Effect of Axial Gas Dispersion on MTO Light–Olefin Yield: Microreactor Data

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Pulsed-tracer experiments conducted for horizontal gas flow through a horizontal duct of rectangular cross section (height = 12.7 mm) containing powder in the coherent-expanded vibrated-bed state have been reported (Benge and Squires, 1995; Squires and Benge, 1995). Axial gas dispersion in the duct can be treated by a simple model: the dispersion is a "spreading" superimposed on plug flow, with no gas bypassing and no lagging gas indicative of dead zones. At a given weight hourly space velocity, a large variation in axial Peclet number (Pe_{ax}) can be achieved by varying length of duct and gas superficial velocity in proportion, with no substantial effect upon gas–solid contacting efficiency. Herein, we report data for the methanol-to-olefin reaction conducted in three ducts at lengths affording Pe_{ax}-values from ~ 2 to ~ 20. The new data display a trend in light-olefin yield vs. Pe_{ax} similar to that reported earlier for three fluid-bed reactors at diameters of 10, 102 and 600 mm.

Introduction

A shallow bed of particles resting on a horizontal plate that is vibrated sinusoidally in the vertical direction can display one of several "states" (Thomas et al., 1989). The coherent-expanded vibrated-bed state of a powder (Geldart Group A) offers the opportunity we are pursuing. Figure 1 is a series of sketches illustrating the behavior of a layer of Group A powder in this state. In the sketches, the layer is fluid-cracking catalyst at ~ 1 mm in depth in a compacted condition. The layer is situated upon a plate vibrated vertically at 25 Hz and with maximum displacement of ~ 2 mm from null position. The upper two sketches in the figure are side views showing the layer's expansion to a height of ~ 4 mm at phase angles between ~ 60° and ~ 150°. The expansion is ~ 4 times the layer's compacted depth; at no point in the cycle is the layer expanded less than by this amount. The second sketch, at 158°, shows the layer beginning to lift. Gas is penetrating the powder to create a gap between layer and plate. The third sketch, at 235°, shows the fully formed gap. Shortly afterward, rapid closure of the gap forces gas to rush upward, causing the powder to expand to a height of 10 mm, as the fourth sketch illustrates. The fifth sketch is a top view of the powder during gap closure: the upward rush of gas causes the powder to sort itself into vertical bands, about a millimeter in width, and at spacings of a few millimeters. Mixing of both gas and powder is intense in the vertical direction, while relatively small horizontally.

Consider a horizontal, vibrated duct of rectangular cross section (height, 12.7 mm; width, 25.4 mm) containing a coherent-expanded layer of powder (vibration parameters being such that powder achieves full duct height in each cycle). We have reported cold-model studies of such a duct (Benge and Squires, 1995; Squires and Benge, 1995). The work confirmed what visual observation had earlier suggested: that the duct provides intimate gas–solid contacting, and that axial gas dispersion therein can be treated by a simple axial dispersion model (Levenspiel, 1972). The parameter of the model is axial Peclet number, Pe_{ax}:

$$Pe_{ax} = \frac{UL}{D_{ax}}, \tag{1}$$

where L = length of duct (cm); U = horizontal superficial gas velocity (cm/s); and D_{ax} (cm^2/s) is an axial dispersion coefficient (combining effects of both molecular diffusion and fluid dispersion). Pulsed-tracer experiments (using helium, argon, and sulfur hexafluoride in nitrogen) established that axial gas dispersion in the duct can be viewed as a simple "spreading" superimposed upon plug flow, with negligible gas bypassing and no lagging gas indicative of presence of dead zones.

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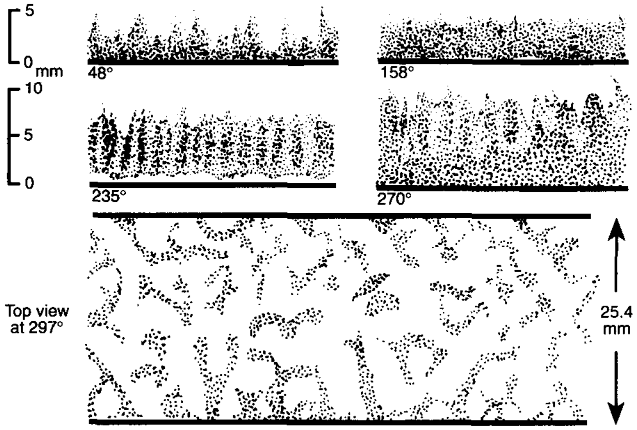

Figure 1. Coherent-expanded state in a vibrated bed of Group A powder.

The upper four sketches are side views. The lower sketch is a top view. The drawings are tracings from photographs (Thomas et al., 1989) of a vibrated layer of fluid catalytic cracking powder (0.96 mm in compacted state) at phase angles noted alongside the drawings. Conditions: 25 Hz; amplitude = 1.99 mm; maximum acceleration = 5 times gravity. If maximum acceleration = ~ 6 to 7 times gravity, the layer expands to more than 13 mm at ~ 270°.

Benge and Squires (1995) reported D_{ax} values for a duct ($L = 20$ cm) charged with glass beads (53 to 74 μm) to a compacted depth of 1 mm. For each of the tracers, measured D_{ax}-values vs. U defined a straight line, each line having a common slope. The three sets of data could be collapsed to a common straight line by subtracting from D_{ax} a quantity proportional to the applicable molecular diffusion coefficient, D_{mol} (cm^2/s). Thus:

$$D_{ax} = D_{vib} + \eta D_{mol} + WU \tag{2}$$

$$D_{ax} = 0.20 + 1.1\ D_{mol} + 0.257\ U. \tag{2a}$$

The quantity D_{vib} reflects a dispersion associated with motion of gas dragged upward and downward by particles moving in the vertical trajectories that characterize the coherent-expanded vibrated-bed state (see Figure 1). The second term, ηD_{mol}, reflects mixing due to molecular diffusion. The third term reflects a "Wilhelm dispersion mechanism" arising from interaction of the flow with particles of the bed (Wilhelm, 1962). Benge and Squires (1995) argued that the parameter η in Eq. 2 can readily take on a value greater than one.

Let $S = U/L = d\rho_{cat}$ WHSV/$(1.27 \times 3{,}600\ \rho_{gas})$, where d = compacted depth of catalyst layer (cm); WHSV = weight hourly space velocity (weight of reactants per hour/weight of catalyst); ρ_{cat} and ρ_{gas} = densities of catalyst (compacted) and reaction gas, respectively. Combining Eqs. 1 and 2a, we have

$$Pe_{ax} = \frac{SL^2}{0.20 + 1.1 D_{mol} + 0.257 SL}. \tag{3}$$

Squires and Benge (1995), using helium tracer in ducts of three lengths, reported experimental confirmation of Eq. 3 at WHSV = 1.

Herein, we report (1) development of a vibrated duct for operation to ~ 550°C, and (2) data showing an effect of axial gas dispersion in the vibrated duct upon light-olefin yield from the methanol-to-olefin (MTO) reaction, in which methanol converts over HZSM-5 catalyst at 482°C and atmospheric pressure to olefins and other hydrocarbons along with water byproduct (Chang, 1984; Chang et al., 1984):

$$CH_3OH \rightleftharpoons CH_3OCH_3 \rightarrow \text{light olefins} \rightarrow$$
$$\text{paraffins, cycloparaffins, aromatics.}$$

We compare our data with fluid-bed results (Gould et al., 1986; Keim et al., 1987).

Our vibrated duct provides a microreactor suitable for conducting a variety of heterogeneously catalyzed or gas–powder reactions at atmospheric pressure. If a newly discovered reaction of this type is thought to have commercial interest, an experiment in a microreactor of large L, affording substantially plug flow, can determine the WHSV necessary to achieve a desired conversion of reactant gas. Experiments in several ducts at shorter lengths, maintaining WHSV constant by varying U proportionately to L, can furnish data over a range of Pe_{ax}, revealing sensitivity of reaction outcomes (conversion, selectivities, etc.) to axial gas dispersion. Squires and Benge (1995) gave our reasons for believing gas–solid mass transfer in the microreactor is so high that its variation with U cannot be a factor in interpreting results from experiments in ducts of various lengths, if the speed of the reaction under study is such that a fluid bed can be considered an appropriate reactor to choose.

Experimental Arrangements

Our vibration system is identical to that described by Benge and Squires (1995). A heated, insulated microreactor duct is placed on a rectangular vibration table supported by horizontal leaf springs tuned to a resonance frequency close to the 24 Hz used in the present work (Tshabalala, 1995). An electromagnetic vibrator drives the table from below by a vertical steel rod, 2.39 mm in diameter. Especially important is maintenance of both strict verticality of the drive shaft and, through leaf-spring balancing, a strict horizontality of the microreactor duct. Achieving these goals requires the weights of the various elements subject to vibration to be distributed symmetrically.

We fabricated three microreactor ducts of 6061-T6 aluminum block (Tshabalala, 1995). Duct lengths are 22.86, 15.24 and 7.62 cm. Each duct has six elements: tops and bottoms for a gas-inlet plenum, for duct proper, and for a gas-exit plenum. Two gas distributor plates, machined from porous stainless steel, separate gas-inlet and gas-exit sections from the duct proper, holding catalyst within the duct. Soft copper sheet is used as gasket material for vertical mating surfaces at the duct's two ends; Chen and Reagan (1979) reported that copper has no catalytic activity toward methanol. New copper gaskets were provided for vertical mating surfaces in each experiment. Since copper corroded severely at 482°C, it is not used everywhere, because its machining requires special care. Grafoil (flexible graphite sheet) is used as gaskets for the horizontal mating surfaces between top and bottom blocks of each of the three sections of the assembly. Although danger of leakage is small, since the duct operates at essentially atmospheric pressure, pressure testing for leaks is routine before each experiment.

Heating the assembly is accomplished with four 9.5-mm cartridge heaters rated at 600 W, 120 V, 25.4 cm in length, and connected in series. Two enter the bottom aluminum-block elements at one end, and two enter the top elements, symmetrically, at the other end. The heaters are fitted with stainless-steel braid to protect the leads from snapping during vigorous vibration.

The microreactor duct is charged with a weighed quantity of HZSM-5 catalyst such that it would create a layer 1 mm in depth, if the catalyst were in its fully compacted state. Density of the catalyst in this state was determined to be 0.7534 g/mL by using the procedure given by Thomas et al. (1989), namely, averaging the weight of six samples of ~10 mL of catalyst in a graduate cylinder after the samples have been compacted by mechanical tapping followed by intense vibration at ~1,000 Hz.

In the work, we require catalyst in the heated microreactor duct to display the coherent-expanded (C-E) vibrated-bed state. In planning our study, we faced the question, how can we ensure that the C-E state exists during an experiment? We considered and rejected ideas for using a quartz microreactor duct in a furnace fitted with a window or for providing a window in an internally heated aluminum duct. Our answer to the question has been to provide a glass reference duct, identical in dimension to the microreactor duct's reaction section, and mounted above the duct-assembly's insulation. A quantity of catalyst is charged to the glass reference duct, which is very like that used in the aluminum microreactor duct. The state of powder in the glass reference duct can be judged by eye under strobe lighting at a frequency slightly below the 24 Hz of our experiments, creating an effect like ultra-slow-motion cinematography.

It can be argued that visual confirmation of the C-E state in the glass reference duct lends confidence that this state also exists in the hot microreactor duct. The viscosity of MTO reactants is ~40% higher than that of air at room temperature, present both in glass reference duct and also in our earlier studies of the transition from the C-E state to the coherent-condensed (C-C) vibrated-bed state (Thomas et al., 1989). This transition is defined as that depth of particle layer at which, when one slowly adds particles, clumps of particles in the C-C state, forming Chladni patterns, first appear on the floor of the duct. Among other factors, gas viscosity affects this transition, an increase in viscosity moving the transition toward greater depth of powder. Observation of C-E state in the glass reference duct, therefore, supports a strong inference that the weight of powder charged to the hot microreactor duct is below that at which transition from C-E to C-C state would occur under MTO reaction conditions.

The glass reference duct is borosilicate glass. It is glued to an aluminum plate using General Electric's silicone adhesive sealant. Great care must be exercised in mounting both glass reference duct and microreactor, to ensure horizontality of both elements, in parallel relationship with the vibration table.

A syringe metering pump, ISCO Model 314, is used to deliver methanol to the microreactor via stainless-steel tubing (3.175-mm outside diameter and 0.51-mm wall thickness). Helium flows through the microreactor while stable temperatures are being achieved therein. Meanwhile, a desired flow of methanol is established via one branch of a four-way valve, by determining the quantity of methanol delivered over a measured time. After the desired temperature and methanol flow have been established, a quarter-turn of the four-way valve diverts helium away from the microreactor and allows methanol to flow through heated tubing and to enter the microreactor in the vapor state. The four-way valve is situated at the highest elevation in the flow system, so that flow of methanol vapor is promptly established at the desired rate, and no gravity-assisted flow of liquid methanol can enter the heated piping, creating an uncontrolled initial pulse of methanol vapor into the microreactor.

Products are analyzed by means of Hewlett-Packard gas chromatograph, HP 5730A, fitted with flame ionization detector (FID) and thermal conductivity detector (TCD), each sending a signal to a separate Hewlett-Packard Integrator, Model 3390A. Two HayeSep D packed columns (Hayes Separations, Inc.) separate products chromatographically; columns are conditioned before initial use (18 hours at 270°C with helium flow). (Columns are 3.175 mm × 3.048 m and operable to 290°C.) Carrier gas is helium, flowing to each detector at 30 mL/min.

Our sample of ZSM-5 powder is substantially identical to that used in fluid-bed studies of the MTO reaction (Gould et al., 1986; Keim et al., 1987). As received by us, the cation in the ZSM-5 is ammonium. The powder is calcined at 538°C for 12 h under flow of air to convert it to the HZSM-5 catalyst for the MTO reaction. It is a Group A powder with spherical particles that display the wide size distribution and average particle size, which are typical of fluid catalytic cracking catalyst.

Two standard gas samples were obtained to calibrate our chromatographic analysis. One sample comprised ethylene, propylene, 1-butene, 1-pentene, and 1-hexene, each at ~1,000 ppm, in helium. A second sample comprised methane, ethane, propane, *n*-butane, *n*-pentane, and *n*-hexane, each also at ~1,000 ppm, in helium. In exploratory work, neither isothermal oven conditions nor a programmed oven temperature gave satisfactory results, and various combinations of isothermal and programmed steps were attempted. Oven conditions settled upon are 2 min at 120°C, followed by temperature rise at 8°C/min, reaching a final temperature of 250°C, followed by cooling to 120°C before another analysis. Duration of an analysis is 32 min. Table 1 lists retention times for this combination of isothermal and programmed steps. A chromatogram obtained for a mixture of the standard olefin and paraffin samples shows good resolution of olefin and paraffin peaks. An adjusted retention time is reckoned as the difference between retention time of a given component and time of the methane peak. Peaks are identified by plotting (1) adjusted retention time against boiling point, and (2) logarithm of adjusted retention time against carbon number. Correlations were developed relating peak areas to quantities of C_2–C_6 hydrocarbons present in a sample.

In MTO experiments, no peaks are seen for C_{7+} hydrocarbons that could be olefinic; C_{7+} hydrocarbons reported hereinafter are believed to be (unidentified) paraffins and cycloparaffins, with (perhaps) small amounts of aromatics. Calibration runs for methycyclopentane, cyclohexane, methylcy-

Table 1. Retention Times for Combination of Isothermal and Programmed Oven Temperature Steps*

Compound	Boiling Point (°C)	Retention Time (min)
Methane	−161.0	1.07
Ethylene	−104.4	2.10
Ethane	−88.0	2.45
Propene	−47.7	5.90
Propane	−42.2	6.57
1-Butene	−6.3	11.27
n-Butane	0.0	12.74
1-Pentene	30.0	15.43
n-Pentane	36.0	16.41
1-Hexene	64.0	19.68
n-Hexane	69.0	20.45

*2 min. at 120°C followed by 8°C/min to 250°C.

clohexane, toluene, iso-octane, ethylbenzene, and *o*-xylene, providing additional retention times, did not prove useful for identifying C_{7+} hydrocarbons.

Results

The MTO reaction was studied at 482°C and at atmospheric pressure prevailing at Blacksburg, VA, ~ 712 mm Hg.

A blank run (with no catalyst present in a microreactor at length 22.86 cm) was conducted, yielding only a methanol peak in an FID chromatogram, and in a TCD chromatogram, only a methanol peak together with a small water peak (reflecting water in the methanol, and not a reaction product).

Table 2 lists conditions for seven runs conducted in three microreactor ducts ($L = 22.86$, 15.24 and 7.62 cm). All runs were conducted at 24 Hz and maximum vertical displacement of ~ 4 mm from null position, affording maximum acceleration of 10 times gravity.

Each run commenced with a fresh sample of HZSM-5 catalyst. Table 3 gives analyses for carbon and hydrogen in three samples of used catalyst. Calculated "yields" of carbon vary from 0.21 to 0.29 wt. %, based on cumulative feed of methanol for a run. The interior of a microreactor was visually inspected after each run. No carbon deposits were seen. Substantially all methanol appears to report to hydrocarbons.

Table 3. Yields of Carbon in Experiments

	Analysis of Catalyst Sample		
Sample Origin	Carbon (wt. %)	Hydrogen (wt. %)	Yield of Carbon (%)*
7.62-cm duct	1.42	< 0.5	0.22
15.24-cm duct	2.84	< 0.5	0.29
22.86-cm duct	1.44	< 0.5	0.21

*Percentage of methanol carbon reporting to carbon deposited on catalyst, based upon total throughput of methanol for the run.

Table 4 lists average hydrocarbon yields for a representative run at each duct length. Figures 2, 3 and 4 plot yields of C_2–C_6 olefins vs. sample time for runs in 22.86-cm, 15.24-cm, and 7.86-cm microreactor ducts, respectively.

Figure 5 plots average light-olefin yield for each of our runs vs. axial Peclet number. The figure also plots yields vs. Peclet number for a series of three fluid beds (Keim et al., 1987; Avidan, 1995). The trend of our data versus Peclet number roughly parallels that seen in the fluid-bed data.

Unlike the fluid-bed researchers, we did not find "Reaction Index" (ratio of propane to propene yield) a useful variable for organizing our data (Tshabalala, 1995).

Discussion

Knowledge of the sensitivity of a gas–powder reaction to axial gas dispersion will be valuable to engineers embarking on reactor development. Since axial dispersion increases sharply with fluid-bed diameter (van Deemter, 1980), knowing how dispersion affects a reaction is important if a fluid-bed research and development (R&D) is to proceed beyond the laboratory stage. A literature has emerged arguing that the simple axial dispersion model is useful for treating gas dispersion in a large catalytic fluid bed (e.g., DeMaria et al., 1961; Avidan, 1982; Bolthrunis, 1989).

Our objective has been to demonstrate that our microreactor can disclose, quickly and at small cost, effects of axial gas dispersion upon a new reaction about which little is known.

For our study, we chose the MTO reaction because fluid-bed data are available showing the reaction's response to Pe_{ax}. See Figure 5, with data from 10-mm and 102-mm beds (Mobil Research & Development Corp.) and from a 600-mm bed (Mobil, Union Rheinische Braunkohlen Kraftstoff AG, and

Table 2. Conditions of Experiments in Three Microreactor Ducts

HZSM-5 (g)	Methanol Flow (mL/h)	Superficial gas Velocity (cm/s)	WHSV	Duration (hr)	Pe_{ax}*
		7.62-cm duct			
1.3757	0.97	0.13	0.54	32	1.3
1.3669	1.96	0.27	1.11	19	2.5
1.3608	1.88	0.26	1.06	29	2.4
		15.24-cm duct			
2.8298	4.05	0.53	1.10	34	9.2
2.8107	3.79	0.50	1.04	25	8.7
		22.86-cm duct			
4.3860	6.50	0.83**	1.15	33	19.8
4.3451	6.20	0.79	1.10	24	19.1

*Calculated from Eq. 3, with $D_{\mathrm{mol}} = 0.5\ \mathrm{cm^2/s}$ and $d = 0.1$ cm.

**The horizontal gas superficial velocity in the 22.86-cm duct is less than an allowable 1.4-cm/s velocity for the MTO reaction, scaled by viscosity ratio from an allowable 2.0-cm/s velocity for air. The latter is the velocity just beyond which first signs of displacement of powder toward microreactor outlet are seen in experiments with air (Thomas and Squires, 1989).

Table 4. Composition of MTO Hydrocarbon Product from Three Microreactors*

Duct Length	22.86 cm	15.24 cm	7.62 cm
Ethylene	12.5%	13.9%	10.2%
1-Propene	19.1	18.8	17.8
1-Butene	28.9	17.5	17.3
1-Pentene	14.8	14.7	8.2
1-Hexene	7.2	5.2	3.4
Total light olefins	82.5%	70.2%	56.9%
Methane	1.3%	1.4%	1.2%
Ethane	0.7	0.4	0.4
Propane	7.4	3.5	4.8
n-Butane	4.5	3.4	3.3
n-Pentane	1.8	3.4	1.5
n-Hexane	1.4	1.2	0.9
Total light paraffins	17.1%	13.3%	12.2%
Heavier hydrocarbons**	0.4%	16.5%	30.8%
WHSV	1.15	1.10	1.06
Pe_{ax}	19.8	9.2	2.4

*Percentage of methanol carbon reporting to various hydrocarbons.
**Paraffins, cycloparaffins, and (perhaps) small amounts of aromatics.

Uhde GmbH). Data like these are rare in the fluid-bed literature. Gathering such data is costly in both money and time, and the data may have a commercial value that precludes their prompt publication. Our microreactor has potential for disclosing a reaction's response to Pe_{ax} at far less cost and far more quickly than building and operating fluid beds over a range of diameters sufficient to reveal this response (e.g., from ~10 to hundreds of millimeters).

Our somewhat higher yields in Figure 5 may reflect (1) our lower pressure; (2) the absence in our runs of the fluid-bed operation's periodic catalyst regenerations, which may affect selectivity to olefins; or (3) absence in our runs of front-to-back solid mixing, a phenomenon known to affect the kinetics of some reactions when conducted in a fluid bed (Squires, 1961, 1973, 1982, 1994; Squires et al., 1985). By providing serrations in the microreactor duct's floor, front-to-back circulation of catalyst powder may be induced in future experiments (Squires and Benge, 1995).

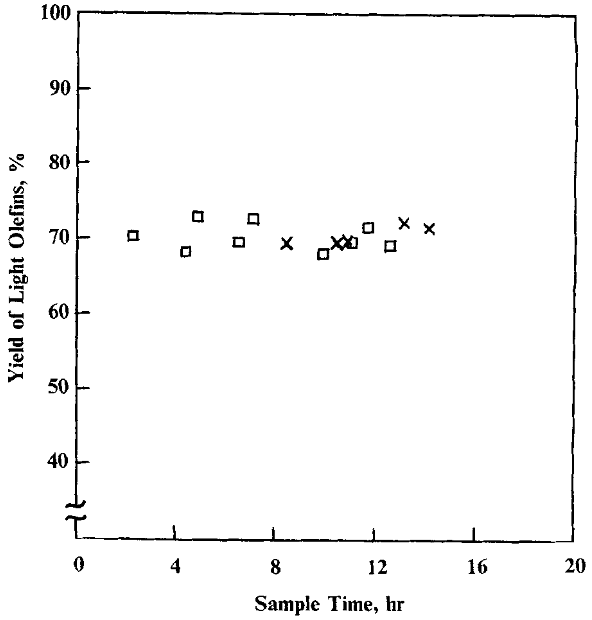

Figure 3. Yield of light olefins from two runs in 15.24-cm microreactor.

Yield of methanol carbon reporting to C_2–C_6 olefins; yields vary between 68.0 and 72.9%. Average yield = 70.2%; WHSV = 1.10; Pe_{ax} = 9.2 (□); average yield = 70.2%; WHSV = 1.04; Pe_{ax} = 8.7 (×).

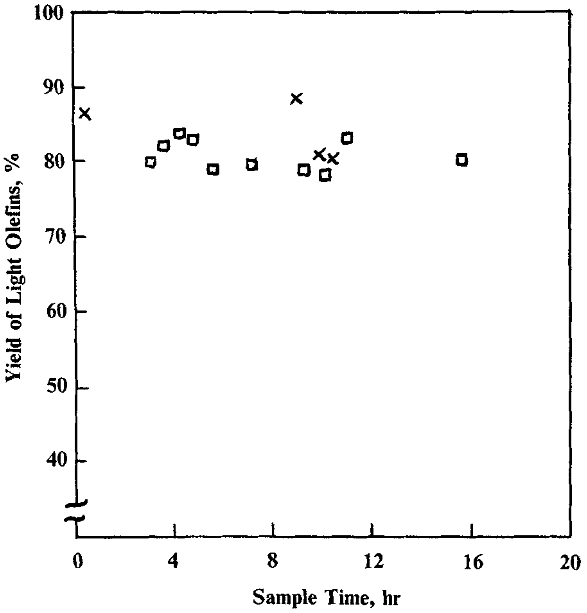

Figure 2. Yield of light olefins from two runs in 22.86-cm microreactor.

Yield of methanol carbon reporting to C_2–C_6 olefins; yields vary between 78.3 and 88.5%. Average yield = 82.5%; WHSV = 1.15; Pe_{ax} = 19.8 (□); average yield = 85.5%; WHSV = 1.10; Pe_{ax} = 19.1 (×).

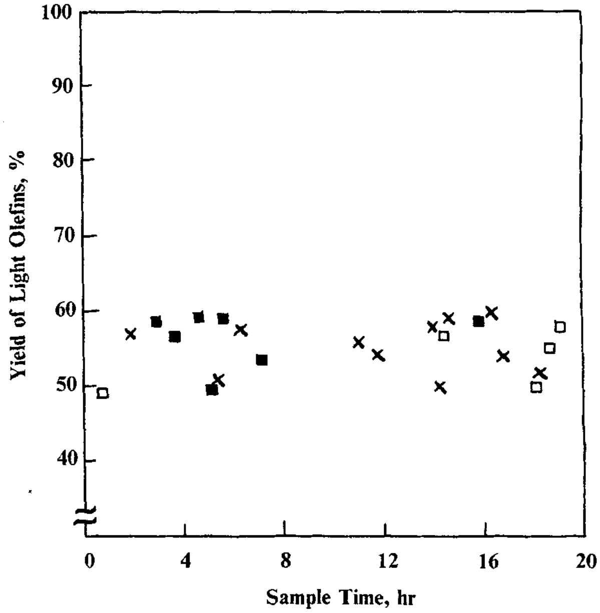

Figure 4. Yield of light olefins from three runs in 7.62-cm microreactor.

Yield of methanol carbon reporting to C_2–C_6 olefins; yields vary between 49.0 and 59.7%. Average yield = 53.6%; WHSV = 0.54; Pe_{ax} = 1.3 (□); average yield = 54.1%; WHSV = 1.11; Pe_{ax} = 2.5 (×); average yield = 56.9%; WHSV = 1.06; Pe_{ax} = 2.4 (■).

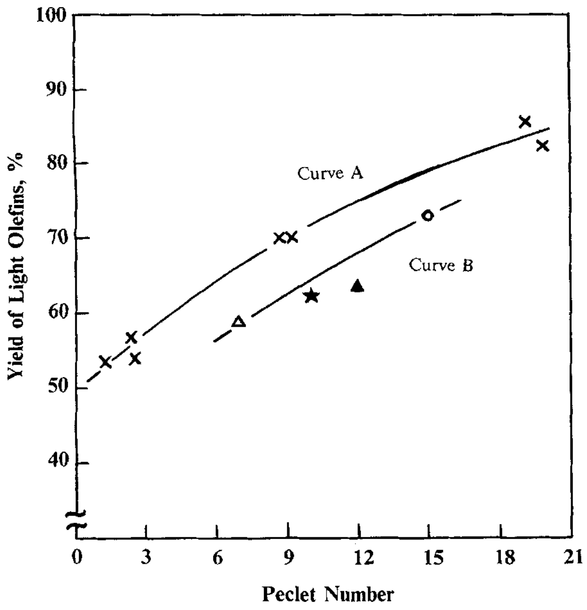

Figure 5. Comparison of yields of light olefins from microreactors and three developmental fluid-bed reactors at WHSV = ~1.

Yield = average percentage of methanol carbon reporting to C_2–C_6 olefins. Curve A = our data (482°C, 712 mm Hg); curve B = fluid-bed data (Keim et al., 1987; Avidan, 1995). Experimental conditions in fluid beds: 482°C and 772 mm Hg in bed of 10-mm diameter (○) and in bed of 102-mm diameter (★). 500°C and 1,876 mm Hg in bed of 600-mm diameter: without baffles (△) with baffles (▲).

In the near future, our microreactor could help R&D managers to avoid the expense of a fluid-bed R&D effort where an economically significant outcome of a reaction is acutely sensitive to axial gas dispersion, and where a fixed bed is an acceptable alternative.

In this circumstance, a circulating fluid bed may provide an alternative more attractive than the fixed bed. Our microreactor data suggest that a circulating fluid bed designed to afford high Pe_{ax} may be a good choice for the MTO reaction (Schoenfelder et al., 1994).

Our hope is that, over time, a body of microreactor data can grow to sufficient size and represent sufficient variety of reaction type such that often, as soon as laboratory fluid-bed data for a new reaction become available, project managers may use previously acquired microreactor data to justify a decision to build a plant around a fluid-bed reactor. The goal would be for such a decision to be made with something like the confidence now attached to a decision for a plant with a fixed-bed reactor.

Responding to a reviewer's comment, we note that a research team seldom, if ever, has the luxury of possessing sufficient bench-scale kinetic data to predict curves like those seen in Figure 5. An analysis of the fall-off in MTO light-olefin yield with increasing axial gas dispersion (declining Pe_{ax}) seems to require information of two kinds: (1) identification of the C_{7+} moieties whose yield increase appears to account for the fall-off, and (2) kinetic data for creation of these species from gases "retarded" by axial dispersion and thereby exposed to MTO reaction conditions over longer residence times.

Although bubble theory has been valuable for designers of fluid beds of Group B and Group D solids (e.g., for combustion), the theory offers little for the reaction engineer wishing to design a catalytic fluid bed employing a Group A powder (Bolthrunis, 1989). At best, bubble theory offers a dubious framework for correlating pilot-plant information. Where a reaction is newly discovered and no kinetic information is yet available, bubble theory cannot project reaction outcomes that an R&D engineer may reasonably hope to achieve in a commercial-scale fluid bed. For a new reaction, a few experiments in our microreactor can quickly answer an important question, one that cannot be answered unequivocally by investing effort focused upon bubble theory: obtaining bench-scale kinetics in fixed beds; developing reaction models and kinetic rate expressions for reactions yielding primary products and, perhaps as well, for reactions that occur in gases retarded by axial gas dispersion, either breaking down products or yielding undesired secondary matter; and applying theory for how axial gas dispersion would influence integral reaction outcomes. To obtain an unequivocal answer from an effort along these lines, it must include unsteady-state reaction kinetic studies disclosing whatever influence (either good or bad) top-to-bottom solid circulation may have.

At least two effects can cause such influence:

First, the circulation causes solids to traverse a wide range of gas environments in times on the order, generally speaking, of 5 to 10 s. Equilibrium adsorption levels of reacting gases upon the solids are not established instantaneously. Equilibrium levels in the time-invariant, progressive gas environments of fixed-bed kinetic studies may bear little relationship to steady-state (or mildly fluctuating) levels on solids in a fluid-bed reactor. Integral reaction outcomes determined (or calculated) for time-invariant, progressive gas environments may of course sometimes give an idea of what to expect from a fluid bed. From our microreactor data (obtained in substantially time-invariant, progressive gas environments, since there was no front-to-back solid circulation), it appears that the MTO reaction may be such a case (although earlier we offered the caveat that absence of such circulation may be a factor accounting, at least in part, for our higher yields in Figure 5 relative to fluid beds).

Second, a fluctuating gas environment can influence the oxidation level of a metal species present in a catalyst. We know, for example, that frequent exposure of an iron Fischer–Tropsch (FT) catalyst to reducing conditions near the bottom of a fluid-bed synthesis reactor can maintain high catalytic activity, despite the fact that the powder spends much of its time in the oxidizing gases present at higher bed elevations (Squires, 1982). Catalyst activity remains high in a well-designed fluid-bed FT reactor (i.e., one employing both suitable gas velocities and a suitable Group A powder), whereas, in a fixed-bed reactor, activity of an iron catalyst will decline to substantially zero over time as FT reaction products oxidize the iron in a wave progressing from gas-outlet to gas-inlet. Unfortunately, large FT synthesis reactors erected around 1950 at Brownsville, TX, employed an unsuitable, Group B powder. Insufficient dwell-time of catalyst in reducing gases led to insufficient levels of reduced iron; the result was a reduction in catalyst activity that accounted (at least in part) for Brownsville's unsatisfactory rate of production, ~1,500 daily barrels of oil vs. an intended 7,000 (Squires, 1982). In any situation of this type, where a fluid-bed catalyst cycles between oxidizing and reducing atmospheres, the balance between catalyst oxidation and reduction would be exceedingly difficult to predict by applying theory to fixed-bed bench-scale data; but a series of microreactor experiments in which solid circulation is varied could reveal the engineering importance of this balance for a fluid-bed catalysis, as well as a good idea of its practical effect.

When our microreactor has been further developed to include the capability of operating at elevated pressure and means for studying solid-circulation effects, we expect it to become the tool of choice for scale-up of a catalytic fluid bed from laboratory fluid-bed data. Reaction engineers specializing in fixed-bed design have long enjoyed the advantage that data for scale-up can be obtained from a laboratory fixed bed of small size. The combination of microreactor and laboratory fluid bed could go a long way toward giving fluid-bed reaction engineers a comparable advantage.

A possible limitation should be mentioned. In studies of an earlier vibrated-bed microreactor (employing the C-C state and differing from the C-E–state microreactor reported herein), Whiting (1985) found it impossible to conduct FT synthesis at 22 atm over an iron catalyst at a temperature below 395°C. At lower temperatures, catalyst mobility declined and ceased over time, apparently as a result of deposition of sticky, waxy hydrocarbonaceous matter. We recognize, therefore, that the usefulness of the new microreactor may be limited if yield from a reaction includes moieties of such high molecular weight that sticky deposits arise, impeding catalyst movement. Two approaches might be taken to study a reaction of this type: large increase in either vibration intensity or catalyst particle size may afford adequate powder mobility. New cold-model experiments may be advisable, yielding new values of D_{vib},η, and W in Eq. 2.

We suggest that reliance on Eq. 3 will meet most engineering requirements. If, however, microreactor results are to be subjected to detailed theoretical analysis, it may be best to acquire both pulsed-gas-tracer data (Benge and Squires, 1995) and integral reaction outcome data simultaneously in the same duct, subjecting both sets of data to automatic workup. A battery of several ducts so instrumented, at various lengths and operating simultaneously, could provide plots of reaction outcomes vs. well-characterized Pe_{ax} values from a single experiment.

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Notation

W = proportionality constant (cm); see Eq. 2
η = proportionality constant (dimensionless); see Eq. 2

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