Korean J. Chem. Eng., **30**(3), 593-597 (2013)
DOI: 10.1007/s11814-012-0220-z

Catalytic performance improvement of styrene hydrogenation in trickle bed reactor by using periodic operation

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(*Received 29 August 2012 • accepted 16 December 2012*)

Abstract−We investigated the catalytic performance improvement of styrene hydrogenation in a trickle bed reactor by using periodic operation. The effects of cycle period and split on relative conversion, which is defined as styrene conversion obtained from periodic operation over that from steady state operation, were examined at various operating conditions including gas and average liquid flow rates, pressure and temperature. The experimental results reveal that both cycle period and split have strong influence on the catalytic performance. The fast mode (short cycle period) is a favorable condition. The improvement by the periodic operation becomes less pronounced for operations at high average liquid flow rate, pressure and temperature. From this study, a maximum improvement of styrene conversion of 18% is observed.

Key words: Trickle Bed Reactor, Periodic Operation, Performance Improvement, Styrene Hydrogenation

INTRODUCTION

The trickle bed reactor (TBR) is a three phase reactor commonly used in industrial applications, such as petroleum, petrochemical and chemical processes, waste water treatment, and biochemical and electrochemical processes. Hydrogenation, oxidation and desulfurization are among the most common reactions used in a trickle read reactor [1,2]. Generally, achieving high conversion requires high operating temperature to favor catalytic activity, and high operating pressure to improve gas solubility and mass and heat transfer rates, to handle gas volumes from high operating temperature at lower capital cost and to slow down the catalyst deactivation [3,4]. Commercial trickle bed reactors are usually operated under steady state mode (constant feed rates) under trickle flow regime (low gas and liquid flow rates), which means that the interaction between gas and liquid is rather poor [4]. Therefore, the gas-liquid mass transfer rate is low. At this condition, it is likely that catalyst particles in the reactor are not completely wet by the liquid [5].

A number of researchers have been trying to improve the catalytic performance of trickle bed reactors. Two common approaches are periodic liquid feed modulation (continuous gas phase) [6-13] and pre-saturated one liquid flow (POLF) [14-17]. Periodic operation has been successfully demonstrated to improve the catalytic performance of TBR in many reactions [4,9,11,12]. Under periodic operation, the liquid velocity is switched either between zero and a given value (on-off mode) or between low and high values (base-pulse mode). For both operation modes, the cycle period can be quite long, usually with an order of magnitude of some minutes (slow-mode), or short, just a few seconds (fast-mode), and the split ratio defined as the ratio of the time with the higher flow rate to cycle period is varied. Tukač et al. [18] studied phenol oxidation under on-off liquid modulation, and found that periodic wetting of external catalyst surface and improvement in oxygen mass transfer from gas phase to catalyst active sites are strongly influenced by operation parameters and by feed modulation parameters such as cycle period and split. Moreover, Lysova et al. [19] concluded that performance enhancement of TBR and increased conversion resulted from the increased temperature of the catalyst bed under periodic operation.

Hydrogenation of pyrolysis gasoline, which is a byproduct from steam cracking of heavier oil fractions to give ethene and propene, is a good example of petrochemical applications for preventing gum formation and catalyst deactivation in the downstream processes [13,20]. After prolonged operation, catalyst activity slightly decreases because polymer or gum coats the active sites on the catalyst surface. The loss of catalytic activity could be compensated by increasing inlet temperature and H_2 pressure. However, increasing inlet temperature for TBR operated in the trickle flow regime can cause serious safety problems, as they can damage the reactor wall and can lead to a reaction runaway. The gum-formation agents are mostly diolefins and styrene. In most research studies, styrene is usually chosen as the model component to be hydrogenated because it is one of the slowest reacting components [20]. There are very limited works in the literature implementing the concept of periodic operation to improve performance of styrene hydrogenation in a trickle bed reactor. Tukač et al. [13] performed a reaction in a pilot-scale trickle-bed reactor packed with palladium on alumina egg-shell catalyst. Improvement as high as 30% over the conventional steady state operation was reported. However, the reaction performance was reported only as the ratio of conversion achieved from the periodic operation over that from the steady state operation for a limited range of operating condition. In addition, important information on con-

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version was not provided.

In this study, we investigated the periodic operation of the styrene hydrogenation in trickle bed reactor. The effects of modulation parameters including cycle period and split ratio, and operation parameters including gas and average liquid flow rate, temperature and pressure were considered to find a suitable operating condition at which the periodic operation outperforms the conventional steady state operation.

EXPERIMENTAL SETUP FOR PERIODIC OPERATION

The schematic diagram of the experimental setup used in this study is shown in Fig. 1. The bench-scale reactor consisted of a jacketed stainless-steel cylinder with a diameter of ¾” packed with a catalyst bed of 0.5 g. Beds of ceramic spheres were set just on top and below the catalyst bed to ensure uniform radial liquid distribution. Activated alumina was loaded on top of catalyst bed to adsorb 4-tert-ButylCatechol (TBC), a polymerization inhibitor in the styrene feed, which could poison the catalyst. The gas lines provided hydrogen and nitrogen to the reactor. A mass-flow controller was located in each gas line. The liquid was then pumped to the reactor by a HPLC pump. The “on-off” liquid modulation was realized through an actuator valve set on the liquid feed line and actuated by a digital timer. During the pulse time (on) the liquid was allowed to reach the reactor, while during the base time (off) it was passed to a back pressure regulator whose pressure was set equal to that of the reactor. During the entire cycle period (τ), the feed pump was operated at a constant flow rate in which the periodic operating parameters were controlled by an actuator valve equipped with digital timer.

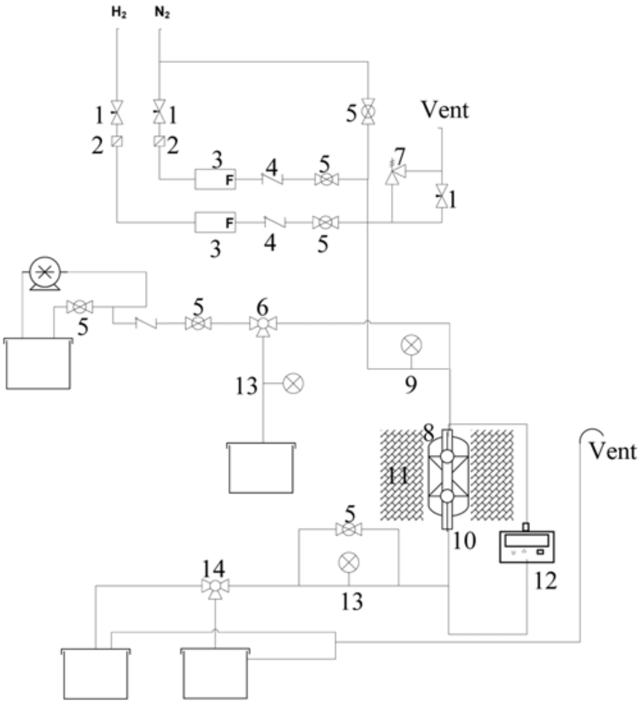

Fig. 1. Schematic diagram of the styrene hydrogenation system.

1. Needle valve
2. Filter
3. Mass flow controller
4. Check valve
5. Ball valve
6. 3-Ways solenoid valve
7. Relief valve
8. Trickle bed reactor
9. Pressure gauge
10. Thermocouple
11. Electric furnace
12. Heater control
13. Back pressure
14. 3-Ways ball valve

A commercial catalyst used in the present work was spherical with 0.3 wt% palladium supported on γ-Alumina (diameter=2 mm, bulk density=0.66 g/cm^3, BASF). Before experiments, the catalyst was in-situ reduced using hydrogen (100 cm^3/min) at 150 °C for 1.5 h. The gas feed (hydrogen 99.99%) and liquid hydrocarbons were introduced to the top of the reactor. The concentration of styrene (99% Sigma Aldrich) in cyclohexane (99% lab scan) was 10% by weight. Samples at the reactor inlet and outlet were analyzed by chromatography with a flame ionized detector (PETROCAL Column). Inlet feed samples were taken from a sampling port set just after the feed tank. Outlet liquid samples were collected in the liquid product tank. The first outlet liquid sample was taken when a transient period of 30 min had elapsed, and then each sample was taken every 15 min. After reaching steady state, the periodic operation experiments were started at desired values of cycle period (τ) and split ratio (S). The cycle period (τ) is defined as the total time for one cycle of liquid modulation under on and off modes, whereas the split ratio (S) is defined as the time of liquid modulation under on mode divided by cycle period. The corresponding liquid flow rate was based on the equivalent average liquid flow rate of the steady state experiment.

The experiments were divided into two modes of operation: slow and fast modes. The ranges of operating condition were as follows: liquid flow rate of 1.5-4.5 cm^3/min, hydrogen flow rate of 50-100 cm^3/min, temperature of 50-75 °C, pressure of 15-25 bar, split ratio of 0.3-0.75 and cycle period of 4 min for slow-mode and of 40-60 s for fast-mode. The operating temperature and pressure used in this study were within the operation range of a commercial hydrogenation of pyrolysis gasoline.

RESULTS AND DISCUSSION

1. Styrene Hydrogenation in Steady State Operation Experiments

Steady state operation experiments were performed at different gas flow rates, liquid flow rates, pressures and temperatures in order to understand the reaction performance of styrene hydrogenation in a trickle bed reactor under conventional operation at an operat-

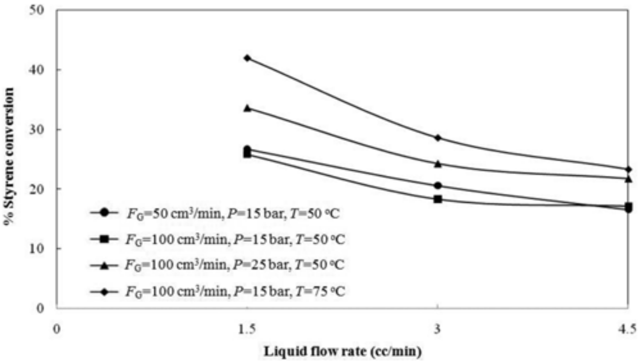

Fig. 2. % Styrene conversion at different operating conditions (steady state operation).

ing temperature of 50 °C. The results (Fig. 2) indicate that the styrene conversion increases with increasing hydrogen pressure due to enhanced solubility of H_2 into the liquid hydrocarbons and gas-liquid mass transfer. With increasing liquid flow rate, styrene conversion decreases due to the shorter residence time of liquid in the catalyst bed, and this also indirectly confirmed that these experiments were not under external mass transfer limit. However, the H_2 gas flow rate does not show significant influence on the conversion. This is in good agreement with the previous work [12]. Styrene conversion could be improved by performing the reaction at a higher temperature to increase reaction rate and to decrease mass transfer resistance [13].

2. Styrene Hydrogenation in Periodic Operation Experiments

Preliminary experiments under periodic operation were performed at the following condition: temperature of 50 °C, pressure of 15 bar, gas flow rate of 100 cm^3/min and average liquid flow rate of 3 cm^3/min. Different values of split ratio (S=0.3, 0.5 and 0.75) and cycle period (τ=40 s, 1 min and 4 min) were varied. The reaction performance is represented in terms of "relative conversion" (X_P/X_{SS}), defined as the styrene conversion obtained from the periodic operation over that from the steady state operation. Fig. 3 shows that both the cycle period and the split ratio have a significant influence on the relative conversion (X_P/X_{SS}). Operation at slow mode or long cycle period (τ=4 min) is not favorable, especially at the low value of split ratio (S=0.3), because at a longer cycle period, both the periods for the operation under high liquid flow rate and no liquid feeding become longer. During the extended high liquid flow rate period, the liquid residence time is shorter, whereas during the extended no liquid feeding period, the reaction is limited by the supply of liquid feed. Consequently, the conversion decreases. This effect is particularly pronounced at low split ratio as observed in Fig. 3 that the relative conversion is significantly decreased at S=0.3. For S=0.5 and 0.75, the maximum relative conversions (X_P/X_{SS}) are observed at the cycle period (τ) of 1 min. However, from this set of experiments, the improvement of conversion from the periodic operation over the steady state operation is still not yet observed.

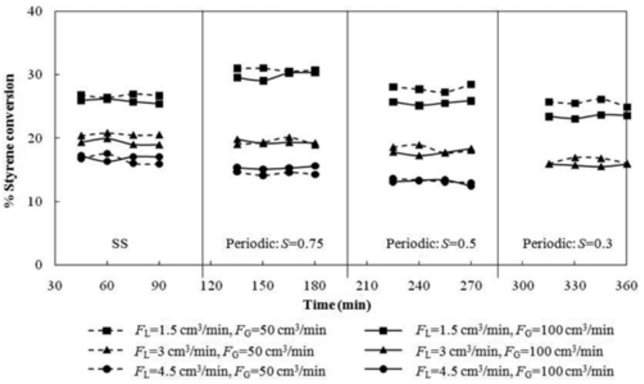

Fig. 4. **% Styrene conversion profiles at different values of split, average liquid flow rate and gas flow rate (periodic operation, T=50 °C, P=15 bar, τ=1 min).**

Another set of experiments was carried out at different values of gas flow rate and average liquid flow rate. The temperature and pressure were maintained at 50 °C and 15 bar, respectively. A suitable cycle period (τ) of 1 min was employed for all subsequent experiments of this study. The reaction was initially performed under steady state mode (S=1) before switching to the periodic operation mode. The first liquid product sample was collected after 30 min of periodic operation, and then the samples were collected every 15 min. Fig. 4 shows % styrene conversion profiles as a function of time. The average liquid flow rate and split ratio have significant influence on % styrene conversion, whereas the gas flow rate does not show pronounced influence on styrene conversion, similar to the previous report [12]. However, at low values of average liquid velocity at low split ratio, the effect of gas flow rate becomes more pronounced. The high gas flow rate (100 cm^3/min) offers lower % styrene conversion than the lower one (50 cm^3/min), probably because too high gas flow rate could decrease liquid holdup and catalyst wetting. For all values of split ratio, increasing average liquid flow rate decreases % styrene conversion. This should be due to shorter residence time, which is consistent with the results of the steady state operation (Fig. 2). The relative conversion (X_P/X_{SS}) shown in Fig. 5 indicates that there are optimum splits for different values of gas and average liquid flow rates. For F_L=4.5 cm^3/min, the relative conversion (X_P/X_{SS}) always decreases with decreasing split. However, for F_L=1.5 cm^3/min, the relative conversion (X_P/X_{SS}) increases initially until reaching a maximum and then decreases with decreasing split. From the experimental results, we observed an improve-

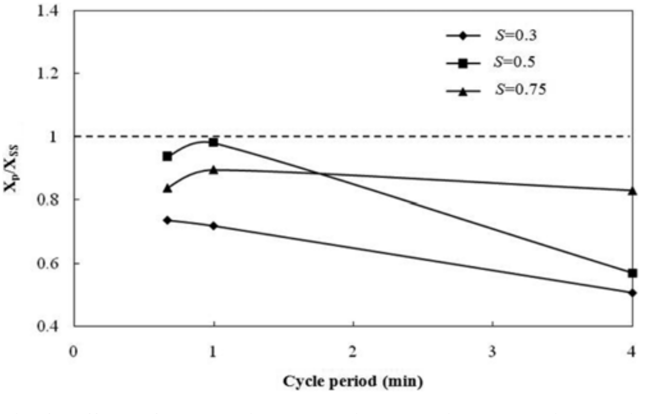

Fig. 3. **Effects of cycle period and split on relative conversion (periodic operation, T=50 °C, P=15 bar, F_L=3 cm^3/min, F_G=100 cm^3/min).**

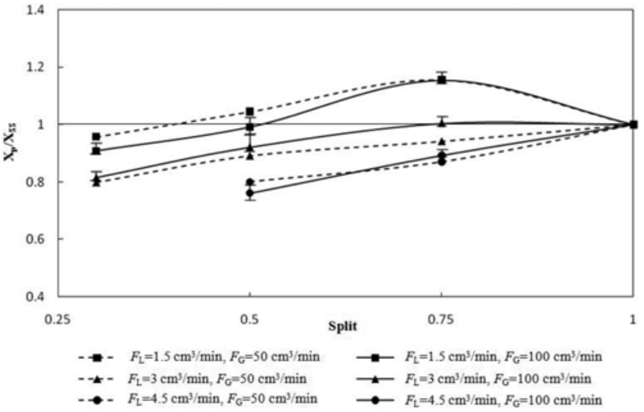

Fig. 5. **Effects of split, gas flow rate and average liquid flow rate on relative conversion (periodic operation, T=50 °C, P=15 bar, τ =1 min).**

ment in conversion from periodic operation over steady operation only at low liquid flow rate (F_L=1.5 cm^3/min). At S=0.75, improvement as high as 18% was achieved. It is obvious that the split is an important operating parameter for periodic operation. When decreasing split, the actual liquid flow rate in "on mode" becomes higher and hence lowers the residence time. Consequently, the conversion trends to be lower. However, the high liquid flow rate helps improve the catalyst wetting, and therefore the active catalyst surface can be more efficiently utilized [6,10]. In addition, the mass transfer limitation is decreased because the thickness of the film surrounding the catalyst particles during the "off mode" is reduced. It was reported in the previous works [7-9,12,21] that the synergistic effect of the improved reaction rate is also partly due to the increased bed temperature during the "off mode." The competing effects mentioned above result in the presence of an optimum split. For low average liquid flow rate, the catalyst wetting is poor. The use of periodic operation shows strong enhancement effect. On the other hand, at high average liquid flow rate, the problem on catalyst wetting and the enhancement from the better mass transfer become less significant. Therefore, no improvement from the periodic operation is observed.

Fig. 6 shows the effect of operating pressure, while Fig. 7 shows the effect of operating temperature on the catalytic performance of styrene hydrogenation in the trickle bed reactor. Considering the styrene conversion from the steady state operation (Fig. 2), higher styrene conversion is achieved when increasing hydrogen pressure and temperature. This is because of the increased gas-liquid mass transfer and gas solubility from the operation at higher pressures [1] and the faster reaction kinetics and mass transfer rate from the operation at higher temperatures [13]. Figs. 6 and 7 reveal that the improvement of the styrene conversion by periodic operation over the steady state operation becomes small at higher pressure and temperature. At F_L=1.5 cm^3/min and S=0.75, the improvement is 18% at P=15 bar and T=50 °C. However, they become about 6% at P=25 bar and T=50 °C and about 3% at P=15 bar and T=75 °C. From the experimental results, the optimum split also varies with operating temperature. The maximum relative conversion (X_P/X_{SS}) appears at a split of 0.5 for F_L=1.5 cm^3/min and T=75 °C while it is 0.75 at T=50 °C. The increased temperature obviously promotes the reaction rate and alters the hydrodynamics of the gas-liquid flow in the bed. It was reported that the liquid holdup and the shear stress at the gas-liquid and liquid-solid interfaces decrease with increasing temperature due to increased gas velocity and decreased liquid viscosity [22]. Therefore, it is likely that at a higher temperature, the optimum split of the periodic operation becomes lower.

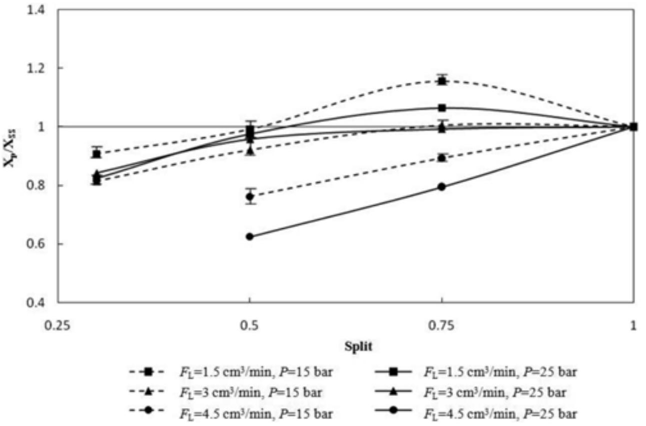

Fig. 6. Effects of split, average liquid flow rate and pressure on relative conversion (periodic operation, T=50 °C, F_G=100 cm^3/min, τ=1 min).

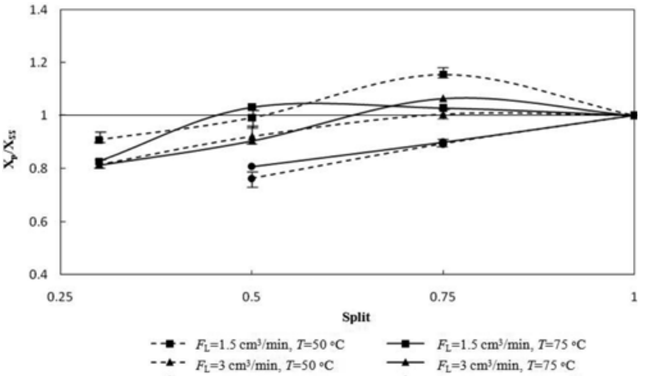

Fig. 7. Effects of split, average liquid flow rate and temperature on relative conversion (periodic operation, P=15 bar, F_G=100 cm^3/min, τ=1 min).

CONCLUSION

Fast-mode periodic operation has been successfully demonstrated to improve catalytic performance of TBR in styrene hydrogenation. A styrene conversion improvement up to 18% can be obtained at an average liquid flow rate of 1.5 cm^3/min, a gas flow rate 100 cm^3/min, a temperature of 50 °C, a pressure 15 bar, a cycle period of 1 min and a split ratio of 0.75. The periodic operation is favorable for reaction systems suffering from mass transfer limitation. The improvement depends on reaction system, operating condition (temperature, pressure, average liquid and gas flow rates) and modulation scheme (cycle period and split ratio).

ACKNOWLEDGEMENT

The authors would like to thank the Royal Golden Jubilee Ph.D. scholarship from TRF and SCG Chemicals, Co., Ltd.

NOMENCLATURE

F_G : gas flow rate [cm^3/min]
F_L : average liquid flow rate [cm^3/min]
P : pressure [bar]
S : split ratio, dimensionless
T : temperature [°C]
X_P : styrene conversion obtained from the periodic operation
X_{SS} : styrene conversion obtained from the steady-state operation

Greek Letter

τ : cycle period [min]

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