

Effects of Diffusion Resistance on Gasoline Selectivity in Catalytic Cracking

The time on stream theory of catalyst decay is applied to gas oil cracking selectivity data from a static bed reactor operating with a diffusion limited catalyst. It is found that intraparticle diffusion affects the reactions leading to the disappearance of gas oil to a much greater extent than the reaction leading to the cracking of gasoline and catalyst poisoning. Reasons for this behavior are postulated. It is also found that the overall kinetic order for the rate of disappearance of gas oil is decreased with the result that maximum selectivity occurs at a higher conversion value than for a corresponding diffusion-free catalyst. It is concluded that probably diffusion limitation is not a serious problem with respect to gasoline selectivity in commercial reactors.

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SCOPE

Diffusional limitations are generally to be avoided in catalytic systems. Various steps are therefore taken to ensure that reactions are not carried out under conditions involving diffusion limitations. Despite such precautions, in some cases it is impossible to avoid the use of a diffusion limited catalyst. One industrial example of this may be the moving bed reactor. Various physical factors conspire to make this reactor configuration a candidate for diffusion problems since they dictate the use of a hard bead catalyst which must be strong enough to withstand abrasion while at the same time large enough to allow proper transport and to forestall large pressure drops through the bed.

The importance of diffusion within porous catalyst systems has long been recognized, and considerable work has been done both in predicting the effect of diffusion on reaction rates and on the selectivity of some simplified systems. One of the earliest such attempts was made by Wheeler (1951, 1955) in which three basic types of selectivity behavior were defined and the effects of diffusion limitations under isothermal conditions on selectivity were described. Wheeler's theoretical analyses were extended and generalized by Carberry (1962) for a series reaction with various combinations of diffusion limitations in the bulk phase, in the pores, and in the micro-macro

pore structure. Weisz and Hicks (1962) extended Wheeler's work to nonisothermal cases while Butt (1966) went on to include Wheeler's type III selectivity. At the same time Hutchings and Carberry (1966) reported some computed results for temperature gradients in the case of Wheeler's type III selectivity.

Unfortunately, predicting selectivity behavior under conditions involving diffusion for a complex system such as gas oil cracking is an even more complex task and is not likely to be treated successfully by the methods used by the above authors. For instance, Johnson et al. (1957) attempted to describe gas oil cracking as following Wheeler's type III selectivity. Subsequently, Campbell and Wojciechowski (1969) and Pachovsky and Wojciechowski (1971) showed that a more complex mechanism is required to describe gas oil cracking and postulated a more complex form of behavior.

In an earlier work reported by Best et al. (1971) it was shown that the hyperbolic aging function (Wojciechowski, 1968) can be used to describe gas oil conversion in both diffusion limited and diffusion free systems. In this paper we will show that their treatment can be extended to describe the effects of diffusion on gas oil selectivity by observing the changes in the parameters of the selectivity model (Pachovsky et al., 1973)

CONCLUSIONS AND SIGNIFICANCE

The gas oil selectivity model is shown to describe adequately gasoline yield data from a static bed reactor operating with a diffusion limited catalyst. A comparison of the model parameters with those from an identical but diffusion free catalyst shows that diffusion limitation has no effect on the mechanism of catalyst decay. The reactions that result in the disappearance of gas oil and which we have called primary reactions are affected to a much greater extent by diffusion than are the reactions involv-

ing the cracking of gasoline and the poisoning of the catalyst (secondary reactions). In addition, diffusion limitation causes the overall order of the primary reaction to decrease, and this results in a shifting of the selectivity maximum to a higher conversion level. The gasoline yield at this maximum, however, is only slightly less than that for a diffusion free catalyst because of the increase of the secondary reaction rate constants relative to the primary rate constants. Furthermore it is shown that diffusion limitation is probably not a serious problem from the point of view of gasoline selectivity in commercial cracking reactors.

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THEORY

In a previous publication (Pachovsky et al., 1973) a general model was developed which describes catalytic conversion and selectivity in a plug flow, static bed reactor. The defining relationships comprising the model are

$$\frac{dX_A}{d\tau} = (k_{10} + k_{20}) \left(\frac{1}{1 + Gt} \right)^N \left(\frac{1 - X_A}{1 + \epsilon_A X_A} \right)^{1+W} \quad (1a)$$

$$\frac{dX_B}{d\tau} = \left(\frac{1}{1 + Gt} \right)^N \left\{ k_{10} \left(\frac{1 - X_A}{1 + \epsilon_A X_A} \right)^{1+W} - k_{30} \left(\frac{1}{1 + \epsilon_A X_A} \right) X_B \right\} \quad (1b)^*$$

$$\frac{dX_C}{d\tau} = \left(\frac{1}{1 + Gt} \right)^N \left\{ k_{20} \left(\frac{1 - X_A}{1 + \epsilon_A X_A} \right)^{1+W} + k_{30} \left(\frac{1}{1 + \epsilon_A X_A} \right) X_B \right\} \quad (1c)^*$$

Equations (1) were derived by assuming that gas oil (A) may crack directly to gasoline (B) or to coke and light gases (C) and that gasoline (B) could be cracked to C.

The catalyst decay in Equations (1) is described using the time on stream theory of Wojciechowski (1968) which yields the expression

$$S^n = S_0^n \left(\frac{1}{1 + (m-1)k_d t} \right)^{\frac{n}{m-1}} = S_0^n (1 + Gt)^{-N} \quad (2)$$

where S is the number of unpoisoned active sites at time t . The other parameters involved are outlined in the notation.

The refractivity of the chargestock (A) has been taken in the above to vary with conversion according to the expression

$$\frac{k}{k_0} = \left(\frac{C_A}{C_{A0}} \right)^w \quad (3)$$

where k is the reactivity of the feed when reactant concentration has dropped to C_A while k_0 is the reactivity of fresh feed. This concept was previously presented in more detail by Pachovsky and Wojciechowski (1971).

Equations (1) are therefore kinetic expressions relating the rate of change of the fraction of A, B, and C to the age of the catalyst and the current fractions of A, B, and C present in the reacting mixture. The instantaneous values of fractional conversion (X_A) and fraction of products produced (X_B, X_C) are related to the average values ($\bar{X}_A, \bar{X}_B, \bar{X}_C$) by

$$\bar{X} = \frac{1}{t_f} \int_0^{t_f} X dt \quad (4)$$

and the contact time τ is related to the time on stream by

$$\tau = bPt_f \quad (5)$$

PROCEDURE

The experimental data to be fitted consisted of fractional conversion, gasoline yield, and undesirable product yield obtained from a static bed reactor. These particular data were obtained by pumping 200 cc of oil over a suitable volume of fresh catalyst for each run. The volume

of the catalyst used in a given run depended on what catalyst to oil ratio (cat/oil) was desired. For a given cat/oil ratio, a typical run consisted of passing the 200 cc volume of oil at a constant rate over fresh catalyst and recording the time taken to pump the 200 cc of oil (catalyst time on stream). By using a different oil feed rate in a subsequent run we changed the duration of the run or the time on stream for the catalyst. The reported data are the measured quantities at the end of a run and hence represent the time averaged quantities. The history of conversion, or instantaneous conversion values, during each test are unknown and unnecessary for our analysis.

The procedure of fitting these multiresponse data by Equations (1) and (2) has previously been described (Pachovsky et al., 1973). The criterion of fit consisted of minimizing the determinant of the covariance matrix between calculated and experimental results as outlined by Box and Draper (1965). The parameters in Equation (1) are N, G, W, k_{10}, k_{20} , and k_{30} . In a previous paper we have reported fitting conversion data for this system and thus obtained values of N, G, W , and $(k_{10} + k_{20})$. These values were retained from this previous work and therefore only k_{30} and k_{20} remained to be determined in order to fit the selectivity data. We have previously reported (Pachovsky et al., 1973) that this procedure saves much computer time and in case of doubt the final parameters thus derived can be checked to see if the values of N, G, W and $(k_{10} + k_{20})$ accepted from the fitting of conversion data alone would change significantly if they were not held constant in fitting selectivity data. Such checks have confirmed the validity of our procedure in this case.

RESULTS

In Table 1 we report the values of the six parameters for the cracking of mid continent gas oil over a 4/10 mesh rare earth exchanged zeolite catalyst at 900°F. For comparison the corresponding values reported previously (Pachovsky et al., 1973) for the cracking of the same feed at identical conditions but using a 30/60 mesh catalyst are also included.

Table 2 gives values of certain constants derived from the model parameters for both 4/10 mesh and 30/60 mesh catalysts. These are compared in size and a set of constants for the ideal case is postulated.

Table 3 gives results of the F-test performed on the selectivity response of the model using the two sets of data and the corresponding parameters from Table 2.

Figure 1 shows a selectivity plot for the 4/10 mesh catalyst. Included in the plot are experimental data points and theoretical selectivity curves obtained using the parameters given in Table 2. This figure shows that increasing time on stream in a fixed bed reactor results in

TABLE 1. COMPARISON OF PARAMETERS FOR 30/60 AND 4/10 MESH CATALYSTS

Catalyst: REHX Stock: Mid Continent gas oil Temperature: 900°F		
Parameter	30/60 mesh	4/10 mesh
k_{10} (hr ⁻¹)	1180.1	107.8
k_{20} (hr ⁻¹)	243.6	26.1
k_{30} (hr ⁻¹)	67.3*	33.3
G (hr ⁻¹)	19.2	9.3
W	0.72	0.0
N	3.60	3.67

* See note concerning Equations (1b) and (1c).

* Note the changes in Equations (1b) and (1c) from previous publications. Here X_B is based on initial conditions. The result is the increasing of k_{30} by a factor of 3.4.

TABLE 2. DERIVED VALUES FOR 30/60 AND 4/10 MESH CATALYSTS

	k_{10}, hr^{-1}	k_{20}, hr^{-1}	k_{30}, hr^{-1}	k_d, hr^{-1}	m	UGE	GE @ max conv.
30/60 mesh	1,180.1	243.6	19.8	7.0	1.27	82.8	72.8
4/10 mesh	107.8	26.1	9.8	3.5	1.27	80.5	61.2
Ideal 4/10 mesh	118.0	24.4	9.9	3.5	1.27	82.8	62.3
Ratio $\frac{30/60 \text{ mesh}}{4/10 \text{ mesh}}$	10.95	9.34	2.01	2.00	1.00	—	—

TABLE 3. TEST FOR ADEQUACY OF GASOLINE YIELD MODEL BY *F*-TEST AND 95% CONFIDENCE LEVEL

	Estimate of pure error variance	No. of data points	Sum of squares of residuals*	Tabulated <i>F</i> -values	Calculated <i>F</i> -values
30/60 mesh	0.000263	41	0.0164	$F(35, 12, .95) = 2.36$	1.69
4/10 mesh	0.000323	19	0.0116	$F(13, 5, .95) = 4.65$	2.76

* A residual is defined as the difference between a calculated response and an experimental response.

an increasing departure from the instantaneous yield behavior.

Figure 2 shows a comparison of the optimum performance envelopes (Campbell and Wojciechowski, 1969) for the 4/10 and 30/60 mesh catalysts, together with the ideal case described in the discussion.

Figure 3 shows a comparison of the predicted selectivity curves at a selected cat/oil ratio for the 4/10, the 30/60 mesh catalysts, and the ideal case.

DISCUSSION

The behavior of gas oil selectivity in fixed bed reactors with aging catalyst has been known for some time to be different from that in continuous reactors, such as moving and fluidized beds (Campbell and Wojciechowski, 1970). Static bed reactor selectivity performance lies within a region bounded by curves called the optimum performance envelope (OPE) and the minimum performance envelope (MPE). The OPE is a locus of the maximum possible selectivities that can be achieved at any particular conversion and the MPE is a locus of the minimum possible selectivities. In a static bed reactor the area between these two envelopes defines the region of possible

operation. In moving and fluidized bed reactors, however, all performance falls on a single curve which coincides with the static bed OPE. For practical purposes then, comparison of selectivity curves even in fixed bed reactors

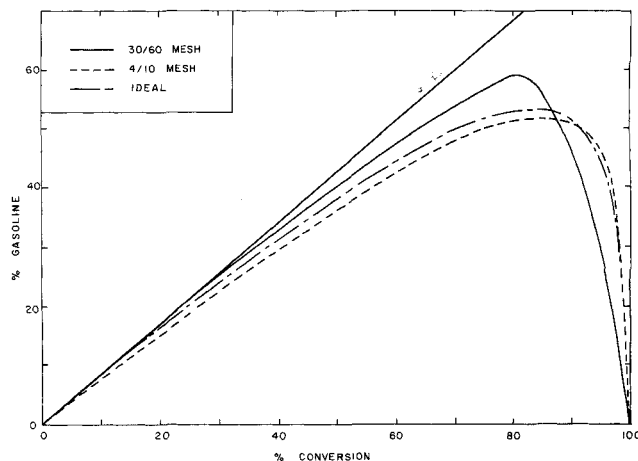


Fig. 2. Comparison of optimum performance envelopes for 30/60 and 4/10 mesh REHX and ideal case.

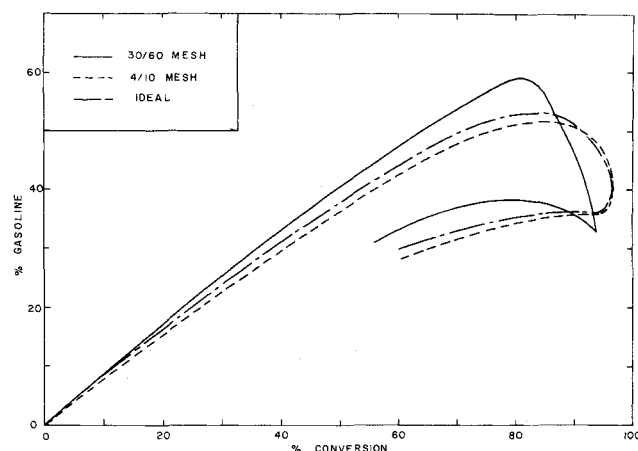


Fig. 3. Comparison of model curves at a constant catalyst to oil ratio of 3.0 for 30/60 and 4/10 mesh REHX and ideal case.

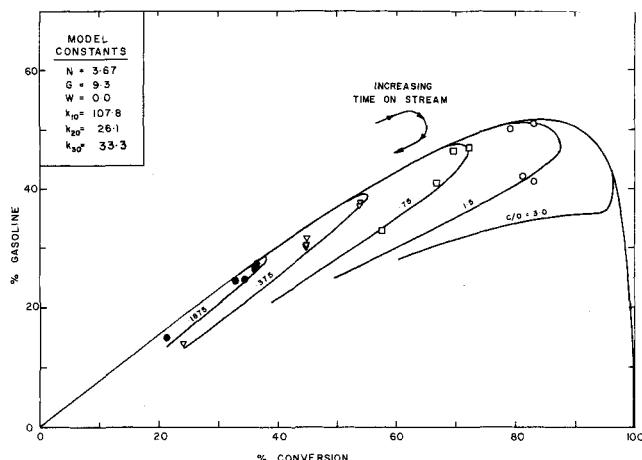


Fig. 1. Comparison of model and experimental data for constant catalyst to oil ratio: Catalyst—4/10 mesh REHX; Stock—Mid-continent gas oil; Temperature—900°F.

should be based on the OPE's.

From Table 3 it is readily apparent that for both the 4/10 mesh and 30/60 mesh data the selectivity model adequately describes the data at the 95% confidence level. In previous publications (Pachovsky and Wojciechowski, 1971; Best et al., 1971), it has been shown that the conversion model also adequately describes the conversion data at the 95% confidence level for both the 4/10 mesh and 30/60 mesh catalysts.

As reported previously (Best et al., 1971) m , the average number of sites lost per deactivating event, does not change in going from the 4/10 mesh to the 30/60 mesh catalysts, and it was argued that therefore diffusion has no effect on the mechanism of aging. For this catalyst and charge stock, therefore, the decay appears to involve both one and two site poisoning mechanisms. This observation casts doubt on the possibility of decay occurring in this case by means of pore mouth plugging even on the diffusion limited catalyst. If pore mouth plugging was the dominant deactivation mechanism we would expect that considerably more than two sites would be lost per deactivating event. In cumene cracking, it has been shown (Campbell and Wojciechowski, 1971) that two sites are involved in every deactivating event. Since in gas oil cracking a great variety of molecules is involved in the reaction, it is not difficult to imagine that some deactivation steps involve other than two sites at a time. The majority of sites, however, must be lost by single site mechanism since the average* number of sites lost per deactivating event, as represented by $m = 1.28$, is less than two. It is worth noting here that some authors (Weekman, 1968; Weekman-Nace, 1970) prefer to describe catalyst aging as following an exponential decay function. By doing so, they in fact assumed that only one site is involved in a deactivating event. From our intuitive understanding of gas oil cracking it appears that this assumption is not justified in general and certainly not in this case.

The interesting fact that the parameter W goes to zero for the diffusion limited case has previously been discussed in detail (Best et al., 1971). We will simply repeat here that a value of zero indicates that there is no preferential cracking of the easy to crack molecules as occurs in a diffusion free catalyst.

From Table 2 it can be seen that k_{10} and k_{20} are approximately ten times larger for the diffusion free catalyst than they are for the diffusion limited one. On the other hand, a similar comparison between the parameters k_{30} and k_d , the decay rate constant, shows that these parameters are only twice as large in the diffusion free case. From these results it appears that diffusion effects the primary reactions, that is, the ones resulting in the disappearance of gas oil, to a much greater degree than it does the secondary reactions which involves the overcracking of gasoline and apparently the decay of catalyst activity. This trend in the behavior of the parameters agrees with our understanding of the mechanism of catalytic cracking. Our proposed explanation for this observation is that during the reaction process the gas oil molecules diffuse into the catalyst particles and react on the catalyst active sites to yield the products. These products are formed inside the catalyst in immediate proximity to active sites and are therefore not as subject to hindrance by diffusion processes as are the gas oil molecules which have to first enter the catalyst particle before they can

react. Consequently, any secondary reaction is not affected by diffusion limitations to the same extent as is the primary process of gas oil cracking. The reaction rate constant for such a secondary reaction will nevertheless be lower than that for a diffusion free catalyst because during the course of reaction each particle of diffusion limited catalyst sees less products of primary reaction than does a particle of diffusion free catalyst. The fact that k_d shows behavior similar to that of the secondary reaction rate constant is also very interesting. We explain this similarity by the fact that since aging occurs due to the products as well as due to reactants it should show a lower dependence on diffusion than the primary reactions.

From the above discussion it seems reasonable to expect that, ideally, in going from a diffusion free to a diffusion limited catalyst, k_{10} and k_{20} should decrease by one factor while k_{30} and k_d should decrease by a smaller factor. At the same time N should not change while W should go to zero. Based on these conclusions, Figures 2 and 3 include curves which are called *ideal* and are calculated by assuming ideal diffusion behavior which results in parameters given in Table 2.

In Figure 2 it is seen that the optimum performance envelope (OPE) for the ideal diffusion catalyst lies between the actual OPE's for the diffusion free and diffusion limited catalyst but considerably closer to the experimental diffusion limited OPE. In fact it is clear from Figures 2 and 3 that our experimental results are close enough to ideal behavior so that subsequent discussion can be based on actual observations rather than the ideal case. Table 2 confirms this procedure with some numerical comparisons between the ideal and the experimental diffusion limited cases. With this in mind we can consider the figures in turn.

Figure 1 shows that the fit between experimental and theoretical results is very good. This fact is further supported by the results of the statistical test reported in Table 3.

Figure 2 shows that the diffusion limited catalyst generally gives lower yields of gasoline at a given conversion but that at high conversions this situation is reversed. The reasons are as follows. The re cracking rate constant k_{30} is less affected by diffusion than the primary constants k_{10} and k_{20} , and hence there is proportionately more re cracking of gasoline on the diffusion limited catalyst. The effect would tend to lower the OPE for the diffusion limited catalyst until it lay entirely below the OPE for the diffusion free catalyst. At the same time, however, W becomes zero for the diffusion limited catalyst, thus making the orders of the primary reactions unity. The effect is to shift the conversion at which maximum gasoline is produced to higher values. The result is that the two OPE's cross at high conversion as shown on Figure 2.

Figure 3 further confirms the effects of decreasing W where it is shown that higher conversions can be obtained at a given cat/oil ratio using diffusion limited catalyst.

PRACTICAL CONSEQUENCES OF DIFFUSION LIMITATION IN CRACKING CATALYSTS

Since commercial catalytic cracking units are invariably of moving or fluidized bed design we will confine our discussion here to these units. It has been shown (Campbell and Wojciechowski, 1970) that such units operate only on the OPE. Looking at Figure 2 and bearing in mind the previous discussion we see that as long as k_{10} and k_{20} change in the same proportion, the highest possible selec-

* It will be shown elsewhere that $m = 1.28$ does not tell us the precise fraction of sites lost by one or two site decay.

tivity is that given by the Ultimate Gasoline Efficiency shown on Figure 2. This line corresponds to the initial slope of the OPE and its slope is given by

$$\text{U.G.E.} = \frac{k_{10}}{k_{20} + k_{10}}$$

Selectivities lying along this line will be obtained if $k_{30} = 0$, in other words, if gasoline re cracking is completely suppressed. Removal of diffusion limitations has been shown here to lead to OPE's lying closer to the U.G.E. at low conversions but peaking to a maximum at lower conversions than does the diffusion limited catalyst. In view of this we judge from Figure 2 that little gain in selectivity can be expected in this system by further subdivision of catalyst particles. In units where such a situation as shown in Figure 2 exists, selectivity will not be a strong function of particle size distribution or of particle porosity. In fact, the reputed loss of selectivity due to diffusion limitations is probably largely due to loss of activity which leads to a lower gasoline yield at a given set of conditions.

The second practical consideration involves the cat/oil ratio required to obtain maximum gasoline production. From Figure 3 and computer simulations it can be seen that this ratio is almost identical for diffusion free and diffusion limited catalysts in the static bed. In the case of moving and fluidized beds we know from previous work (Pachovsky and Wojciechowski, 1972) that the moving bed gives higher conversions at any given cat/oil for the same particle size and the same time on stream. Thus we can conclude that maximum gasoline production will be obtained at a lower cat/oil in the moving bed reactor. If we then consider the riser-cracker as a moving bed reactor with a very short catalyst time on stream we see that operating such a reactor at a suitably high cat/oil will also lead to maximum gasoline production.

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NOTATION

G	= rate constant parameter of the aging function ($= (m - 1)k_d$), hr.^{-1}
N	= exponent of aging function
P	= cat/oil ratio (vol cat/vol feed)
W	= refractivity parameter
X_A	= instantaneous fraction of gas oil converted
X_B	= instantaneous fraction of gasoline produced
X_C	= instantaneous fraction of coke and C_4 -gas produced
\bar{X}	= time averaged fraction
b	= ratio of vaporized oil density to liquid oil density
k_{10}	= initial rate constant for conversion of gas oil to gasoline, hr.^{-1}
k_{20}	= initial rate constant for conversion of gas oil to coke and C_4 -gas, hr.^{-1}
k_{30}	= initial rate constant for conversion of gasoline to coke and C_4 -gas, hr.^{-1}
k_d	= NG = the rate constant for catalyst decay
m	= number of sites lost per deactivating event
n	= number of sites engaged in a cracking event
t_f	= catalyst time-on-stream, hr.
t	= any intermediate time-on-stream during an experimental run, hr.

ϵ_A	= volume expansion correction term
τ	= gas oil contact time measured at initial conditions of flow, hr.
θ	= fraction of active sites remaining at any time, t
GE	= gasoline efficiency ($= \frac{\% \text{ gasoline yield}}{\% \text{ conversion}}$)
MPE	= locus of minimum selectivities observable in a fixed bed reactor with aging catalyst
OPE	= locus of maximum selectivities observable in a fixed bed reactor with aging catalyst also the curve defining moving bed and fluidized bed selectivities
UGE	= ultimate gasoline efficiency ($= \frac{k_{10}}{k_{10} + k_{20}}$)

Subscripts

A	= gas oil
B	= gasoline
C	= coke and dry gas

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