Comments on the Note by Edelson and Allara

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Edelson and Allara have correctly pointed out some of the problems concerned with the modeling of pyrolysis data, but we believe the problems are even more complicated than indicated by their paper. In developing a highly accurate (and theoretical) model, problems occur both in choosing all the reaction steps of importance to include in the model and also in selecting accurate parameters (energies of activation and pre-exponential terms) for each reaction step.

Considering first the reaction steps in the models, it is currently difficult to identify all important reaction steps occurring during pyrolysis. Most of the many reactions occur in the gas phase, but some reactions also occur at the walls of the reactor. Recent work in our chemical engineering laboratories at Purdue University has shown that at least six types of reactions occur on the walls of tubular reactors. Yet no known models have included terms for such surface reactions.

Considering now the energies of activation to be used in modeling the gas-phase free-radical steps for the pyrolysis, the values reported in the literature may be in error by at least 1 kcal/g-mole. Such an error may have a large effect on the predicted rate values for at least some of the reactions. Furthermore as suggested earlier by Herriott et al. (1972), the energies of activation vary to at least some extent with temperature. Values to be used at 750° to 900°C may be different than values determined experimentally at much lower temperatures. In addition, the exact mechanism of some of these specific reaction steps that may involve hot or activated radicals, or molecules may change somewhat as temperature is increased.

As additional information is being obtained so that theoretical models can be developed, semiempirical (or even semitheoretical depending on one's state of optimism) models have proven reasonably successful. The model developed by Herriott et al. using 15 free-radical gas-phase reaction steps is obviously not truly theoretical, but it does seem to be a step in the right direction. Herriott et al. recognized there were limitations to the model and emphasized the need for expanded models in the future. Of interest, energies of activation in this model did generally agree fairly well with relatively well accepted values that in some cases had been obtained independently at lower temperatures. However we agree completely with Drs. Edelson and Allara that the energies of activation of this model are not necessarily accurate values. They are probably reasonable approximations that should only be used with caution in making any theoretical predictions.

Drs. Edelson and Allara are definitely moving in the right direction when they use an expanded model containing more reaction steps than that used by Herriott et al. It is most encouraging that their model fits the experimental data of Leathard and Purnell, who operated at extremely mild (for pyrolysis) conditions, namely low temperatures, low pressures, low conversions, in the absence of steam, and in a quartz reactor operated batchwise. Side reactions were presumably minimal, and surface reactions in the quartz reactor were probably much different and were of relatively lesser importance as compared to those in commercial reactors. As a side note, batch data for free-radical reactions are difficult to interpret since the contributions of wall reactions often are quite different than those in flow reactors.

We agree with Drs. Edelson and Allara that theoretical models for pyrolysis made at much more severe conditions such as obtained by Herriott et al. will be considerably more complicated than those made at mild conditions. We plan, however, to test the expanded propane model proposed by Edelson and Allara when it is published and hence becomes available; we would like to determine how use of somewhat modified parameters predict data obtained at more severe conditions. Eventually we hope to incorporate terms for the surface reactions into our pyrolysis models.

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Effect of Transport Processes on Conversion in a Trickle-Bed Reactor

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Reactors containing three phases (gas, liquid, and solid) are becoming more important not only for pollution control but also to the petroleum, plastics, and chemical industries for the production of new and better products. The trickle-bed reactor, as the term is used here, is one in which a liquid-and a gas-phase flow concurrently downward through a fixed bed of catalyst particles. Trickle-bed reactors are used in the petroleum industry for such processing as hydrodesulfurization of heavy oil fractions, hydrocracking of high boiling point stocks, hydrotreating and refining and lubricating oils and waxes (Frye and Moxby, 1967; Hoog et al., 1953; McAfee, et al., 1955). However, surprisingly little is known about the variables involved in trickle-bed operation and their influence on performance. Reiss (1967) obtained experimental data for a variety of packings for concurrent gas-liquid contacting in packed columns including pressure loss, liquid holdup, radial distribution, and ammonia absorption and oxygen desorption. Engineering correlations for both gas- and liquid-side mass transfer coefficients based on the energy dissipation per unit volume were presented. Hockman and Effron (1969) studied both liquid- and gas-phase residence-time distributions in concurrent trickle flow and found that although radial variations were small, axial dispersion in both phases was considerably greater than in single-phase flow. Increased gas-phase dispersion was attributed to bridging of the liquid on the packing and increased liquid-phase dispersion to transfer between free flowing and stagnant liquid. Correlations were given for both gas and liquid Peclet numbers and the effect of the gas flow rate on the liquid Peclet number was small for the gas-continuous flow regime investigated. The performance of a trickle-bed reactor also depends on the extent of liquid maldistribution (Ross, 1965). However, there is disagreement on this effect due to the widely differing experimental conditions of the various studies (Baket et al., 1935; Schiesser and Lapidus, 1961). Another important consideration is the fluid flow regime. The recent study of Bemesch and Kessler (1971) has shown that the gas and liquid mass fluxes control the flow regime obtained and that the pulsing flow regime is the most extensive, although in most previous work the gas-continuous regime was investigated such that the complexities of radially segregated slug flow were absent.

Satterfield et al. (1968, 1969, 1972), in a series of papers, have studied various aspects of three-phase reactor performance. In the first of these papers, they studied the hydrogenation of α-methylstyrene on two sizes of palladium-alumina catalyst pellets and powdered catalyst. They found that the intraparticle effectiveness factor could be obtained for the case of liquid filled pores in a manner analogous to that for the gas-solid reactor. Satterfield et al. (1969) also studied the hydrogenation of α-methylstyrene on palladium-alumina catalyst. The reaction was studied in a powdered-slurry reactor, a pellet-stirred basket reactor and in a simulated trickle-bed reactor. They found that external mass transfer was important in the trickle-bed reactor. Satterfield and Way (1972) studied the effect of the addition of an inert liquid into a gas-phase catalytic reaction. They studied the isomerization of cyclopropane to propylene on a silica-alumina catalyst using three liquids in a trickle-bed reactor. The addition of the liquid phase lowered the measured reaction rate demonstrating the importance of mass transfer effects. In addition, adsorption of the liquids on the catalyst was found to have an enormous retarding effect on the reaction rate by effectively deactivating the catalyst.

The purpose of this communication is to develop a procedure which will show the combined effects of axial dispersion, external diffusion, intraparticle diffusion, and surface reaction on the conversion for a first-order irreversible reaction in an isothermal, trickle-bed reactor and to evaluate the procedure with existing experimental data. The procedure is analogous to that developed by Suzuki and Smith (1970) for gas-solid, fixed-bed reactors. Suzuki and Smith (1971) derived the equations for the zeroth, first, and second moments of the reactant concentration in the effluent from a gas-solid fixed bed reactor in response to a pulse introduced in the feed. These equations include the effects of all transport resistances for isothermal operation and first-order surface reaction. The equation for the zeroth moment can be related to the conversion X at steady state by Equation (1)

$$1 - x = \frac{C}{C_0} = \exp\left[\frac{-uZ}{2E_z}(\gamma^{1/2} - 1)\right] \tag{1}$$

where

$$\gamma = \frac{1 + 4E_z k_T}{u^2}\left(\frac{3(1-\alpha)}{\alpha}\right)$$
$$\left[1 - \frac{k_T R_p/D_e}{R_p\sqrt{k_r\beta/D_e}\coth\left(R_p\sqrt{k_r\beta/D_e}\right) - 1 + k_T R_p/D_e}\right] \tag{2}$$

and the overall external, mass transfer coefficient is given by (Sylvester and Carberry, 1972)

$$\frac{1}{k_T} = \frac{1}{k_g H H^*} + \frac{1}{k_L} + \frac{1}{k_s}$$

The derivation of Equations (1) and (2) are given in Suzuki and Smith (1970 and 1971).

Equations (1) and (2) can be written in the following form:

$$1 - X = e^{-\Lambda_3 w} \tag{4}$$

$$\Lambda_3 = \frac{N_{pe}}{2}\left[\sqrt{1 + 4\Lambda_2/N_{pe}} - 1\right] \tag{5}$$

$$\Lambda_2 = \frac{1}{1/\Lambda_1 + 1/S} \tag{6}$$

$$\Lambda_1 = \frac{3}{F}\left[\sqrt{\Lambda_0 F}\coth\sqrt{\Lambda_0 F} - 1\right] \tag{7}$$

In these equations Λ_2 is a dimensionless global reaction rate which includes the effects of external mass transfer (S), intraparticle diffusion (F), and surface rate (Λ_0).

When axial diffusion is negligible N_{pe} is large with respect to Λ_2 so that $\Lambda_3 \cong \Lambda_2$. If the external mass transfer resistances are negligible, S is large compared with Λ_1 so that $\Lambda_2 \cong \Lambda_1$. When the intraparticle diffusion resistance is negligible, F is so small that $\Lambda_1 \cong \Lambda_0$. If all three transport resistances are negligible, $\Lambda_3 \cong \Lambda_0$, and Equation (4) is the usual expression for conversion in terms solely of the kinetics of the reaction. Λ_3 may be regarded as a pseudo global rate, which includes the effect of axial dispersion as well as the other transport processes. The asymptotic relations indicated above are not obvious from inspection of Equations (5) to (7), but they are readily seen in Figure 1 which shows the relationships determined numerically.

Figure 1 is a graphical representation of Equations (4) to (7), where each section displays the effect of a single transport resistance. Figure 1a shows the relation between Λ_0 and Λ_1, and thus the importance of intraparticle diffusion; Figure 1b relates Λ_1 and Λ_2, indicating the importance of external diffusion; Figure 1c relates Λ_2 and Λ_3 and so gives the effect of axial dispersion; Figure 1d relates Λ_3 and conversion for a given particle size and reactor length. This plot should be helpful in the interpretation of laboratory kinetic studies and for reactor design. In using the figure for reactor design, the intrinsic rate constant k_r would be known so that Λ_0 can be calculated. The effect of each transport process is estimated from estimates of F, S and N_{pe} and the conversion for a given reactor or the reactor length for a given conversion determined. The figure is also useful for a rapid estimate of the intrinsic constant from the observed conversion. In this case, X is known and the figure is used in the reverse direction to eliminate the transport effects of Λ_0 and thus k_r. In all cases, it is assumed that the liquid phase is uniformly distributed.

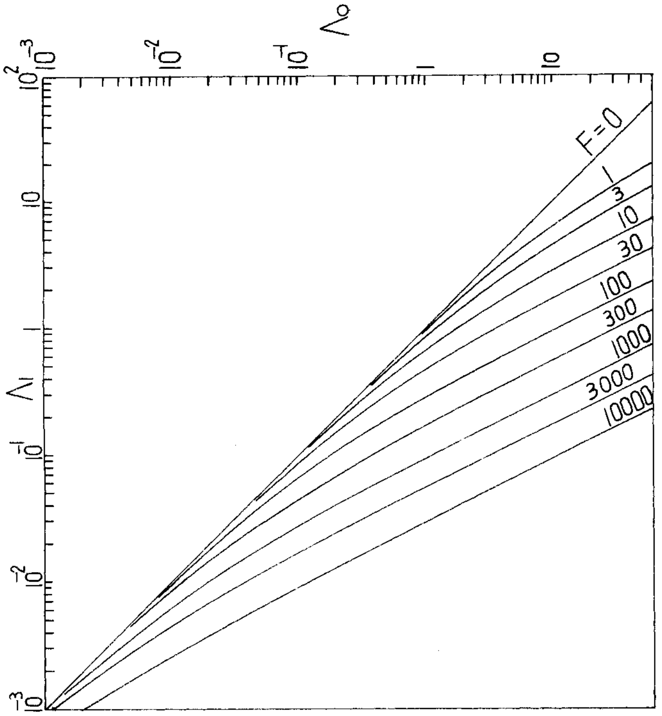

Fig. 1a. Effect of transport process in trickle-bed reactors: Effect of intraparticle diffusion.

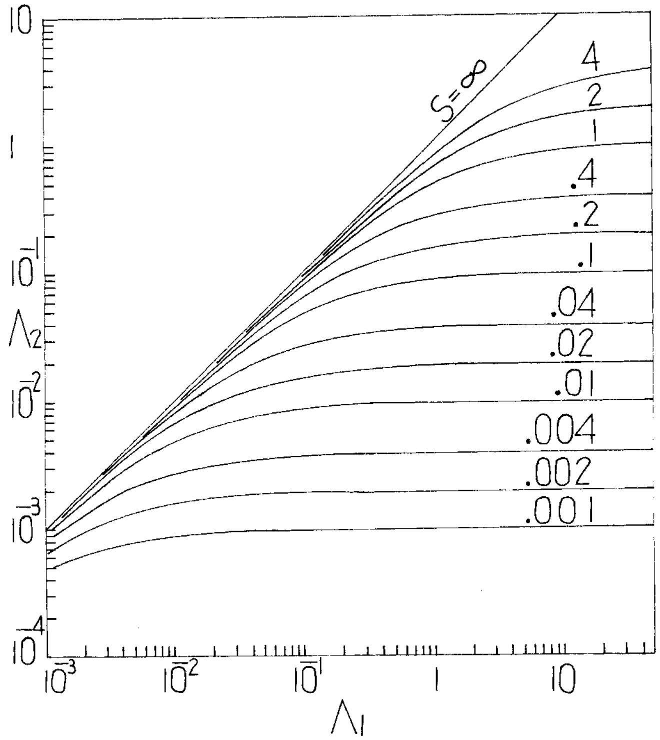

Fig. 1b. Effect of transport process in trickle-bed reactors: Effect of external diffusion.

The utility of the procedure is demonstrated by applying it to the experimental data of Way (1971). Way studied the isomerization of dilute gaseous cyclopropane to propylene in a fixed bed of pelleted silica-alumina catalyst. This same reaction was then carried out on the same catalyst in the presence of a trickling flow of one of three liquids (Nujol, Isopar L, and Solvesso). Each liquid was inert to reaction, but each had different chemical and physical properties. In all cases the reaction rate was reduced due in varying degrees to mass transfer limitations either in the outside film or within the pores of the catalyst and also to adsorption phenomena which apparently blocked some portion of the active sites of the

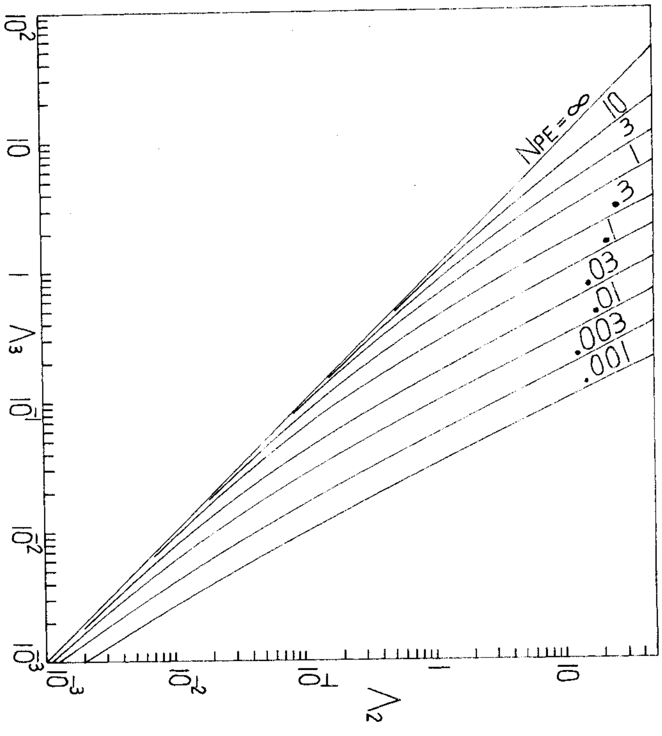

Fig. 1c. Effect of transport process in trickle-bed reactors: Effect of axial dispersion.

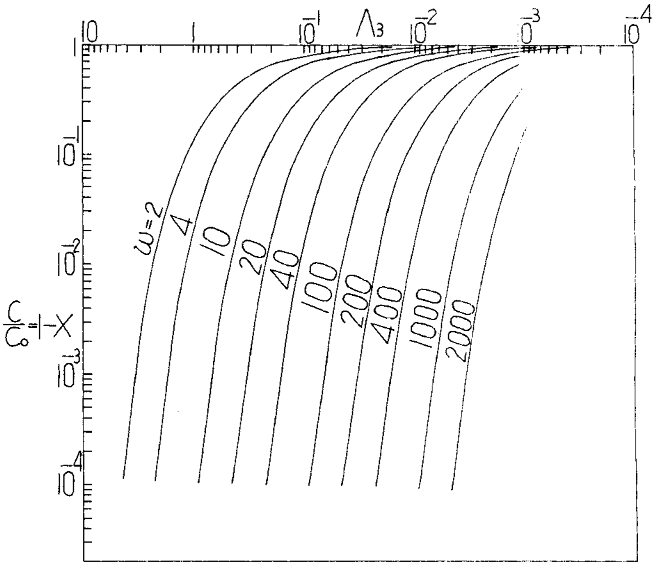

Fig. 1d. Effect of transport process in trickle-bed reactors: Effect of reactor length to catalyst particle size.

catalyst.

Tables 1 to 4 show the comparison between the experimental conversions and the relative importance of the various transport resistances. The predictions of Tables 2 to 4 are based on Way's original data obtained in the gas-solid system alone, in which mass transfer effects were negligible. Due to the absence of experimental information on axial dispersion in trickle-bed reactors, a Peclet number of 100 was used in all calculations, essentially ignoring the effects of axial dispersion.

Table 1 shows the two-phase reactor results. The predicted conversions are somewhat lower than those measured at all temperatures which is due to the difficulty of reading part four of Figure 1 in the upper right-hand corner where the lines are highly curved. Mass transport is seen to be unimportant except for the highest temperatures. Table 2 shows the three-phase reactor results with Nujol as the liquid phase. Here the predicted conversions are somewhat higher than measured indicating that some catalyst deactivation has taken place. For this highly

TABLE 1. TWO-PHASE REACTOR

Gas concentration: 2% cyclopropane in nitrogen
Catalyst *A*: ⅛-in. × ⅛-in. cylinders
θ/τ, correction factor = 0.2
Peclet number = 100

Temp., °C	x measured	x predicted	Catalyst effective factor, Λ_1/Λ_0	External mass transfer resistance, Λ_2/Λ_1	Axial dispersion, Λ_3/Λ_2
50	0.078	0.029	0.995	1.000	0.882
60	0.146	0.064	0.989	1.000	0.977
70	0.268	0.125	0.978	0.999	0.991
80	0.445	0.228	0.957	0.999	0.995
90	0.657	0.360	0.925	0.998	0.995
100	0.844	0.529	0.875	0.997	0.998
110	0.957	0.706	0.803	0.995	0.997

TABLE 2. THREE-PHASE TRICKLE-BED REACTOR

Liquid: Nujol
Gas: 2% cyclopropane in nitrogen, 418 cc/min. @ 18°C
Catalyst A: ⅛-in. × ⅛-in. cylinders
θ/τ correction factor = 0.2
Peclet number = 100

Temp., °C	x measured	x predicted	Catalyst effective factor, Λ_1/Λ_0	External mass transfer resistance, Λ_2/Λ_1	Axial dispersion, Λ_3/Λ_2
50	0.0209	0.0684	0.179	0.737	0.976
61	0.0403	0.1211	0.148	0.716	0.969
71	0.0579	0.1947	0.124	0.694	0.988
81	0.0837	0.2922	0.105	0.671	0.991
91	0.1243	0.4205	0.091	0.651	0.995
101	0.1706	0.5579	0.078	0.625	0.997

TABLE 3. THREE-PHASE TRICKLE-BED REACTOR

Liquid: Isopar L
Gas: 2% cyclopropane in nitrogen, 450 cc/min. @ 30°C
Catalyst A: ⅛-in. × ⅛-in. cylinders
θ/τ, correction factor = 0.2
Peclet number = 100

Temp., °C	x measured	x predicted	Catalyst effective factor, Λ_1/Λ_0	External mass transfer resistance, Λ_2/Λ_1	Axial dispersion, Λ_3/Λ_2
50	0.0177	0.2371	0.471	0.957	0.988
60	0.0309	0.3622	0.372	0.941	0.995
70	0.0502	0.5073	0.294	0.923	0.996
80	0.0884	0.6556	0.231	0.901	0.999
90	0.1528	0.7885	0.184	0.876	0.998
101	0.2296	0.9000	0.143	0.844	1.000
111	0.3056	0.9574	0.116	0.814	1.000
120	0.3707	0.9831	0.096	0.785	0.999

Table 4. Three-Phase Trickle-Bed Reactor

Liquid: Solvesso
Gas: 2% cyclopropane in nitrogen, 440 cc/min. @ 19°C
Catalyst A: 1/8-in. × 1/8-in. cylinders
θ/τ, correction factor = 0.2
Peclet number = 100

Temp., °C	x measured	x predicted	Catalyst effective factor, Λ_1/Λ_0	External mass transfer resistance, Λ_2/Λ_1	Axial dispersion, Λ_3/Λ_2
50	0.00296	0.1284	0.501	0.955	0.989
60	0.00369	0.2014	0.396	0.938	0.982
70	0.00458	0.2981	0.310	0.917	0.993
90	0.01166	0.5372	0.194	0.866	0.998
110	0.03660	0.7729	0.126	0.804	0.998

viscous liquid both internal and external mass transport effects are important. Table 3 shows the three-phase results with Isopar L as the liquid phase. Here the predicted conversions are again higher than measured even though the effects of mass transport are not as important as for Nujol. Once again the liquid is seen to deactivate the catalyst. Table 4 shows the results with the highly aromatic Solvesso as the liquid phase. Here the predicted conversions are more than an order of magnitude larger than measured confirming the significant catalyst deactivation due to the adsorption of Solvesso on the catalyst. Although mass transport effects are not negligible they are not as important as for Nujol. These comparisons not only demonstrate the utility of the method presented to the analysis of laboratory reactor data and to design but also show that unexpected effects like catalyst deactivation due to liquid adsorption can also be diagnosed and accounted for in design.

ACKNOWLEDGMENTS

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NOTATION

C = reactant concentration, g-mole/cc
C_0 = feed reactant concentration, g-mole/cc
D_p = catalyst particle diameter, cm
D_{AB} = molecular diffusivity in mixture of A and B, cm^2/s
D_e = effective diffusivity in catalyst particle cm^2/s
E_z = axial dispersion coefficient, cm^2/s
H = Henry's law constant
H^* = Gas phase holdup, cm^{3}gas/cm^{3}reactor
k_T = overall external mass transfer coefficient defined by Equation (3), cm/s
k_g = gas-side mass transfer coefficient, cm/s
k_L = liquid-side mass transfer coefficient, cm/s
k_s = solid-liquid mass transfer coefficient, cm/s
k_r = intrinsic reaction rate constant, 1/s
R_p = particle radius, cm
X = conversion
U = superficial velocity, cm/s
Z = axial distance from reactor inlet, cm

Greek Letters

α = porosity in catalyst bed
β = porosity of catalyst particle
μ = viscosity, g/cm s
g = gas density g/cc
ω = Z/Rp
γ = defined by Equation (2)

Dimensionless Groups

$F = uRp/De(1-\alpha)$
$N_{pe} = Rp\,U/E_z$
$S = 3(1-\alpha)k_T/u$
$\Lambda_0 = \dfrac{(1-\alpha)\,\beta K_r R_p}{u}$
$\Lambda_{1,2,3}$ = defined by Equations (5) and (7)

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