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Effect of pulsing on reaction outcome in a gas–liquid catalytic packed-bed reactor

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Abstract

A novel experiment is described for studying the effect of flow regime on reaction outcome for a consecutive-parallel reaction. By taking advantage of the convective nature of disturbances that grow into pulses in gas–liquid packed-bed reactors, it is shown that it is possible to compare reaction behavior for pulsing and trickling at the *same* flow rates. This contrasts previous studies where effects of regime were found, but at different flow rates. This experiment is accomplished by packing the column with mostly inert particles and confining the catalytically active region either near the inlet, where pulses have not yet formed, or near the end where they have developed. It is found that for the reaction of phenylacetylene to styrene and ethylbenzene over a platinum/alumina catalyst, where pulses are present in the bottom of the reactor but not at the top, about a 15% increase in styrene concentration, as an intermediate, occurs under pulsing conditions. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Trickle bed reactors; Pulsing flow; Gas-liquid flow in packed beds

1. 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 [1] first proposed a regime map for their operation. Consistent with other flow regime maps before 1954 ([2] for gas–liquid pipe flow) and since 1974 (e.g., [3] 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 [1] 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. [4] 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. [5] describe pulses mathematically as traveling waves and Krieg et al. [6] 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

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at increasing distance in the flow direction) and so Krieg et al. [6] 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 [7] or roll waves [8] in horizontal gas–liquid flows, it is necessary to determine if disturbances are growing or decaying with distance.

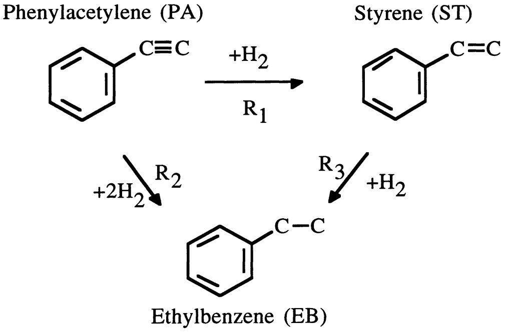
Wu et al. [9] pointed out that pulsing could be even more important than recognized by prior researchers, who were interested primarily in the increased *average* heat and mass transfer rates that occur. Wu et al. [9] used a theoretical model to demonstrate *qualitative* changes in the reaction outcome, for sequential or competitive reactions, when the timescale 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 predictions of Wu et al. 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 [9].

2. Experimental

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



(1)

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 h during which time liquid samples were collected about every 1–3 min. Constant temperature was maintained during the course of each run. A schematic of the column showing the reaction zones is given in Fig. 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. For the experiments presented here, the initial phenylacetylene concentration was 0.0455 M. Experiments at different initial concentrations and separate reaction kinetic

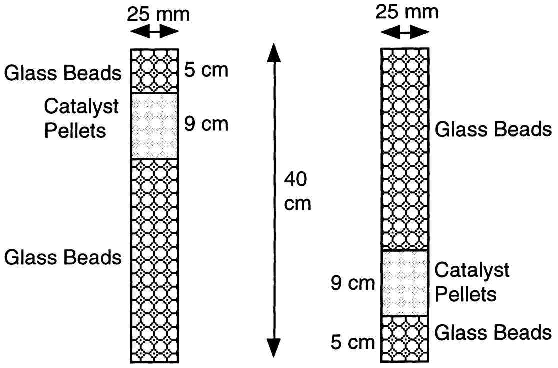


Fig. 1. Geometries for catalyst packing configurations: upper and lower packings.

studies confirmed that hydrogen is present in excess and does not limit the reaction.

3. Results

When the reactor system was first built, a regime study was conducted to determine the boundaries of pulsing and trickling, as well as the nature of the transition. It was found that when compared with air–water on the superficial mass flow coordinates of Weekman and Myers [1], changing the gas to H_2 requires substantially lower mass flow rate to get similar transition behavior. Switching from water to *n*-tetradecane causes the trickle-pulse transition to move to about a 30% lower liquid mass flow rate. Additional details are available elsewhere [10].

For gas and liquid flow rates (G_V=0.00196 kg/m^2 s, L_V=15.1 kg/m^2 s), 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=0.00283 Kg/m^2 s, L_V=29.1 kg/m^2 s) 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.

Fig. 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 Fig. 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.*

Numerous replicate experiments showed comparable tendencies as that in Fig. 2(a) and detailed results are available in [10]. 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

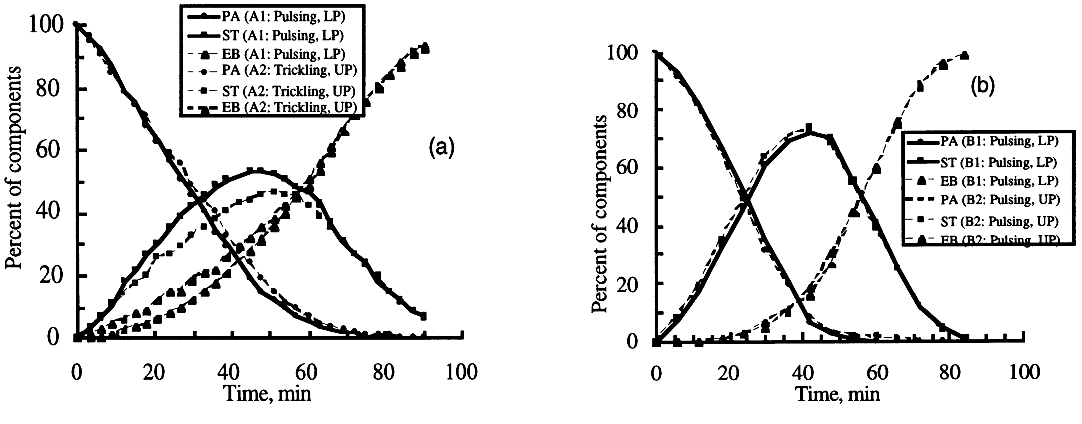


Fig. 2. Species concentrations as functions of time for series A and B experiments.

limited, so the observed changes in reaction outcome should be related to mass transfer fluctuations.

4. Discussion

The experiments presented here, and in [11], demonstrate that even at the same average flow rates, changes in mass transfer behavior of trickling as compared to pulsing cause differences in the reaction behavior. There are two possible reasons for this. First, it could be that the *dynamic* nature of the mass transfer fluctuations in pulsing flow interacts with reaction on similar timescales, causing enhancement of only the selected reactions. This result is similar to that predicted theoretically by Wu et al. [9]. A second possibility is that the average mass transfer behavior is increased once pulses have formed and this causes the changes in reaction outcome. Since no previous work has reported mass transfer coefficients in trickling versus pulsing at the *same* flow rates, we cannot differentiate between these possibilities with a single reaction system.

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 if dynamic effects of mass transfer are responsible for differences in reaction behavior, it may be possible to *tune* the frequency of pulsing to optimize the reaction selectivity. Krieg et al. [6] 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.

5. Conclusions

A new experiment for studying the effects of hydrodynamics on reaction in a gas–liquid packed-bed reactor is described as that takes advantage of the convective nature of the disturbances that form pulses. It is shown that for identical flow rates, the reaction outcome changes if the active catalyst is located at the top of the column, where pulses have not yet formed, or at the bottom where pulses occur. While the difference is surely the result of different mass transfer behavior, it has not been determined yet if it is the *dynamic* effect of pulses or just an increased average mass transfer coefficient that is responsible for the differences.

Acknowledgements

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