

Effect of Pulsing on Reaction Outcome in a Gas-Liquid Catalytic Packed-Bed Reactor

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Introduction

There has been continuous interest and fascination with the fluid dynamics of trickle-beds (i.e., cocurrent gas-liquid packed-bed reactors) at least since Weekman and Myers (1964) first proposed a regime map for their operation. Consistent with other flow regime maps before (Baker, 1954; for gas-liquid pipe flow) and since (e.g., Mandhane et al., 1974; for pipe flow), visual observations were used to identify the existence of qualitatively different *regimes* of operation. *Trickling* was characterized, much as the name implies, by gentle to moderate bubbling and liquid fluctuations. At more severe flow conditions, strong, organized, traveling, disturbances of high liquid fraction, termed *pulses* are observed. Most industrially important reactions are carried out in one of these two flow regimes. Weekman and Myers (1964) noticed that pulses took some distance to appear and so defined the existence of the pulse regime when pulsing was observed at a particular point. Chou et al. (1977) also adopted this criterion which makes sense from a reaction point of view. Pulsing affects the heat and mass transfer rates, and thus reaction rates, hence it is necessary to verify its existence in the reaction zone.

However, Dankworth et al. (1990) describe pulses mathematically as traveling waves and Krieg et al. (1995) show that the transition to pulsing occurs by the continued growth with distance of very small amplitude disturbances. These small disturbances are convectively unstable (meaning that *growth* of disturbances is observed *only* when they are viewed at increasing distance in the flow direction) and so Krieg et al. (1995) point out that the transition to pulsing cannot be reliably determined by observing the flow at a fixed location. Similar to the transition to slugging

(Fan et al., 1993) or roll waves (Bruno and McCready, 1988) in horizontal gas-liquid flows, it is necessary to determine if disturbances are growing or decaying with distance.

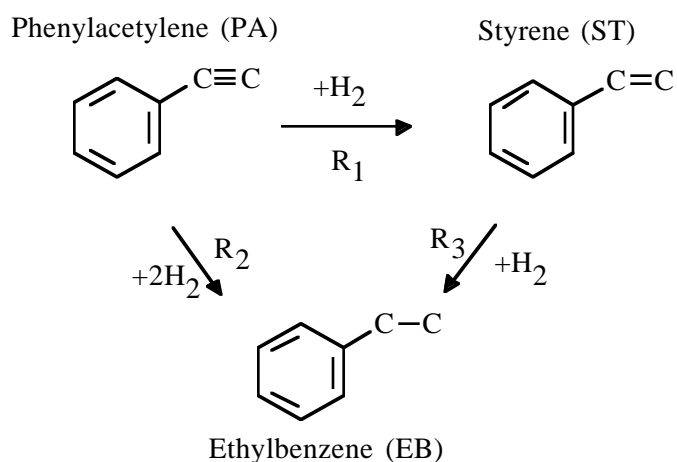
Wu et al. (1995) pointed out that pulsing could be even more important than recognized by prior researchers, who were interested primarily in the increased *average* heat and mass transfer rates that occur. Wu et al. (1995) used a theoretical model to demonstrate *qualitative* changes in the reaction outcome, for sequential or competitive reactions, when the time scale of pulsing was comparable to the reaction scales. In some cases, very significant changes in selectivity or yield could occur. These results suggest both the opportunity and challenge of finding a way to *tune* the pulsing to produce the most desirable product mix for a given reaction in a real system. However to-date there is no experimental confirmation that Wu et al.'s predictions will occur in experimental systems, so the first step is to design an experiment that will demonstrate the predicted effects of pulsing on reaction outcome.

This paper describes our initial efforts at conducting such an experiment to verify the theoretical predictions and shows that a direct dynamical link exists between reaction and pulsing. It would not be sufficient to conduct one set of experiments at flow conditions where pulsing did not occur and others where pulsing did, because differences in the reaction result could be attributed to different flow rates. Likewise it would not be adequate to demonstrate the effect with a microscale experiment that employs a small catalytic surface which is contacted by flowing liquid and gas. It is necessary to demonstrate the effect in a real packed bed. To accomplish this we exploit the convective nature of the disturbances that lead to pulsing. For a chosen range of gas and liquid flow rates, pulses are not present at the top of the column but form with distance and can be observed near the bottom. Thus an experiment can be conducted where the column is packed largely with inert particles, but with a small catalytically active region located either near the top where the pulses have not yet formed and flow is uniform, or at the bottom, where developed pulses exist. In either case, the average flow rates for gas and liquid are the same.

Our preliminary results indicate that significant differences in reaction outcome exist between the cases where the catalyst is at the top and where it is at the bottom. This paper outlines the experimental procedure and system, and describes some preliminary results we have obtained that prove the general premise contained in Wu et al. (1995).

Experimental

Hydrogenation of phenylacetylene (PA), dissolved in n-tetradecane, to styrene (ST) and then ethylbenzene (EB) over Pt/alumina was selected as the example system.



Styrene was viewed as the *desired* product and ethylbenzene as the undesired one. Thus we endeavor to operate the reactor to get the highest yield of styrene.

Hydrogen was flowed through the reactor only once and was vented. The liquid was continuously recycled through the reactor and the progress of the reaction was monitored using gas chromatography. Typical runs lasted about 2 hours during which time liquid samples were collected about every 1-3 minutes. Constant temperature was maintained during the course of each run. A schematic of the column showing the reaction zones is given in Figure 1 where, as described above, the catalyst was located either near the top of the column, where pulses were not

present or near the bottom, where pulsing occurred. In both packing configurations, 20 g of 0.5 wt% Pt/alumina spheres (~ 3 mm diameter) were used, and the rest were glass beads of the same size as the catalyst pellets.

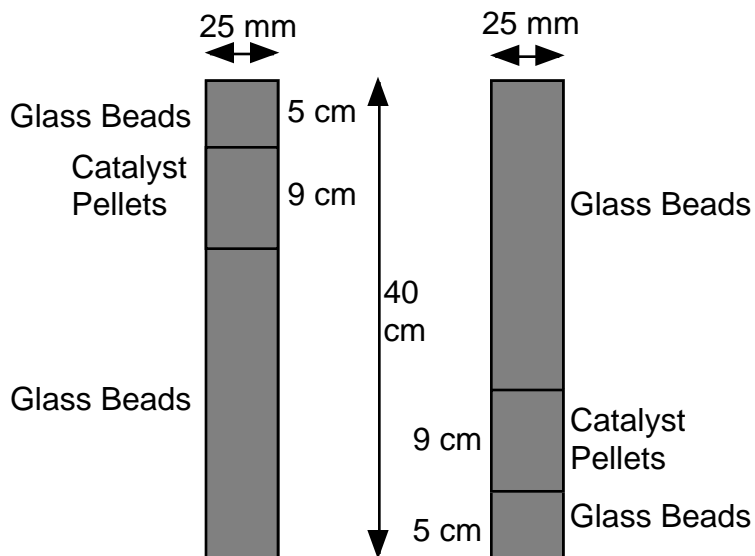


Figure 1: Geometries for catalyst packing configurations: upper and lower packings

Results

For gas and liquid flow rates ($G_V=239$ ml/min, $L_V=167$ ml/min), trickling flow occurs in the upper region and pulsing in the lower part of the column as desired. Experiments A_1 (lower) and A_2 (upper) were conducted using these flow rates. In these two experiments, all the reaction conditions were kept identical except the flow regime to which the catalyst was exposed. To provide a contrast, another set of gas and liquid flow rates ($G_V=346$ ml/min, $L_V=321$ ml/min) was selected under which the whole column was in pulsing-flow regime. Two experiments (B_1 and B_2), with lower and upper catalyst packing, respectively were conducted. In these two experiments, all the reaction conditions including the flow regime (both pulsing) were identical, hence the reactor performance was expected to be similar.

Figure 2(a) shows the results for Series A experiments at 90°C. As expected, there are apparent differences in the reaction outcome, especially in the generation of styrene and ethylbenzene. As a contrast, the reaction behavior for Series B experiments shown in Figure 2(b) indicates little difference in reactor performance for the two catalyst packing locations. Thus it appears that *different flow regimes influence reaction outcome, particularly selectivity*.

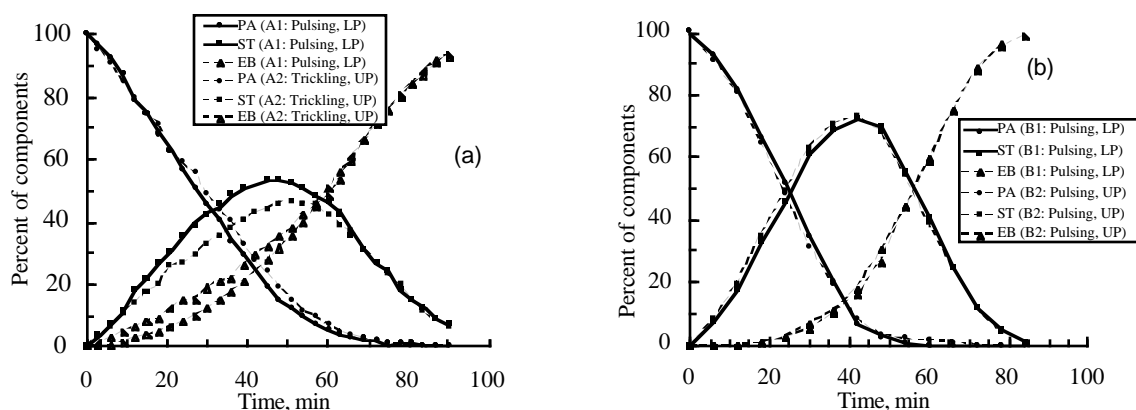


Figure 2: Species concentrations as functions of time for Series A and B experiments

Numerous replicate experiments showed comparable tendencies as that in Figure 2(a) and detailed results are available in Wu (1997). When temperature was increased, similar results were obtained and an apparent activation energy of about 3-7 kcal/mol was determined. This confirms that the system was mass transfer limited, so the observed changes in reaction outcome should be related to mass transfer fluctuations.

Discussion

The experiments presented here, and in Wu et al. (1997), confirm that the *dynamic* behavior of mass transfer fluctuations, as manifested by pulsing, occurs on time scales and with sufficient strength to directly affect reactor performance. Thus the theoretical predictions of Wu et al. (1995) are supported. A more realistic reactor model that provides good *quantitative* agreement with the experimental results is described in Wu et al. (1997).

There are two major implications of the results presented here. First, test reactors for catalysts are typically small in both diameter and length. Thus pulsing will never occur in these. However, process scale reactors are well-known for their pulsing and thus some of the reaction outcome differences that are observed between the two, may be due to this newly identified *dynamic* effect of pulsing. The second implication is that it may be possible to *tune* the frequency of pulsing to optimize the reaction selectivity. Krieg et al. (1995) note that the frequency of pulsing varies substantially with the diameter of a reactor and to some extent with the size of the packing. If a sufficiently good understanding of all important aspects of the mass transfer behavior of pulsing packed beds could be obtained, it should be possible to design process scale reactors with significant selectivity enhancements.

Acknowledgement

This work was supported by the Monsanto Fund, by a grant to the Center for Bioengineering and Pollution Control at the University of Notre Dame.

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