Intensification of Phase Transition on Multiphase Reactions

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Chemical reactions, generally conducted under full gas or liquid phases, are problematic for volatile liquid reactants. For such reactants, the presence of phase transition can be favorable, since evaporation of the liquid could not only balance the reaction heat but improve the effectiveness factor of the porous catalyst. This principle was applied to engineering applications. Experiment was carried out to investigate effects of catalyst activities, flow directions, operation pressures, gas and liquid flow rates, and reactant concentrations on the reactor behavior. Quench operation with a cold-injection side stream was initiated to prevent an excessive temperature rise, which was shown to be effective and flexible. With this novel optimizing method, the reactor temperature could be kept around 270°C under 1.0 MPa, even with a benzene concentration of 35%. Research on phase transition of benzene hydrogenation proved successful and could be extended to reaction systems with a similar range of process intensification.

Introduction

Chemical reactors are generally operated under constant phase conditions without or with only a little phase transition, but this may no longer be appropriate for liquid reactants with substantial volatility, because if the reaction is carried out in a fixed bed for gas operation, the reactant has to be vaporized before it is fed into the reactor. Nevertheless, a great deal of cooling energy should be supplied to remove the reaction heat, and this energy consumption is unreasonable. On the other hand, if the reaction is carried out in a trickle bed under liquid condition, the reaction rate would unfortunately be largely lowered, since the catalyst interior is completely filled with liquid; however, removal of reaction heat cannot be avoided if the reaction is exothermic.

The purpose of this work is to investigate the underlying principles in scope of intensification of multiphase reactions through phase transition. However, previously this has been considered dangerous, since vaporization of the liquid phase usually leads to partial wetting of the catalyst pellets and thus the inception of gas-phase operation, with a possible large rise in temperature and even damage to the catalyst (Eigenberger and Wegerle, 1982; Hanika et al., 1986).

In spite of the large amount of research that has been done on catalyst efficiency under partial wetting conditions, research on phase transition is still scarce. Important contributions in this latter field, for example, are those of Kim and Kim (1981a,b), Hu and Ho (1987), Bhatia (1988, 1989), Jaguste and Bhatia (1991), and Waston and Harold (1993, 1994). These researchers have only investigated the hysteresis phenomenon on the pellet scale, and an important conclusion from their work is that hysteresis is a route-dependent phenomenon—that is, the internal wetting condition is not exclusively determined by the temperature of the catalyst—that also depends on the catalyst being heated or cooled, as described by the Kelvin or the Cohan equations. Studies on reactor scale were also made by only a few investigators, under narrow operating conditions (such as Satterfield and Ozel, 1973; Sedriks and Kenney, 1973; and Hanika et al., 1975, 1976, 1977). These experiments were all conducted under 1 atm in a glass column under the trickling flow condition. The researchers found that phase transition was very dangerous, as it could cause reactor runaway. Theoretical analysis of phase transition on the reactor scale was given by Hanika et al. (1986), Kheshgi et al. (1992), and Khadilkar et al. (1999), who simulated the transition and hysteresis phenomena observed

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by Hanika et al. (1975). It seems more experimental work using close to industrial conditions as possible should be conducted to fulfill the gap between engineering application and theoretical understanding on the phase transition.

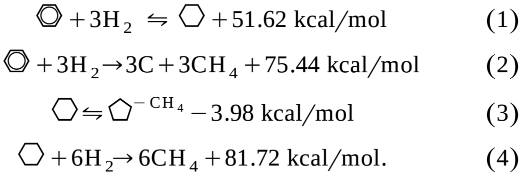
Regardless of the possibility of runaway reactors, phase transition nevertheless could provide an alternative to process intensification, since it has been observed that the reaction rate under gaseous condition is seven times as large as that under liquid conditions (Sedriks and Kenney, 1973: Hanika et al., 1975). To prevent the danger posed by phase transition, a concentration shift operation has been proposed in the literature (Lange et al., 1994; Hanika, 1999). It should be noted that concentration oscillation would inevitably lead to operational complexity, and even worse, to unstable product quality.

In this work, the hydrogenation of benzene to cyclohexane is carried out as the working system because of both its industrial importance and the inherent academic significance of the outcome. Additionally, the hydrogenation product, cyclohexane, has physical properties similar to benzene and is stable during the reaction, so that benzene hydrogenation can be treated as a single-component system in order to simplify the theoretical analysis.

Principles

Thermodynamics of the reaction system

Hydrogenation of benzene is a complex process, as is indicated by the following network:



In the above equations, the reaction heat is given at 500 K. Equation 1 is called the principal reaction in producing cyclohexane, and Eq. 2 accounts for the hydrocracking of benezene, with carbon and methane as the final products. Equations 1 and 2 are parallel for the conversion of benzene.

Because of the high reaction heat, a substantial temperature rise will occur in the reactor. The temperature effects on the four reactions are different, as can be seen by the equilibrium constants listed in Table 1. The equilibrium constant for the principal reaction is found to decrease substantially under high temperatures, and it seems that the temperature suitable for benzene conversion cannot exceed 600 K. At temperatures lower than this, the benzene conversion will be seriously restricted, thus leaving much of the benzene unconverted. However, the coexistence of benzene hydrocracking provides additional conversion because of its high equilibrium constant. Additionally, high temperatures also favor the conversion of cyclohexane to other byproducts. Therefore, the temperature should not be too high to guarantee the conversion of benzene into cyclohexane.

Table 1. Equilibrium Constants of the Benzene Hydrogenation Network

T	Reaction, log K_P			
K	1	2	3	4
300	16.932	49.092	−0.686	58.629
400	7.842	35.632	0.036	44.296
500	2.259	27.448	0.472	35.485
600	−1,527	21.916	0.759	29.458
700	−4.257	17.922	0.957	25.050
800	−6.311	14.896	1.097	21.669
900	−7.910	12.518	1.198	18.976
1,000	−9.183	10.605	1.270	16.785

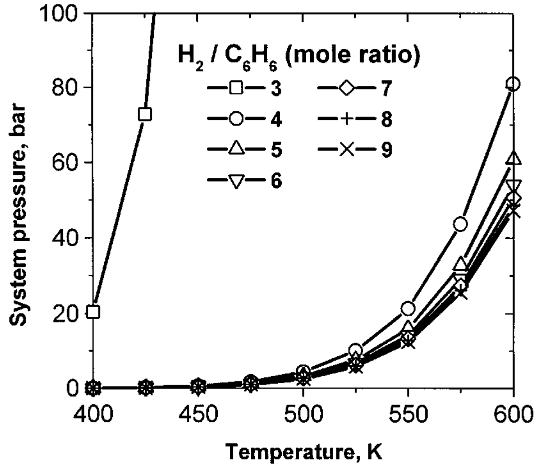


Figure 1. Thermodynamic conditions for benzene conversion to 99.95%.

To provide the most available reaction rate, the reaction temperature can approach the equilibrium value, as is determined from the following assumptions:

1. The conversion of benzene to cyclohexane is as high as 99.95%.
2. The side reactions are assumed negligible under a wide temperature range.

Assumption 1 is also a constraint that has to be satisfied for industrial operation, since the boiling point of cyclohexane approaches that of benzene; otherwise, the separation of these two components will be very difficult. The second assumption is made to simplify the theoretical analysis, and should be expected in view of the rapid development of new catalysts.

A thermodynamic diagram based on these assumptions is shown in Figure 1. Specifically, in order to obtain 99.95% conversion from benzene to cyclohexane under an operation pressure of 1.0 MPa at a molar ratio of $H_2/C_6H_6 = 9$, the operation temperature should not exceed 270°C.

Gas–liquid equilibrium inside of the catalyst interior

The liquid filling condition in the catalyst interior is closely related to the effectiveness factor of the porous catalyst. According to the capillary effect, as described by the Kelvin equation (Eq. 5), the gas–liquid equilibrium in the catalyst interior will be much different from the bulk phase:

$$\ln\frac{p_i^0}{p^0}=\frac{2\sigma M}{RT\rho}\left(\frac{-1}{\hat{r}_i}\right) \qquad (5)$$

In Eq. 5, $\hat{r}_i$ is the average gas–liquid interface radius, and is

Table 2. Capillary Effects on Phase Transition within Catalyst Pores*

	Evaporation		Condensation	
d_i (Å)	p_i^0 (bar)	T_i^e (°C)	p_i^0 (bar)	T_i^c (°C)
30	7.65	197	8.85	189
50	8.60	190	9.39	185
120	9.53	184	9.89	182

*The bulk phase condition is $T^0 = 180°\text{C}$; $P^0 = 1.025$ MPa.

expressed by

$$\frac{2}{\hat{r}_i} = \left[\frac{1}{r_1} + \frac{1}{r_2}\right] \tag{6}$$

where $\hat{r}_i$ depends on the system being heated or cooled, and is obtained according to Jaguste and Bhatia (1991):

$$\hat{r}_i = \begin{cases} r_i, & \text{where } r_1 = r = r_i \text{ for evaporation} \\ 2r_i, & \text{where } r_1 = r_i, r_2 = \infty \text{ for condensation.} \end{cases} \tag{7}$$

The gas–liquid equilibrium data within the capillary is shown in Table 2, where pressure p_i^0 indicates the equilibrium vapor pressure of the liquid in the pores under bulk temperature, T^0. Here T_i^e and T_i^c correspond, respectively, to the bulk phase temperatures, under which the liquid in the pores starts to evaporate or to the vapor in the bulk phase starts to condense within the pores. The difference between T_i^e and T_i^c forms a hysteresis cycle from evaporation to condensation.

Experimental Studies

According to the hydrodynamic analysis of Ng (1986) and Cheng and Yuan (1999), liquid maldistribution has been one of the major problems in the trickle-bed operation, especially prior to the inception of the pulsing flow. In the literature, maldistribution has been considered one of the origins of operational uncertainty (Stanek et al., 1981; Funk et al., 1990). To get a uniform liquid distribution without the tedious catalyst dilution procedure, we prefer the concurrent upward flow of the gas–liquid.

To get a steady hydrogen flow rate over a long period, the process is facilitated with a G2V-5/20 diaphragm compressor (20.0 MPa and 5 Nm^3/h) for hydrogen recycling and making up. The reactor, which is made of a stainless steel pipe, has a wall thickness of 2.5 mm, is 1.6 m in length, and has an inside diameter of 20 mm. Twelve thermocouples, 10 cm distant from each other, are inserted across the reactor wall and are connected to a data-acquisition computer. Side-stream concentration analysis and quench operation are also facilitated. The reactor wall is wrapped with a 1.5-kW electrical heating band and is insulated by a thick layer of glass wool. A flowsheet diagram of the whole process is shown in Figure 2.

Two different catalysts, 0.5% Pd over Al_2O_3 (catalyst A) and amorphous Ni-B alloy catalyst (catalyst B), are employed in the present work. It is assumed that catalyst B is several times more active than catalyst A. The catalysts are 2–3 mm in diameter, and are packed to a height of 1.0 m between two inert packing layers 30 cm on both ends, in order to offer uniform distribution and saturation of the reaction mixture by hydrogen, and eventually the temperature is leveled off to satisfy the Danckwerts' boundary condition. The reactor is designed to operate simultaneously downward and upward for the two fluids. A two-stage gas–liquid separator is installed to accomplish a complete phase separation. The reactor pressure is controlled through a back-pressure regulator installed next to the first-stage separator.

Results and Discussion

To conduct the benzene hydrogenation effectively, the choice of catalyst and flow direction should be the fundamen-

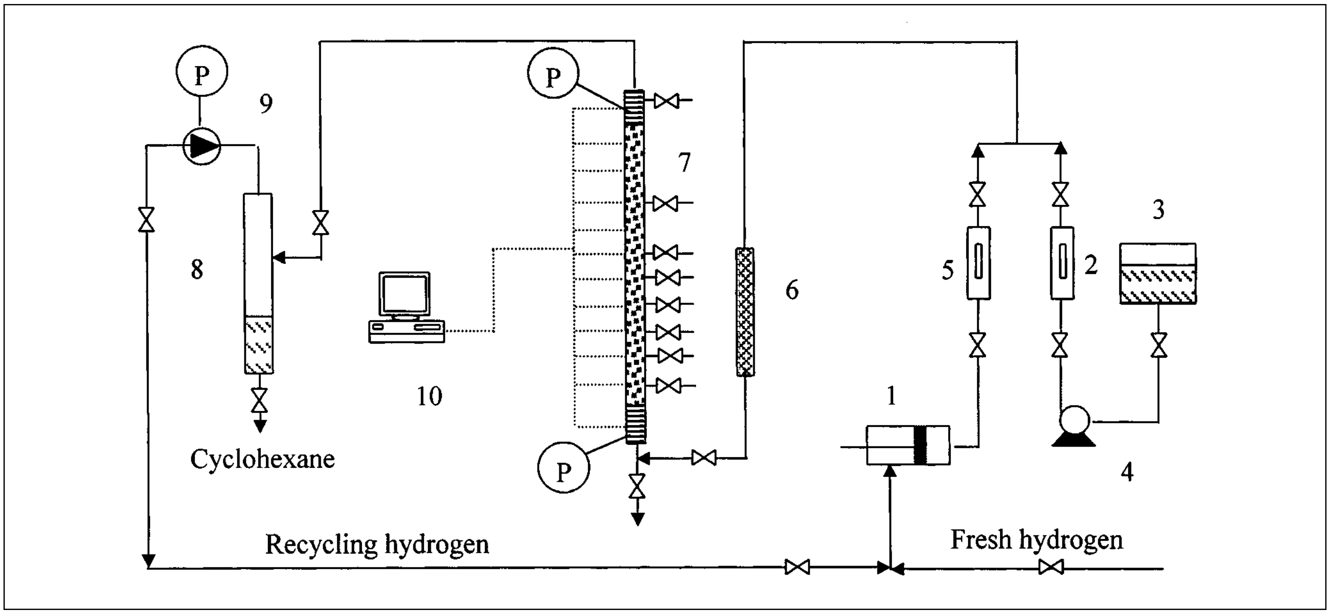


Figure 2. Experimental flow sheet.

1—Compressor; 2—liquid flowmeter; 3—liquid tank; 4—liquid pump; 5—hydrogen flowmeter; 6—preheater; 7—reactor; 8—gas–liquid separator; 9—back-pressure control valve; 10—computer; ⋈—valve; ⓟ—pressure gauge.

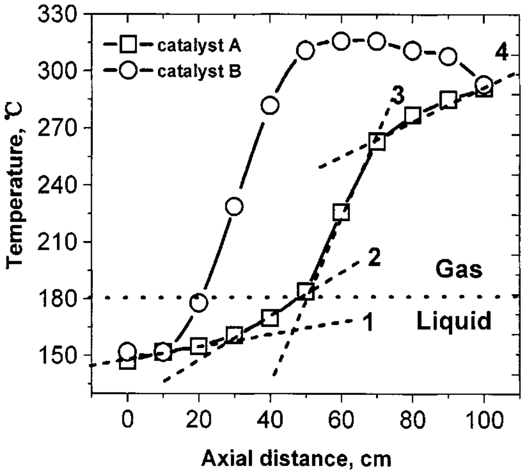


Figure 3. Effect of catalyst activity on the reactor temperature profile under upward flow.

$P = 1.0$ MPa; $T_{in} = T_w = 150°C$; $C_B^0 = 25\%$; $L = 1.24$ kg/h; $G = 15.5$ nL/min; conversion: ○; □—100%.

tal task. A comparison of catalyst activity is shown in Figure 3, where the reactor temperature increases for catalyst A from 150°C to 291°C and to 316°C for catalyst B. It is also found, under the same operating conditions, the hot spot for catalyst B is about 50 cm ahead of that for catalyst A.

The existence of phase transition can be verified in Figure 3 from the boiling point of benzene/cyclohexane mixture, which is 180°C at 1.0 MPa. The liquid will therefore not exist above this temperature in the bulk phase in the back of the reactor. It should be noted that, due to the capillary effect, the liquid may possibly exist in the catalyst pores. From Table 2, it is expected that the liquid can be stored in the pores at temperatures between 184 and 197°C as the pore diameter decreases from 120 Å to 30 Å.

A plot of temperature against reactor length in Figure 3 shows four different slopes. Slope 1 denotes the reaction rate at the reactor inlet under the liquid condition. With some liquid evaporation, the catalyst's external surface will be partially dried and the reaction rate increases to slope 2. Above the boiling point of 180°C, the catalyst becomes partially wetted internally and leads to a stepwise increment in the reaction rate, as denoted by slope 3. Slope 4 corresponds to a reduced reaction rate, since at the end of the reactor, the reactant concentration is much lower, which causes a drop in reaction rate. Different temperature profiles are obtained for catalysts A and B under the same 100% reactant conversion, and this should be attributed to the side reaction of benzene hydrocracking, for providing additional reaction heat. Such an explanation could be verified if carbon deposits were found on the catalysts.

As Figure 4 shows, a phase-transition diagram is outlined according to the preceding analysis, with five progressive reaction regions classified along the flow direction.

The effect of flow direction is shown in Figure 5. It is likely that the downward flow leads to a reduced utilization of catalysts, since it is seen that the conversion of benzene is even lower than that for catalyst A under the upward flow condition. The reduced conversion under downward flow comes from the lower liquid holdup. The flow rates of liquid and gas under the experimental condition just mentioned ($T = 150°C$ and $P = 1.0$ MPa) are $u_L = 1.25 \times 10^{-3}$ m/s and $u_G = 0.127$ m/s, which suggests that the flow condition is bubbling flow or trickling flow for the upward and downward flow patterns (Charpentier and Favier, 1975; Shah, 1978; Cheng and Yuan, 1999). The dimensionless liquid holdups are estimated to be 0.33 and 0.25, respectively, according to Turpin and Huntington (1967) and Ellman et al. (1990).

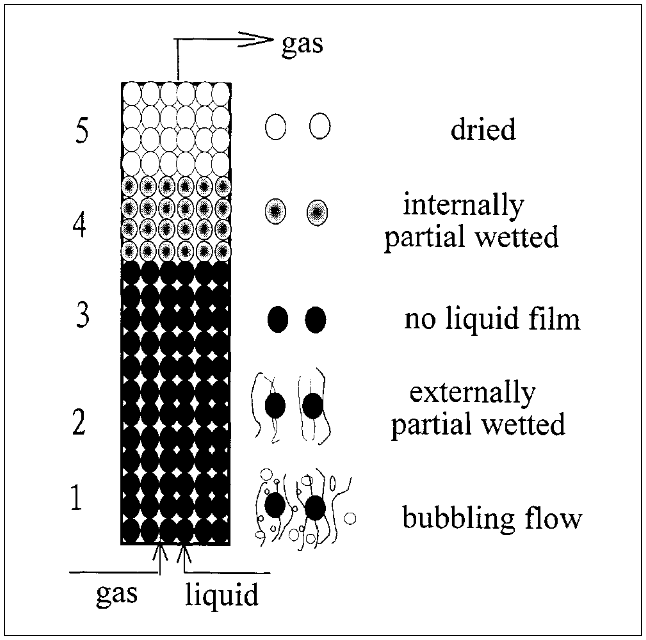


Figure 4. Phase-transition diagram with vaporization of the liquid component.

Catalyst states: 1, 2, 3—fully wetted; 4—partially wetted; 5—dried.

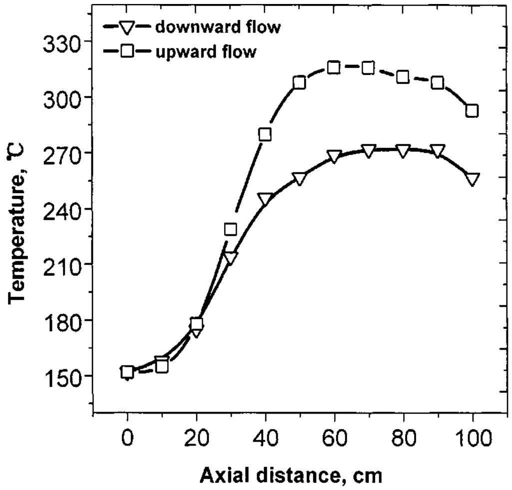


Figure 5. Effect of flow direction on the reactor behavior for catalyst B.

$P = 1.0$ MPa; $T_{in} = T_w = 150°C$; $C_B^0 = 31.5\%$; $L = 1.24$ kg/h; $G = 15.5$ nL/min; conversion: △—69%; □—100%.

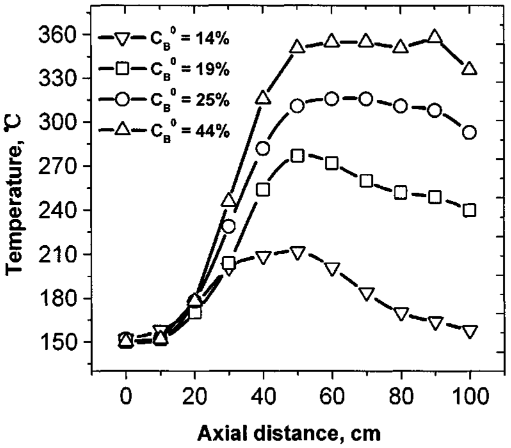


Figure 6. Effect of reactant concentration on the bed temperature profile.

$P = 1.0$ MPa; $G = 15.5$ nL/min; $L = 1.24$ kg/h, $T_{in} = T_w = 150$°C; conversion: ○, □, ▽, △—100%.

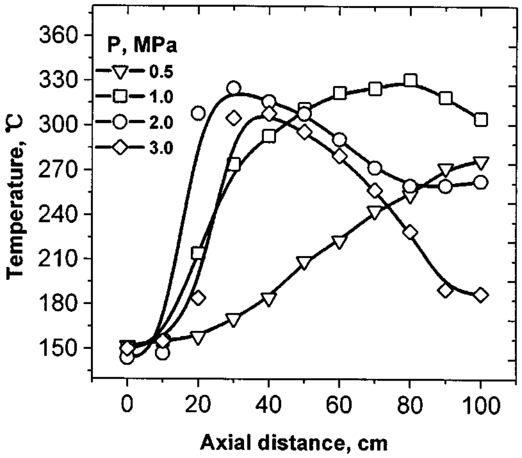


Figure 7. Effect of operation pressure on phase transition.

$C_B^0 = 25\%$, $T_{in} = T_w = 150$°C, $G = 15.5$ nL/min; $L = 12.4–1.30$ kg/h; conversion: ▽—73.8%, ○, □, ◇—100%.

Operations under concurrent upflow

In the following paragraphs, the reactor is operated under upward flow and packed with catalyst B to have a higher catalyst activity and uniform liquid distribution.

No concentration effect is observed in Figure 6 under liquid-phase condition, although the reactant concentration varies from 14% to 44%. This means that the reaction order to benzene in the liquid phase is almost 0, which could be explained by the large excess of benzene relative to hydrogen in the liquid phase. The concentration effect appears at above 180°C, which indicates that the reaction order to benzene in the gas phase is greater than 0, and this is ascribed to the shortage of benzene compared with hydrogen in this case.

The operation pressure influences both the reaction rate and phase transition. Since the operation pressure represents a total of the hydrogen and benzene, an increase in this variable increases the concentration of the reactants, and thus the reaction rate. In addition, under a fixed mass flow rate, the increase in operation pressure would lead to a longer residence time and higher conversion. These two effects are combined to give different temperature profiles, as is observed in Figure 7.

In spite of the similarities in the temperature profiles in the front of the reactor at 1.0, 2.0, and 3.0 MPa, a large difference is observed downstream, as is indicated by the significant temperature declines at 2.0 and 3.0 MPa. The reason for this is that at high pressures, significant condensation of the gas phase, and thus increased heat loss, will occur because of the large thermal conductivity of the liquid phase.

The effect of hydrogen flow rates is shown in Figure 8. Under a hydrogen flow rate of 5.4 nL/min, the conversion is only 56%, which is almost half of the other two cases. The low conversion comes from the insufficiency in hydrogen, since the actual flow rate is less than the stoichiometric value of 5.6 nL/min. The reactant conversion under 5.4 nL/min indicates that the hydrogen converted in the reaction is only half the stoichiometric value. In this proportion, the complete conversion of benzene requires twice the stoichiometric value for hydrogen, and it was verified by the experiment with $G = 10.5$ nL/min. It seems that, in view of the equilibrium limitation, extra hydrogen is needed to ensure high benzene conversion.

Figure 9 depicts the effect of the liquid flow rate on the temperature profiles. At a liquid flow rate of 4.74 kg/h, the maximum temperature is 180°C, which means that the reaction is carried out under full liquid condition. At a liquid flow rate of 3.24 kg/h, a critical temperature profile is observed which indicates the transition from liquid-phase operation to gas phase. At liquid flow rates of 2.16 and 1.24 kg/h, the operations shift rapidly to gas and exhibit a similar temperature trend. At a liquid flow rate of 2.16 kg/h, however, the conversion is only 53.6%, although the temperature profile is similar to that at 1.24 kg/h. The reason for this is that benzene hydrogenation is inhibited by equilibrium at high temperatures, and the high temperature region contributes only a little to the conversion of benzene.

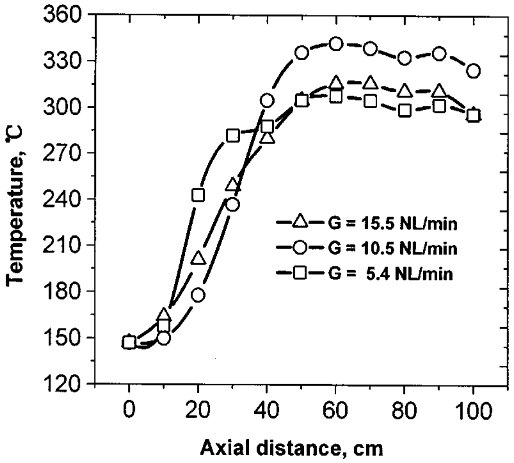


Figure 8. Effect of hydrogen flow rate on the bed temperature profile.

$P = 1.0$ MPa; $C_B^0 = 31.5\%$; $T_{in} = T_w = 150$°C; $L = 1.24$ kg/h; conversion: ▽ ○—100%, □—56.5%.

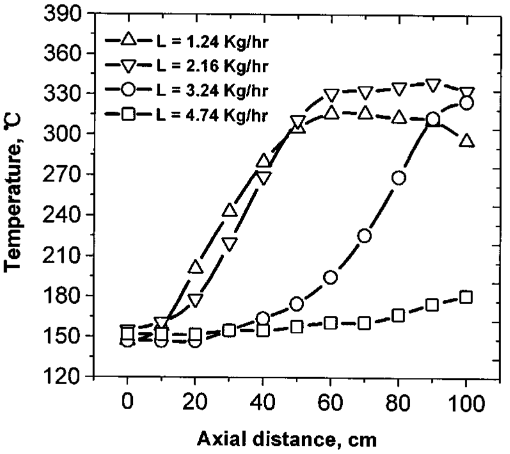


Figure 9. Effect of liquid flow rate on phase transition.

$P = 1.0$ MPa; $C_B^0 = 31.5\%$, $T_{in} = T_w = 150°C$; $G = 15.5$ nL/min; conversion: △—100%, ▽—53.6%; ○—41%; □—14%.

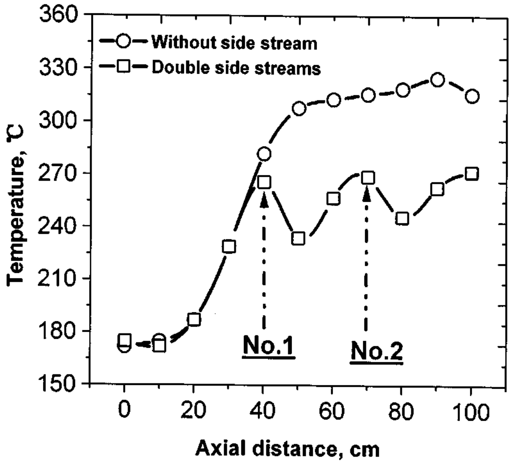


Figure 11. Side-stream optimization with two injection points.

$P = 1.0$ MPa, $C_B^0 = 31.5\%$, $T_{in} = T_w = 150°C$; $L = 1.24$ kg/h; $G = 15.5$ nL/min; ○— $L_1 = L_2 = 0$, $X = 100\%$; □— $L_1 = L_2 = 6$ mL/min, $X = 100\%$.

The relationship between the liquid flow rate and conversion is plotted in Figure 10. It is estimated from the extrapolations that the reaction rate under liquid phase is one half that with a substantial phase transition, which implies the contribution of the gas-phase reaction to the conversion of benzene.

Optimization with quench operation

To achieve a conversion from benzene to cyclohexane of 99.95%, the temperature should not exceed 270°C, provided the operation pressure is 1.0 MPa. Above this temperature, benzene will be converted to C and CH_4 through hydrocracking, although the conversion still reaches 100%. To control the reaction temperature within 270°C, it is found from the preceding paragraphs and as depicted in Figure 6 that the reactant concentration should not exceed 18%. Nevertheless, this would reduce the processing capacity of benzene. It is believed that this problem arises from the low utilization of the reactor space. From Figure 6 it can be concluded that the reactions only take place in the front of the reactor, with almost a half of the reactor space not used.

To produce a uniform temperature profile over the reactor length, quench operation is employed (Cheng et al., 2000). It is found from Figure 11 that the operation with two injection points is more flexible than with only one point as shown in Figure 12. The local maximum temperatures in the operation with two injection points are 226°C, 269°C, and 272°C, all of them approaching the thermodynamic temperature limit of 270°C. The perfect temperature control has provided promising product quality and benzene conversion. From the GC

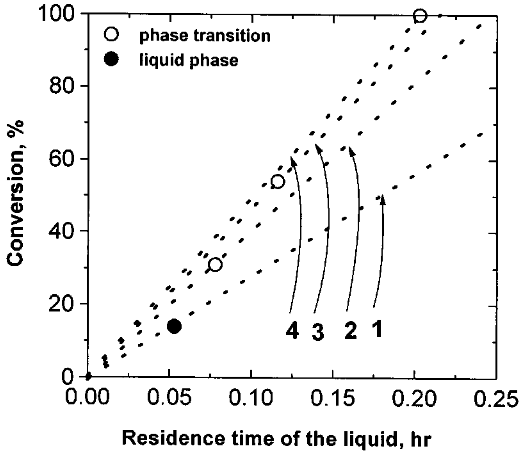


Figure 10. Effect of phase transition on conversion of the reactant.

$P = 1.0$ MPa; $C_B^0 = 31.5\%$; $T_{in} = T_w = 150°C$, $G = 15.5$ nL/min; liquid flow rates (kg/h):1—4.74; 2—3.24; 3—2.16; 4—1.24.

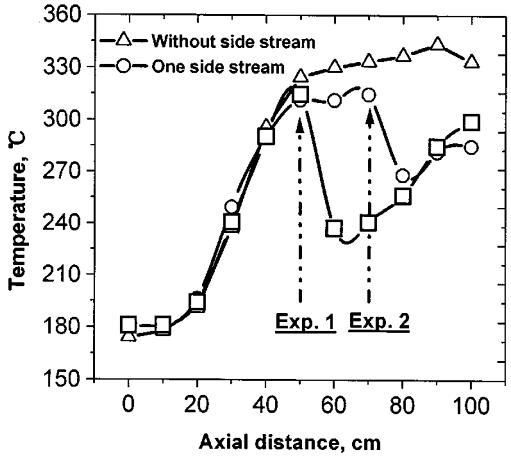


Figure 12. Side-stream optimization with one injection point.

$P = 1.0$ Mpa; $C_B^0 = 31.5\%$; $T_{in} = T_w = 150°C$; $L = 1.24$ kg/h; $G = 15.5$ nL/min; △— $L_1 = 0$, $X = 100\%$; ○— $L_1 = 6.7$ mL/min, $X = 100\%$; □— $L_1 = 18.4$ mL/min, $X = 82.7\%$.

Table 3. Benzene Hydrogenation among Different Technologies

Parameter	Trickle Bed	Magnetically Suspended Slurry	Phase Transition Operation	
Catalyst	Ni–Cu–Cr 2–3 mm	Ni–Re–P alloy 0.2 mm	Pd/Al_2O_3 2–3 mm	Ni–B alloy 2–3 mm
Inlet temp., °C	150	230	150	150
Hydrogen vs. benzene by mol	>100	>100	6–9	6–9
Liquid space vel. of benzene, h^{-1}	1.62	3.2	1.6	3.4
Benzene in feedstock, vol. %	21.5	25.1	16–40	16–40
Benzene in product, vol. %	<1	0.73	<0.01	<0.01

analysis, it is found that the product purity in cyclohexane is greater than 99.98% and that the conversion of benzene approaches 100%. Additionally, with the temperature control satisfied, no carbon deposits have been found on the catalyst surface.

The quench operation has also made the operation available at the high benzene concentration of 35%. The reduction in reaction rate due to the liquid entering the catalysts is not expected around the injection points, since the local temperature minima are 234°C and 246°C, both are greater than the values for vapor condensation, as shown in Table 2. The side-stream operation was proved successful, as can be seen by a comparison with other technologies shown in Table 3 (Cheng et al., 2000).

Conclusions

It may be concluded from the present work that for liquid reactants with substantial volatility such as benzene, an operation associated with phase transition would exhibit multifunctional effects. Advantages due to this new development are summarized as follows:

1. The energy requirement is reduced, since the reaction heat is to a certain extent counterbalanced by the liquid evaporation.
2. Phase transition improved the overall reaction rate by 100% in comparison with the full liquid-phase operation.
3. The reactant concentration can be much higher than in the conventional gas-phase operation and with no risk of hot-spot formation.
4. The reactor operation is flexible and could be optimized through side-stream injection.

The research work initiated on benzene hydrogenation proved successful in applying the phase transition principle to the intensification of multiphase reactions.

Acknowledgment

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Notation

C_B^0 = inlet benzene concentration in dilution by cyclohexane, vol. %
d_i = catalyst pore diameter, m
G = gas flow rate, nL/min
K_P = equilibrium constant
L = liquid flow rate, kg/h
M = molecular weight
L_1 = liquid flow rate of side stream at position 1, kg/h
L_2 = liquid flow rate of side stream at position 2, kg/h
P = operation pressure, bar
p^0 = bulk phase pressure, bar
p_i^0 = vapor pressure of the liquid inside the catalyst, bar
r_1, r_2 = principal radii of the gas–liquid interface, m
$\hat{r}_i$ = average radius of the gas–liquid interface, m
T = temperature, °C
T^0 = bulk-phase temperature, °C
T_i^c = condensation temperature of vapor inside of the catalyst, °C
T_i^e = evaporation temperature of liquid inside of the catalyst, °C
T_{in} = inlet temperature of the reactant mixture, °C
T_w = reactor wall temperature, °C
u_G = linear velocity of the gas, m/s
u_L = linear velocity of the liquid, m/s
X = conversion of the reactant

Greek letters

σ = surface tension, N/m
ρ = density of the liquid, kg/m^3

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