Enhancing Performance of Three-Phase Catalytic Packed-Bed Reactors

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Our previous theoretical work predicted the possibility of enhancing three-phase packed-bed reactor performance by operating in the pulsing-flow regime. This article deals with the experimental study of the beneficial effect of pulsing flow on reaction outcome. Hydrogenation of phenylacetylene, dissolved in n-tetradecane over Pt/alumina catalyst, was chosen as the experimental reaction system. This is a triangular reaction, with styrene and ethylbenzene as the desired intermediate and final products, respectively. With properly designed experiments, the reaction performance in pulsing flow and trickling-flow regimes was compared directly. The effects of process variables such as temperature, feed flow rates, and reactant concentration on reaction behavior were studied. A simplified model to describe the qualitative trends was also developed. Both experiments and calculations show that the yield of styrene is higher in pulsing flow than in trickling flow, which confirms the advantages of pulsing-flow operation predicted by the theoretical work.

Introduction

Multiphase reactions, in which gas and liquid reactants are selectively converted into desired products using solid catalysts, provide the basis for a large number of chemical, petrochemical, biochemical, and polymer processes (Mills et al., 1992; Dudukovic et al., 1999). A common configuration for carrying out such reactions is a three-phase packed bed reactor, involving a stationary packed-bed of catalyst over which gaseous and liquid reactants flow in either a cocurrent or countercurrent manner. Due to complexity of this type of operation, many factors influence reactor behavior. These include liquid distribution, contacting efficiency and partial wetting, which have received prior attention in the literature (Jiang et al. 1999; Al-Dahhan and Dudukovic, 1995; Watson and Harold, 1994).

In cocurrent three-phase packed-bed reactors, four major flow regimes have been identified: trickling flow, pulsing flow, spray flow, and bubble flow (Ng and Chu, 1987), depending on factors such as gas and liquid flow rates, physical properties, and the nature of the reactor packing. These flow regimes result in different behavior (such as holdup and transport) around the catalyst, which could affect the overall reaction outcome. Specifically, when the reactor is operated in pulsing-flow regime, liquid-rich slug (pulse) and gas-rich slug (base) regions are formed, and they move down the column alternatingly. The strong interactions between the phases within the pulses result in significant enhancement in overall mass and heat transfer rates (Blok and Drinkenburg, 1982; Chou et al., 1979), and the alternation between pulses and bases introduces a periodically changing flow environment around the stationary catalyst, with the overall reactor operating under stationary conditions.

By carrying out experiments in columns packed with different heights of active catalyst, Sims et al. (1994) made a direct comparison of H_2O_2 conversion in catalytic decomposition of H_2O_2 under pulsing-flow and trickling-flow regimes of a three-phase packed-bed reactor. With different heights of active catalyst and by varying the flow rates, the experiments can have the same space time, but operate under different flow regimes. It was shown that operation in pulsing-flow regime can significantly increase the conversion of H_2O_2, as compared to trickle-flow operation at the same space time. Our earlier theoretical work (Wu et al., 1995) predicted that reactor performance (that is, conversion or selectivity) could

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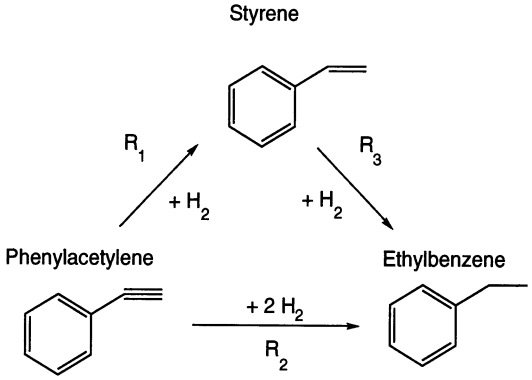
be enhanced by operating the reactor in pulsing-flow regime and that optimization is possible by "tuning" the pulsing frequency prudently.

In the present work, an experimental demonstration of the beneficial effect of pulsing-flow regime is made. In addition, a simplified model is developed to qualitatively examine the influence of flow regimes on reactor performance. The results of this work provide a general understanding that can be applied to a variety of gas-liquid-solid reacting systems.

Reaction System

Proper selection of the reaction system is crucial to experimentally investigate the effect of flow regimes. The system should be a multiphase catalytic reaction, have multiple products (preferably two, for selectivity study) and proceed at reasonable rates under relatively low temperatures and atmospheric pressure, so that mass transfer is the limiting step. Further, evaporation of reactant and solvent should be negligible, to minimize losses and enhance contacting efficiency in the packed bed. Finally, the reaction mixture should be easy to analyze by standard analytical methods such as gas chromatography (GC).

After screening a number of potential reaction systems using the above criteria, hydrogenation of phenylacetylene (PA), dissolved in *n*-tetradecane, to styrene (ST) and then ethylbenzene (EB) over Pt/alumina was selected.



This system involves three phases: gas (H_2), liquid (phenylacetylene solution); and solid (Pt / alumina catalyst), and has two products, styrene and ethylbenzene. The reaction proceeds at a measureable rate at 40°C and atmospheric pressure (Kawakami and Kusonoki, 1976). The boiling points for phenylacetylene (144°C), styrene (146°C), ethylbenzene (136°C) and n-tetradecane (254°C) are all relatively high, and the reaction mixture is easy to analyze using standard GC method.

It should be noted that further hydrogenation of ethylbenzene to ethylcyclohexane can also occur. This generally takes

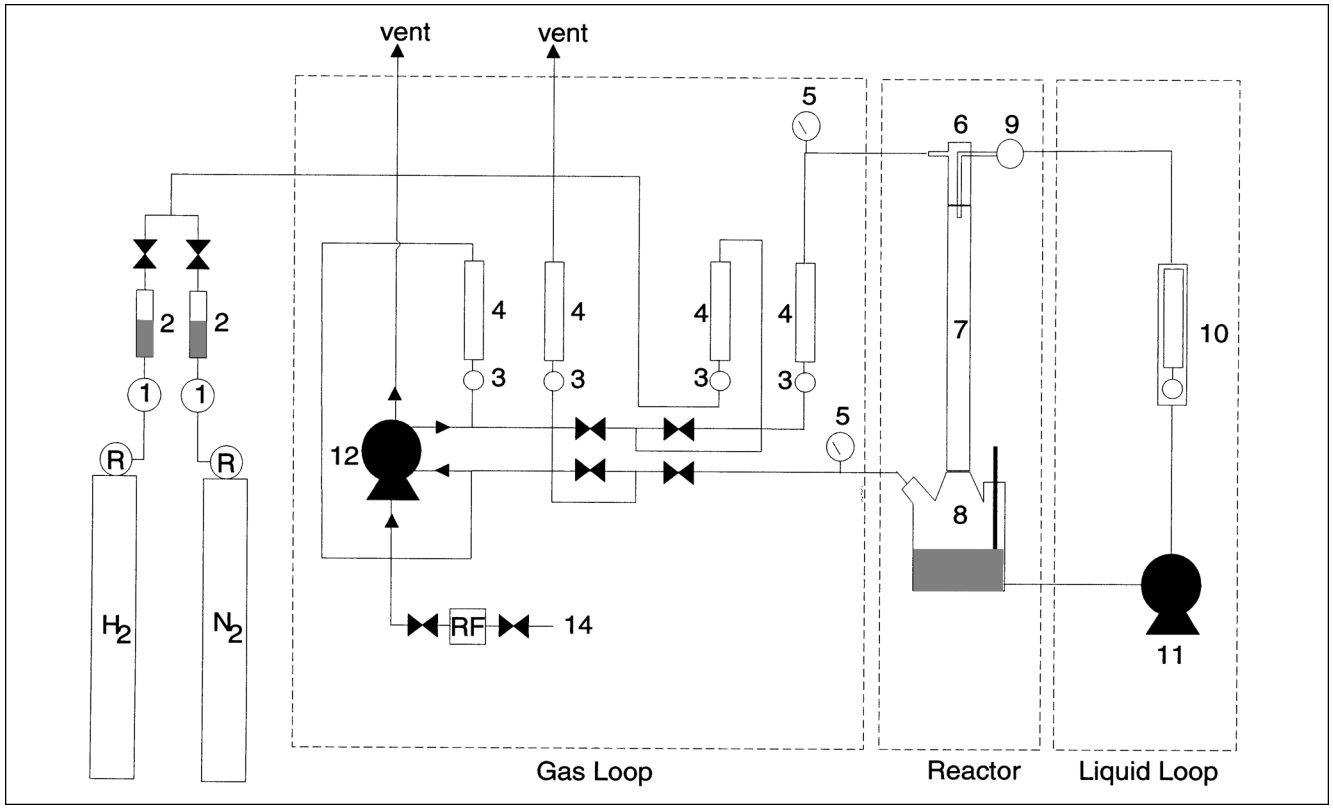


Figure 1. Experimental setup.

1. Pressure regulator; 2. gas purifier; 3. needle valve; 4. rotameter; 5. bourdon gauge; 6. inlet section; 7. reactor section; 8. reservoir section; 9. sample port; 10. liquid flowmeter; 11. liquid pump; 12. air bellows pump; 13. RF unit; 14. house air supply.

place after the phenylacetylene is essentially fully converted to ethylbenzene. For the experimental conditions and durations investigated in the present work, phenylacetylene conversion to ethylcyclohexane was always less than 4%.

The selected reaction system is also an important industrial process (Priddy and Roe, 1983; Maurer and Goldardes, 1989). In styrene polymerization, pure styrene feedstock is needed to preserve the catalyst. A small amount of phenylacetylene in the styrene stream can deactivate the catalyst; hence, its reduction to less that 10 ppm is necessary. For this reason, a number of investigations related to this process have been reported in the literature.

Earlier works involving this reaction system include investigations of both kinetic and transport effects. The reaction kinetics on Pd catalysts were reported by Aramendia et al. (1990) and Duca et al. (1995). Mochizuki and Matsui (1976) studied the effect of liquid–solid mass transfer, and found that improvement in the liquid-solid mass transfer increased the styrene yield. Kawakami and Kusunoki (1976) investigated the effect of intraparticle diffusion on styrene yield using a stirred-basket reactor, and found it to be detrimental. Visser et al. (1994) attempted to enhance selectivity and conversion by pulsing the gas feed externally, which generates transient state. However, due to the dampening effect of viscosity, the advantage of gas pulsing was insignificant. These earlier studies provide a background for the present work.

Experimental Studies

Experiments were conducted to demonstrate the expected influence of flow regime on reaction outcome and the superiority of pulsing flow over trickling-flow regime. Two types of catalyst packing configuration (upper and lower) were introduced to take advantage of the coexistence of two flow regimes (upper-part in trickling and lower-part in pulsing) under certain gas and liquid flow rates (Wu et al., 1999). Experiments were conducted with all the reaction conditions kept identical, except the catalyst packing location, such that the catalyst was exposed to different flow patterns. In this manner, a *direct* comparison was made for the reaction behavior under the two flow regimes. The reactor response to changes in process variables (temperature, liquid input flow rate, and initial reactant concentration) was also investigated. These experiments provided a general understanding of the system, and helped to explain the reactor performance under different operating conditions.

Experimental apparatus

The reactor was designed such that both the liquid and gas phases were recycled during operation. Single-pass conversion of phenylacetylene was estimated at $<10\%$; thus, recycling of the liquid feed was necessary to study the reaction to complete phenylacetylene conversion. Further, because liquid reactants escape with the gas phase, it was necessary to recycle the gas to prevent liquid reactant loss.

The experimental setup (Figure 1) was composed of three sections: a gas loop, a liquid loop and the reactor. Gas and liquid entered the reactor through a glass core-annular inlet section. The reactor column was 2.54 cm ID $\times$ 40 cm length glass unit connected to a 2 L flat-bottomed reservoir with fittings for thermocouple, gas, and liquid outlets. The reservoir was wrapped with heating tape up to the liquid height, and, subsequently, with insulating tape. Heat zones were controlled by an Omega CN76000 auto-tuning PID control and SSR240AC10 digital relay. Agitation to ensure mixing of the liquid phase was provided by a $0.5'' \times 2''$ (12.7 mm $\times$ 50.8 mm) stirring bar and Corning model PC-210 stirring plate. The liquid side consisted of a Baldor 0.7-HP pump, a Gilmont Accucal GF-4540 flowmeter, and a sampling bulb, directly upstream from the inlet section. The gas side utilized four Gilmont No. 14 flowmeters and a Mace model 928 air-bellows pump, driven by house air at 40 psi. Bourdon gauges were positioned at the reactor inlet and outlet to monitor operating pressure. A check valve set to a cracking pressure of 6 psi (41 kPa) was placed at the reactor inlet to avoid accidental pressure buildup in the system, and one-way valves were placed on the supply and vent lines to prevent flow reversal.

Experimental procedure

The catalyst used was 2.5 mm diameter, 0.5 wt. % Pt/Al_2O_3 (ESCAT-26, Engelhard), with the platinum metal dispersed in an eggshell distribution (thickness 0.23 mm) to minimize intraparticle diffusion limitations. For each experiment, catalyst was pretreated and characterized prior to loading the reactor. The pretreatment consisted of heating to 400°C in flowing Argon at 100 mL/min for 2 h. Hydrogen was then passed over the catalyst at 100 mL/min for approximately 12 h, to ensure complete reduction to metal, followed by cooling in flowing Argon. The platinum dispersion was measured to be 80 $\pm 5\%$ using the hydrogen chemisorption technique.

For each experiment, the column was packed with 20 g catalyst in either the upper- or lower-packing configuration (Figure 2). 1-L tetradecane solvent and 1 mL decane GC internal standard were introduced to the reservoir. The liquid-phase was then circulated at the desired flow rate through the column for about 10 min, ensuring complete wetting of the catalyst. Nitrogen was passed through the gas loop for $\sim$15 min at 500 mL/min to purge trapped air. The gas loop was then sealed and nitrogen fed to the column at 500 mL/min for 30 min, while the reactor reached operating temperature. Once purged and heated to the desired temperature, phenylacetylene reactant was introduced to the reservoir by syringe and the reactor sealed. The gas loop was then loaded with hydrogen and sealed. The reaction was initiated by flowing hydrogen through the reactor to vent for 20 s to displace nitrogen, then closing the vent to allow the reactor to pressurize for 60 s. The gas loop was then opened to the reactor and the pump initiated circulation of reactant gas. During operation, the gas outlet remained closed to prevent losses due to volatilization, while additional hydrogen was supplied to the system to compensate for reaction consumption. Samples were taken from the liquid phase at regular intervals via syringe and stored for later analysis. At the end of the experiment, the reaction was terminated by shutting off the pump, heaters, and hydrogen supply, purging the reactor column and gas loop with nitrogen, and allowing the reactor to cool.

Analysis of liquid samples was performed by a Hewlett-Packard 5890 gas chromatograph using a 30 mm $\times$ 32 mm $\times$ 25μm model HP-5 packed column. Peak areas of the four

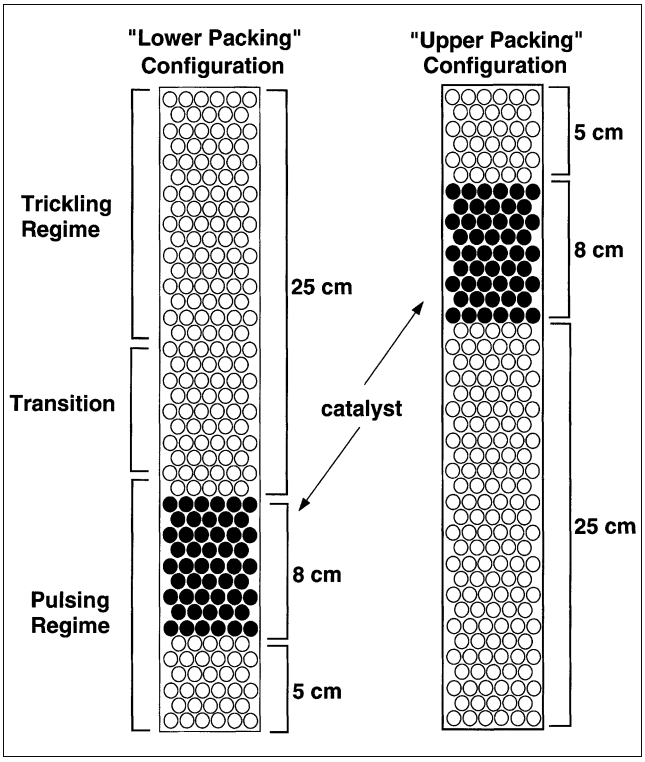


Figure 2. Lower- and upper-packing configurations.

compounds of interest were normalized relative to decane and converted to concentrations via calibration curves generated experimentally, following the internal standard technique. Species concentrations in each sample were analyzed to verify mass balance, typically within $\pm 2\%$.

Direct performance comparison for pulsing and trickling flow regimes

Krieg et al. (1995) have shown that visual and pressure measurements yield consistent identification of the flow regime. For this reason, the presence of trickling or pulsing flow was determined by visual observation. It was found that with certain fixed gas input flow rate, and at relatively low-liquid flow rate, the whole reactor was in the trickling-flow regime. As the liquid flow rate increased, the unsteady, pulsing flow began to develop first at the lower part of the column, and its extent grew further with increasing flow rates until the entire column was in fully-developed pulsing flow regime. As Krieg et al. (1995) noted, this behavior is consistent with pulses forming from a linear *convective* instability. In such systems, for sufficiently large flow rates, weak (linear) disturbances grow in strength as they travel. Therefore, the location where they are strong enough to be detected varies with the disturbance growth rates and speed, both of which change with the liquid and gas flow rates.

The phenomenon that, under certain gas and liquid flow rate combinations, the upper part of the reactor is in steady trickling flow, while the lower part is in pulsing flow, is of special interest. This corresponds to the transition region at flow rates not high enough for the entire column to be under pulsing conditions. It allows the experiments to be carried

Table 1. Reaction Conditions for Series of Experiments A, B and C

	A		B		C	
Experiment	A_1	A_2	B_1	B_2	C_1	C_2
Packing Configuration*	L	U	L	U	L	U
Temperature (°C)	75	75	75	75	75	75
Pressure (atm)	1	1	1	1	1	1
Liquid Flow Rate (cm^3/min)	223	223	223	223	167	167
Gas-Flow Rate (cm^3/min)	3,000	3,000	3,600	3,600	5,400	5,400
$C_{PA,0}$ (M)	0.030	0.030	0.030	0.030	0.030	0.030

*L = lower; U = upper configuration.

out in two different flow regimes, while maintaining all other conditions identical. The column was packed in two configurations, *upper packing* and *lower packing* (Figure 2). In the former, the catalyst was packed near the top of the column, while the rest was packed with glass beads of the same size as the catalyst pellets. In the lower packing, the catalyst was packed near the column bottom.

A set of gas and liquid flow rates was selected, for which two flow regimes coexist: trickling in the upper, and pulsing in the lower part of the column. Owing to the transparent nature of the reactor, packing materials and fluids used in the study, along with the nonfoaming nature of tetradecane-H_2 system, the two flow regimes were identified by visual observations. Experiments A_1 (lower) and A_2 (upper) were conducted using these flow rates (see Table 1). In these experiments, all reaction conditions were kept identical except the flow regime to which the catalyst was exposed. Figure 3 shows the results for these experiments at 75°C. It is seen that there are significant differences in reaction outcome. The rate of phenylacetylene consumption is about 10% faster, and the maximum styrene yield is about 10% higher, for pulsing flow (A_1) as compared to trickling flow (A_2).

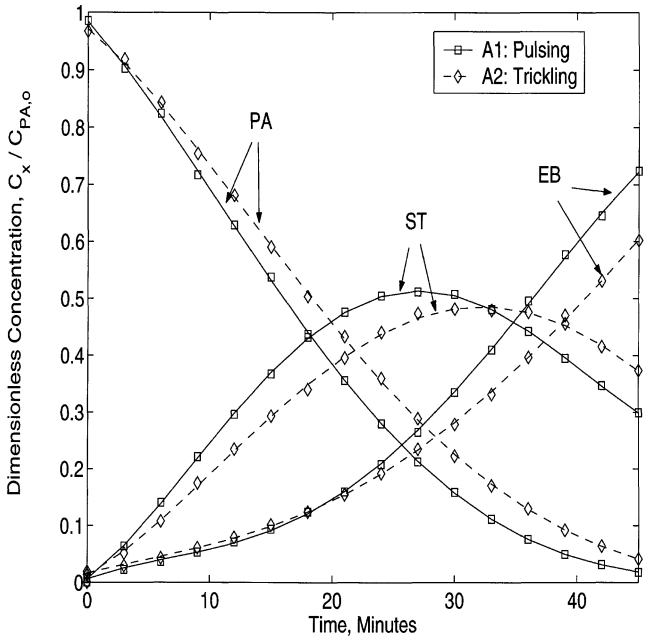


Figure 3. Reactor performance for Series A experiments.

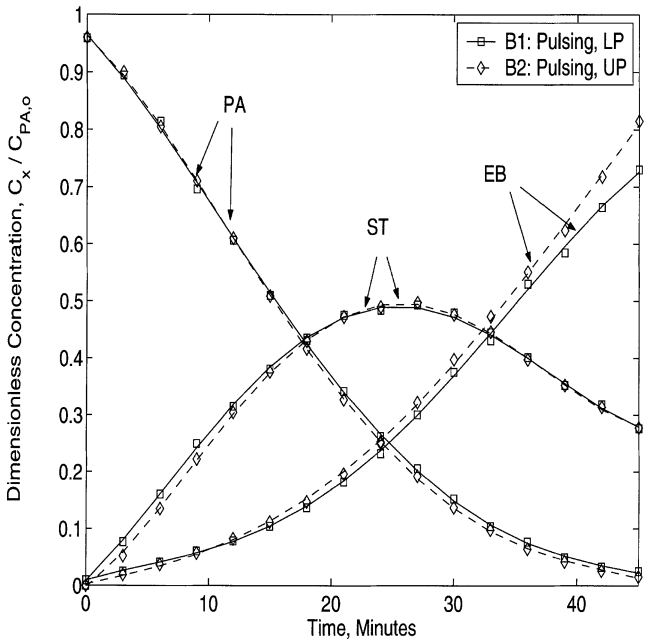


Figure 4. Reactor performance for Series B experiments.

Next, the gas-flow rate was increased such that the entire column was in pulsing-flow regime. Again, two experiments (B_1 and B_2, see Table 1), with lower- and upper-catalyst packings, respectively, were conducted. In these experiments, all reaction conditions including the flow regime (both pulsing) were identical; hence, the reactor performance was expected to be similar. The experimental results, shown in Figure 4, confirm this expectation. Taking the results of Series A and B experiments together confirms that changes in reaction performance are due to differences in flow behavior. Further, the results verify that under the used transition flow conditions (Series A), two distinct flow regimes exist in the upper- and lower- half of the column. Thus, *different flow regimes influence reaction outcome, particularly selectivity and reaction rate.* These experiments were carried out several times to ensure repeatability, which was comparable to that observed in Figure 4.

Another way of visualizing the results of Series A experiments is by a plot of styrene yield vs. phenylacetylene conversion. Figure 5 clearly shows that *pulsing flow is superior to trickling-flow*. Therefore, mass-transfer enhancement in the pulsing-flow regime results in improved reactor performance. If mass-transfer limitation were negligible as compared to the reaction rates, then the reaction would follow the intrinsic kinetics at the reactor level in *both* the trickling and pulsing cases, and the result would be a direct scale-up of the intrinsic kinetic pathway. When this limitation is severe, desired styrene is converted to undesired ethylbenzene in the catalyst pellet, before it is transported to the bulk phase. In general, the greater the mass-transfer limitation, the lower the yield of styrene.

Liquid flow rate study

Experiments were performed next to determine whether the superiority of pulsing-flow operation over trickle-flow was consistent at different sets of flow rates. A second liquid and corresponding gas-flow rate were selected, such that trickling-flow existed in the upper half and pulsing flow in the lower half of the column (see Table 1). Results from these experiments are shown in Figure 6. At these conditions, the reaction rate of phenylacetylene to styrene is almost 30% faster for pulsing as compared to trickling flow. From the series A and C experiments, it is clear that *superiority of puls-*

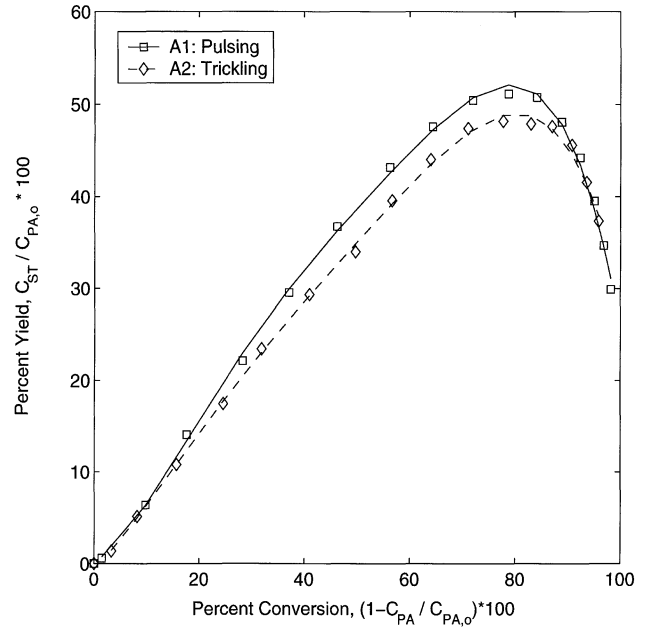


Figure 5. Conversion vs. selectivity for Series A experiments.

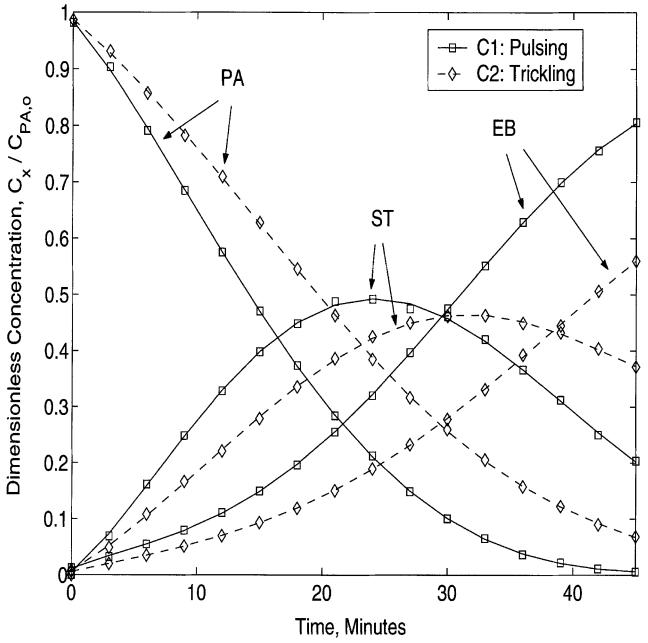


Figure 6. Reactor performance for Series C experiments.

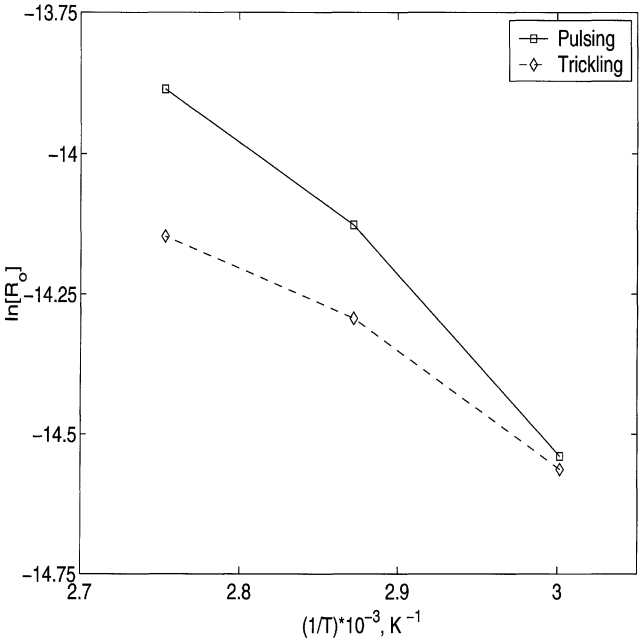


Figure 7. Arrhenius plot for series A conditions.

ing-flow over trickling-flow operation is consistent over different sets of flow rates.

Temperature effect study

In order to demonstrate the dominance of mass-transfer process and to further compare the two flow regimes, experiments were performed over a range of temperatures, keeping all other operating conditions the same. As in the above studies, gas and liquid flow rates were *identical* for both flow regimes, with only the catalyst location changing, that is, upper packing for trickling flow and lower packing for pulsing flow.

From the experimental data, the initial rate of phenylacetylene consumption was determined. If the initial rate follows an expression such as $R(C_{PA,0}) = k_{p0}\ \exp(-E_{ap}/\mathrm{RT})C^n_{PA,0}$, where E_{ap} is the apparent activation energy of the entire process (that is, combined reaction and mass transfer) then

$$\ln R(C_{PA,O}) = \ln k_{p0} + n \ln C_{PA,0} - E_{ap}/RT. \qquad (1)$$

Since $\ln\ k_{p0} + n\ \ln\ C_{PA,0}$ is a constant, a linear relationship exists between $\ln\ R(C_{PA,0})$ and $1/T$, and, from its slope, the apparent activation energy E_{ap} can be calculated. The obtained results are shown in Figure 7 and Table 2, where it may be seen that the apparent activation energy values are different not only for both temperature ranges (60°−75°C, 75°-90°C), but also for the two flow regimes.

Table 2. Apparent Activation Energy Values for Different Temperature Ranges: Series A Conditions

	E_{ap}, kcal/mol	
Range	Trickling	Pulsing
60−75°C	4.2	6.4
75−90°C	2.5	4.0

Among the many steps in a process, the progress of the rate controlling step determines the rate of the entire process. In the present system, liquid−solid external mass transfer, internal diffusion, and reaction are the important steps. Further, reaction R_1 is initially the dominant one (Duca et al., 1995; Arena et al., 1998) with activation energy ~ 9 kcal/mol (Aramendia et al., 1990). Under intrapellet diffusion control, the apparent activation energy E_{ap} should decrease by a factor of two. Indeed, from Figure 7 and Table 2, for lower temperatures (60−75°C), the activation energy in trickling-flow (4.2 kcal/mol) is roughly one-half the intrinsic value. Owing to increased external mass transfer, the corresponding pulsing-flow activation energy (6.4 kcal/mol) decreases less from the intrinsic value, as expected. For higher temperatures (75−90°C), the reaction becomes closer to external mass-transfer control, leading to E_{ap} values closer to zero. However, even in this case, from Table 2 we note that the E_{ap} value is greater for pulsing as compared to trickling-flow, because the latter has even greater external mass-transfer limitation. These results indicate that *internal diffusion and external mass-transfer steps are important for the process, and that the process is closer to kinetic control in the pulsing-flow regime.* Therefore, the pulsing regime at least partially removes limitations on reaction due to internal and external mass-transfer steps that are present in the trickle-flow regime.

Under different operating temperatures, the importance of the mass-transfer step changes, which affects the yield and selectivity of styrene. Figure 8 shows that for both flow regimes, the maximum styrene yield decreases as temperature increases, since mass transfer becomes more limiting.

Initial concentration study

The initial concentration of phenylacetylene could affect the reaction outcome. Since for lower initial concentration,

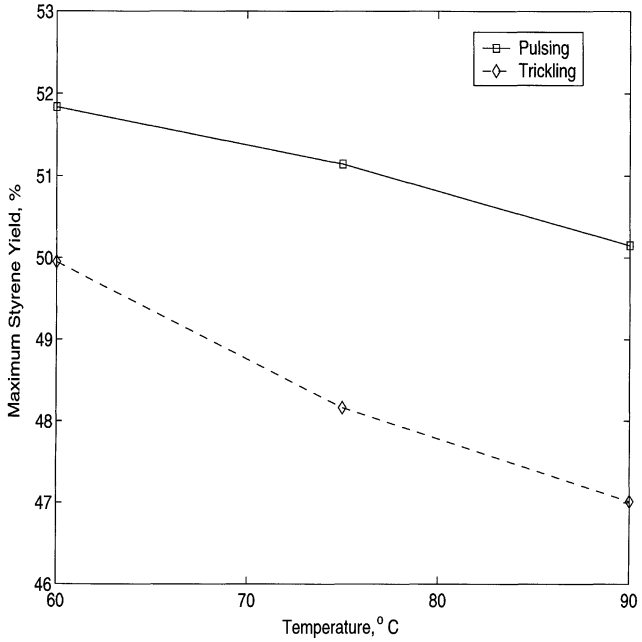


Figure 8. Maximum styrene yield vs. reactor temperature for Series A conditions.

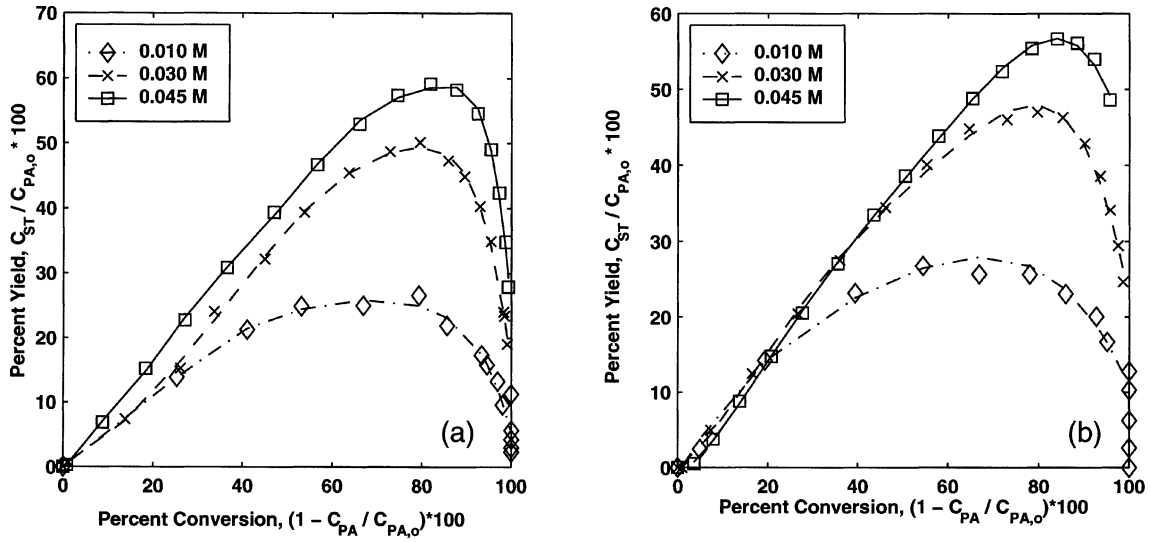


Figure 9. Conversion vs. selectivity for various initial phenylacetylene concentrations for Series A conditions.
(a) Pulsing; (b) Trickling.

there would be less phenylacetylene available near the catalyst surface to react and more active sites left for styrene to degrade to ethylbenzene, the styrene yield is expected to increase with increasing initial phenylacetylene concentration. Experiments with different initial phenylacetylene concentrations were conducted and all other conditions were maintained identical. The results, shown in Figure 9, confirm the expectation for both pulsing (Figure 9a) and trickling conditions (Figure 9b). The maximum styrene yield values corresponding to these experiments, shown in Figure 10, demonstrate that pulsing flow remains superior to trickling flow for the various reactant concentrations investigated.

Simplified Model

To qualitatively demonstrate the experimental trends, including the superiority of pulsing-flow regime over trickling-flow regime, a simplified model was developed with the assumptions given below:

- Since intrinsic reaction kinetics are not known, all reactions are assumed to be first-order with respect to the organic species, irreversible and isothermal.
- The reactions occur in catalyst pellets of slab geometry, with external mass-transfer resistance.
- The liquid is well-mixed in the reactor, that is, a CSTR.
- The effective liquid-solid mass-transfer coefficient for pulsing-flow regime is twice its value in the trickling-flow regime. This assumption is justified by the experimental results of Rao and Drinkenburg (1985).

The mass-balance equations for each liquid phase species were formulated in the reactor and the catalyst pellets. These equations, along with the simulation parameters, are given in the Appendix. The transient diffusion-reaction equations were solved using the Laplace Transform technique (Varma and Morbidelli, 1997), and the solutions are also given in the Appendix.

As shown in Figure 11, the simulation results clearly demonstrate that pulsing flow exhibits higher styrene yield than trickling flow. This is especially true under more severe mass-transfer limitations that occur at higher reaction temperatures. Furthermore, phenylacetylene conversion is also higher under pulsing flow regime, due to the alleviation of mass-transfer limitation. These simulations confirm the experimental findings that the maximum styrene yield increases as temperature decreases, and that pulsing enhancement becomes more significant at higher reaction temperature.

Conclusions

Using catalytic hydrogenation of phenylacetylene as an example, by placing the catalyst in either the lower or upper portion of the packed column, a direct comparison was made

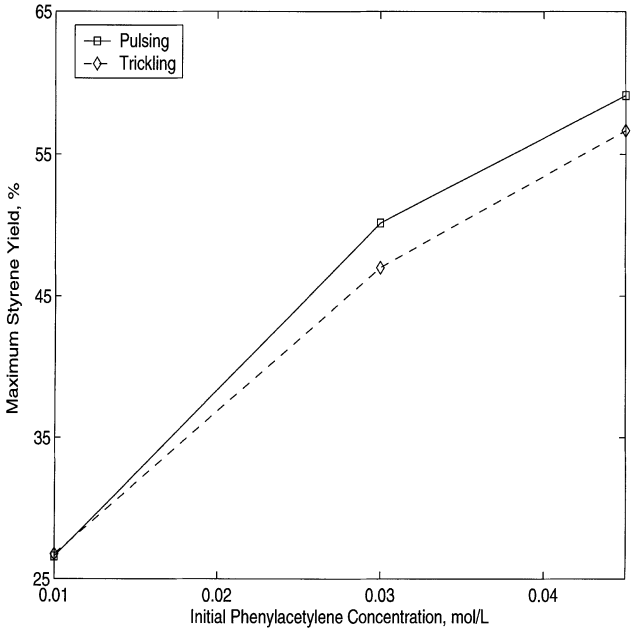


Figure 10. Maximum styrene yield as a function of initial phenylacetylene concentration.

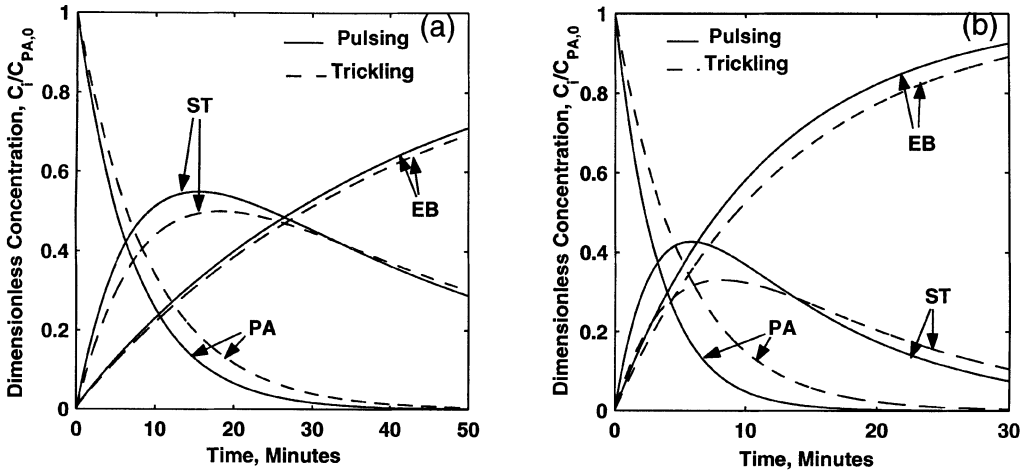


Figure 11. Simplified model calculations.

(a) Lower temperature; (b) higher temperature.

between reactor performance in pulsing-flow and trickling-flow regimes. The experimental results reveal that the flow regimes *significantly* influence the reaction outcome. Up to a 30% increase in reaction rate and a 10% increase in styrene yield were observed. It is noted that a recycle reactor is not the optimal configuration to produce the maximum styrene yield and that other reactor configurations may exhibit yield enhancements consistent with this 30% rate difference.

The apparent activation energy approach used in this study provides valuable information about the extent of mass-transfer limitation in the process. Although this limitation exists in all cases, the experimental results show that the apparent activation energy for pulsing-flow regime is higher than that of trickling-flow regime, indicating that the system is closer to kinetic control in the former case.

A simplified model was developed to qualitatively describe the experimental trends. The model predictions supported the experimental findings and demonstrated that *flow regimes influence the reaction outcome, and that there may be significant advantage by operating the reactor in the pulsing-flow regime*.

Multiphase reacting systems are complex, with spatial and temporal heterogeneities. This work provides an example of tuning the flow pattern inside the reactor for improved performance, and this concept should also be applicable to other multiphase reacting systems.

Acknowledgments

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Notation

A = total catalyst external surface area
$Bi = Kc \cdot R/De$, Biot number for mass transfer
C_i = concentration of species i
D_e = effective diffusivity
K_c = liquid-solid mass transfer coefficient
k_i = intrinsic kinetic constant
$\bar{k}_i = k_i/\epsilon_p$
R = catalyst pellet radius
r = radial position in pellet
s = Laplace transform variable
s_n = roots of $q_1(s)$
s_m = roots of $q_2(s)$
t = time
V = volume
X, Y, Z = dimensionless PA, ST, and EB concentrations

Greek Letters

$\alpha = Kc \cdot A/V_r$
$\beta = De/\epsilon_p \cdot R^2$
ϵ = void fraction
$\gamma_1 = [(\bar{k}_1 + \bar{k}_3 + s)/\beta]^{1/2}$
$\gamma_2 = [(\bar{k}_2 + s)/\beta]^{1/2}$

Subscripts

EB = ethylbenzene
p = catalyst pellet
ps = on pellet surface
PA = phenylacetylene
r = in reactor
ST = styrene

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Appendix

Simplified model equations and solutions

Reactor:

$$V_r \cdot \frac{dC_{PA_r}}{dt} = K_{c,PA} \cdot A \cdot \left(C_{PAps} - C_{PA_r}\right)$$

$$V_r \cdot \frac{dC_{ST_r}}{dt} = K_{c,ST} \cdot A \cdot \left(C_{STps} - C_{ST_r}\right)$$

$$V_r \cdot \frac{dC_{EB_r}}{dt} = K_{c,EB} \cdot A \cdot \left(C_{EBps} - C_{EB_r}\right).$$

Pellet:

$$\epsilon_p \cdot \frac{\partial C_{PA_p}}{\partial t} = D_{e,PA} \cdot \frac{\partial^2 C_{PA_p}}{\partial r^2} - \left(k_1 \cdot C_{PA_p} + k_3 \cdot C_{PA_p}\right)$$

$$\epsilon_p \cdot \frac{\partial C_{ST_p}}{\partial t} = D_{e,ST} \cdot \frac{\partial^2 C_{ST_p}}{\partial r^2} + \left(k_1 \cdot C_{PA_p} - k_2 \cdot C_{ST_p}\right)$$

$$\epsilon_p \cdot \frac{\partial C_{EB_p}}{\partial t} = D_{e,EB} \cdot \frac{\partial^2 C_{EB_p}}{\partial r^2} + \left(k_2 \cdot C_{ST_p} + k_3 \cdot C_{PA_p}\right)$$

along with the initial conditions:

$$C_{PA_p} = C_{ST_p} = C_{EB_p} = 0$$

and boundary conditions:

- $r = 0$:

$$\frac{\partial C_{PA_p}}{\partial r} = \frac{\partial C_{ST_p}}{\partial r} = \frac{\partial C_{EB_p}}{\partial r} = 0$$

- $r = R$:

$$D_{e,PA} \cdot \frac{\partial C_{PA_p}}{\partial r} = K_{c,PA} \cdot \left(C_{PA_r} - C_{PA_p}\right)$$

$$D_{e,ST} \cdot \frac{\partial C_{ST_p}}{\partial r} = K_{c,ST} \cdot \left(C_{ST_r} - C_{ST_p}\right)$$

$$D_{e,EB} \cdot \frac{\partial C_{EB_p}}{\partial r} = K_{c,EB} \cdot \left(C_{EB_r} - C_{EB_p}\right).$$

The above system of equations was solved by the Laplace Transform technique (Varma and Morbidelli, 1997). By further assuming that the effective diffusion and mass-transfer coefficients for all species are the same, we obtain

$$X_r(t) = \sum_{n=1}^{\infty} \frac{p_1(s_n)}{q_1'(s_n)} \cdot e^{s_n t}$$

$$Y_r(t) = \frac{\bar{k}_1}{\bar{k}_1 + \bar{k}_3 - \bar{k}_2} \cdot \left[\sum_{m=1}^{\infty} \frac{p_2(s_m)}{q_2'(s_m)} \cdot e^{s_m t} - \sum_{n=1}^{\infty} \frac{p_1(s_n)}{q_1'(s_n)} \cdot e^{s_n t} \right]$$

where

$$p_i(s) = \gamma_i \cdot \sinh(\gamma_i) + Bi \cdot \cosh(\gamma_i)$$

$$q_i(s) = (s + \alpha) \cdot \gamma_i \cdot \sinh(\gamma_i) + s \cdot Bi \cdot \cosh(\gamma_i)$$

and the various quantities are defined in the notation. $Z_r(t) = 1 - X_r(t) - Y_r(t)$ is obtained based on the assumption that only a small amount of catalyst is used ($V_p/V_r \ll 1$). The simulation parameters used are shown in Table A1.

Table A1. Simulation Parameters

Common Parameters			Lower Temp.	Higher Temp.
V_r 1,000 cm^3	A	660 cm^2	k_1 50 1/min	k_1 800 1/min
R 0.128 cm	ϵ_p	0.5	k_2 1 1/min	k_2 16 1/min
K_c 0.387 cm/min	D_e	1.524×10^{-3} cm^2/min	k_3 2 1/min	k_3 32 1/min

The values of V_r, R, A, and ϵ_p were taken from experimental reactor and catalyst dimensions, while K_c and D_e were evaluated from correlations in the literature. In the absence of intrinsic kinetic data, the rate constants k_i were selected such that the simulations reflected maximum styrene yields and reaction time scales comparable with the experimental data.

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