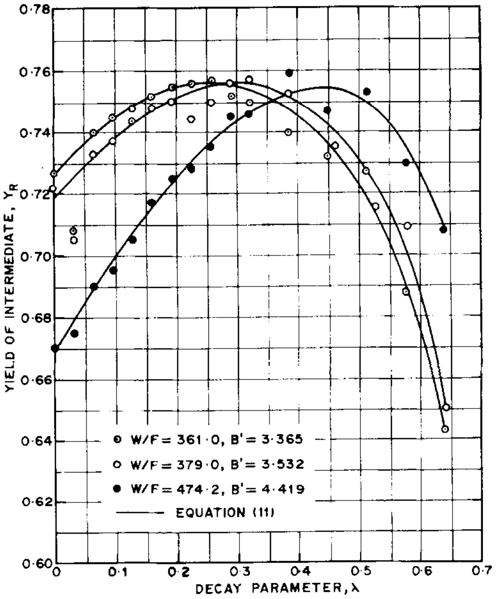

FIG. 5. Comparison of model represented by Eq. (11) with experimental data.

OPTIMAL FEED POLICY

An important factor in the design of a fixed-bed reactor operating under condi-

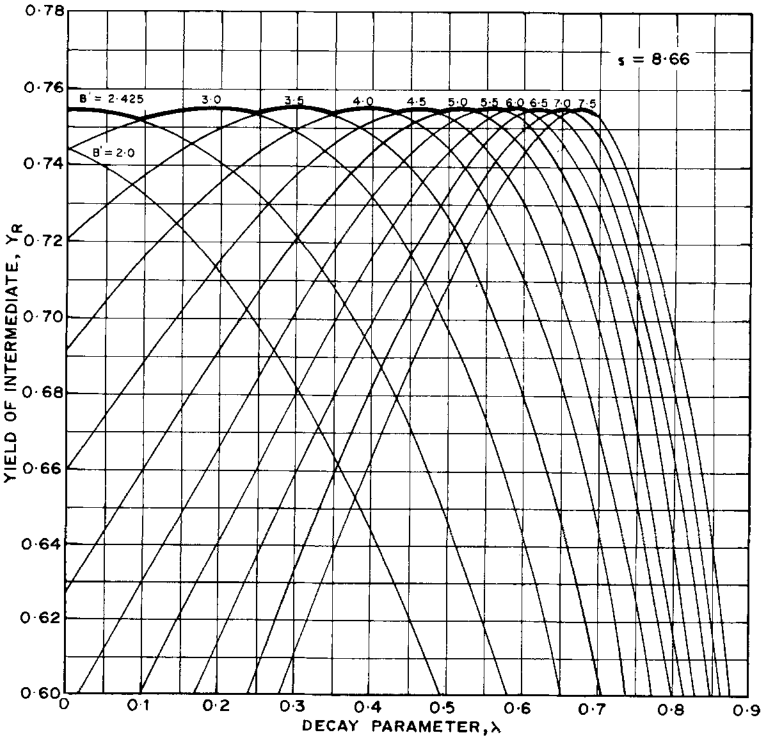

FIG. 6. Formulation of an optimal feed policy for a fixed-bed reactor operating with a decaying catalyst.

tions of catalyst decay is the optimization of process on-stream time t_m. The lower the t_m, the higher the frequency of regeneration and greater the operational costs. It has already been shown (*19*) that an optimum value of λ exists for the maximum yield of the intermediate y_R. Since $\lambda = \alpha\ t_m$ it follows that for a constant value of the fouling parameter α, an optimum value of t_m also exists. But for the type of consecutive reaction considered B' also exhibits an optimum, and in fact differentiation of Eq. (11) with respect to B' and equating the derivative to zero also leads to Eq. (12). Hence it may be concluded that B' and λ should not be considered in isolation for optimization of process time. Equation (12) shows that y_R is maximum when the product $B'\ (1 - \lambda)$ is constant and is equal to $[s/(s - 1) \ln s]$ which is determined only by the kinetics of the reaction. It is therefore possible to maintain y_R at the maximum level corresponding to $B'_0 = [s/(s - 1) \ln s]$ by manipulating B' when λ changes. During the course of the reaction this can be done only by adjusting the feed rate to the reactor such that

$$B' = \frac{B'_0}{1 - \lambda\theta}. \tag{13}$$

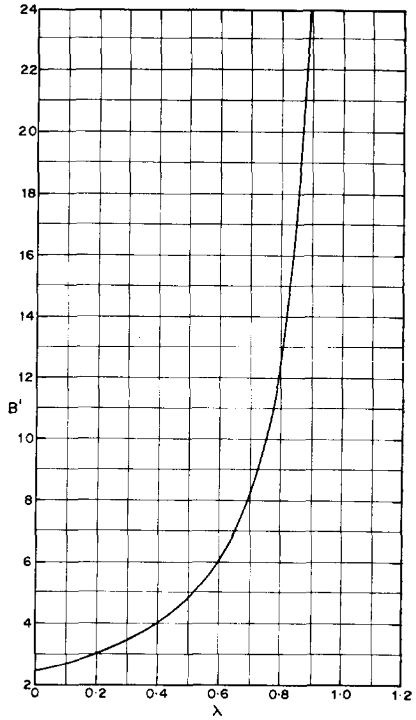

FIG. 7. Variation of B' with λ for optimal policy [Eq. (13)].

Figure 6 illustrates how this can be done over a finite number of stages. It is obvious from Fig. 7, which is a plot of Eq. (13), that when λ takes values very close to unity, B' tends to become infinity and the feed rate tends to zero. Thus the maximum utility of the cycle time can be achieved with the minimum number of regenerations by continuously varying the feed rate according to Eq. (13). Obviously there is no need for averaging the yield of intermediate over time, and in the limit the thick portions of the curves in Fig. 6 become a straight horizontal line with ordinate equal to $y_{R,\max}$.

Recently, Levenspiel (*27*) has suggested that a similar policy, viz, keeping the conversion constant by varying the feed rate, can be used as an effective experimental technique to determine the decay parameters when the decay is concentration dependent. In fact, by automatic controlled variation of the feed, the system can be made to generate a decay function similar to Eq. (14). Thus the concentration effect, which in this case is limited to the main reaction, is eliminated, and only the fouling effect is captured in the run. It may be noted, however, that in the present investigation, this procedure has not been followed, and the rate and fouling constants have been uncoupled by the procedure already described.

For obtaining the optimum value of t_m Eq. (13) may be rewritten in terms of feed rate as follows:

$$\bar{F} = F_0(1 - \lambda\theta). \tag{14}$$

Assuming that the process time is equal to regeneration time (any similar assumption can be made), the total cycle time is 2 t_m and the frequency is $1/(2\ t_m)$. If the plant were to operate at $y_{R,\max}$ always, the rate of production of R at any instant in a cycle is $\bar{F}\ y_{R,\max}$. Or, by using Eq. (14), the total plant capacity may be written as

$$C = \frac{1}{2t_m} \int_0^1 F_0 y_{R,\max} t_m (1 - \lambda\theta) d\theta \tag{15}$$

$$= \frac{1}{2} F_0 y_{\mathrm{R,max}} \left(1 - \frac{\lambda}{2}\right). \qquad (16)$$

Clearly, F_0 is a fixed quantity and is given by

$$F_0 = \frac{(s-1)Wk_{1.0}}{s \ln s} = \frac{Wk_{1.0}}{B'}. \qquad (17)$$

The total capacity at $t_m = 0$, which is purely hypothetical, is equal to $\frac{1}{2}F_0 y_{\mathrm{R,max}}$, and that at $t_m = 1/\alpha$, corresponding to $\lambda = 1$, is $\frac{1}{4} F_0 y_{\mathrm{R,max}}$. [Note that in Eq. (15), as t_m tends to zero, though the frequency tends to ∞ and cycle capacity tends to zero, their product tends to a finite nonzero limit.] Thus, we have a quantitative indication of how the plant capacity diminishes with increasing t_m.

Assuming that the plant is originally designed to operate at F_0 disregarding the catalyst decay, the cost of production can be minimized from considerations of catalyst decay. Let the unit cost be expressed as the sum of two functions $\psi\ (t_m)$ and $\phi\ (t_m)$, where $\psi\ (t_m)$ represents the increase in cost due to capacity reduction and $\phi\ (t_m)$ the decrease in cost due to reduced frequency, both of which are the result of increased t_m. Since $\psi\ (t_m)$ is an increasing function and $\phi\ (t_m)$ a decreasing function, there should exist an optimum value of t_m, corresponding to the minimum cost, which may be found from

$$\frac{\delta[\psi(t_m)]}{\delta t_m} + \frac{\delta[\phi(t_m)]}{\delta t_m} = 0. \qquad (18)$$

The only requirement for using this equation is a prior knowledge of the two cost functions which can be easily worked out.

It must be noted that the optimal feed policy suggested is only valid when the time of the regeneration part of the cycle is independent of the operating or reacting part of the cycle. Thus, if the carbon laid down during the operating cycle is a function of the feed rate, then the optimal feed policy must account for the burning time or the regeneration part of the cycle.

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