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The Effects of Impeller Characteristics in the Hydrogenation of Aniline on Ru/C Catalyst

Hong-Baek Cho and Yeung-Ho Park†

Division of Material Science and Chemical Engineering, Hanyang University,
1271, Sa-1-Dong, Ansan-Si, Kyonggi-Do 425-791, Korea
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Abstract−Effects of impeller characteristics have been studied in the hydrogenation of aniline on Ru/C catalyst. Dual impellers were employed and the experiments were performed at 300 rpm using a lab-scale reactor. Reaction with disk turbines (DT) resulted in the higher cyclohexylamine (CHA) selectivity and higher reaction rate compared to that with pitched blade turbines (PBT). When a combination of PBT and DT impellers was employed, high product selectivity and reaction rate were obtained and the selectivity was maintained constant. Changes in the product selectivity with the impeller geometry were explained in terms of the relative rates of the side reactions depending on the hydrogen concentration in the reaction mixture.

Key words: Impeller Characteristics, Hydrogenation of Aniline, Reaction Rate, Product Selectivity, Hydrogen Concentration

INTRODUCTION

In solid catalyzed gas-liquid reactions like hydrogenation, the mass transfer effect can be more important than the reaction itself. Especially, in the case of the industrial reactor, we face many scale-up problems such as an extended reaction time and a large amount of byproducts due to the insufficient mixing in the reactor. With this kind of multiphase reaction, the selection of the agitator is critical to the design of an industrial reactor. It has been reported that the reaction time in the industrial reactor decreased more than twice and the catalyst life increased five times by changing the impeller [Kaufman, 1998]. Thus proper guides for the impeller selection are needed for industrial reactor design.

These guides can be directly obtained by studying the effect of impellers in large-scale reaction experiments, which is not easy due to the high cost. The effects of impeller types on the characteristics of some reactions might have been examined in a pilot scale in the course of process development, but those results have not been published for commercial reasons, as they could have resulted in the insufficient understanding of the role of impellers in the reaction.

Many general guides on the selection of impellers for the tank reactors have been published [David and John, 1976; Lewis et al., 1975; Richard and Lewis, 1976; Van't Riet et al., 1976; Lu et al., 1999; Jo et al., 1996], but they are mostly based on the data of fluid mechanics and mass transfer. Some of the guides for batch reactors were reviewed as follows. For a dead-end type hydrogenation reactor, which is widely used in the industry, the impeller that can induce the gas from the liquid surface was recommended since gaseous reactant is mostly supplied from the headspace of the reactor [Oldshue, 1980]. A gas-inducing agitator of hollow tube type is known to be effective, but its effect is insignificant in a large scale reactor. Rather, agitators of multi-stirrer type are used more frequently [Nagata, 1975]. In addition, it was reported that the impellers producing a vortex effectively induce the gas from the gas-liquid interface into the liquid [Nagata, 1975]. Oldshue [1980] suggested that in using dual impellers in a dead-end hydrogenation process, it is more efficient to install an axial-flow impeller on the upper position and a radial-flow impeller on the lower position with a half-baffle. In spite of these general guides, there is still a lack of the knowledge on how agitation parameters affect the specific reactions, which is necessary for the design of individual reactor.

Even though no report has been published on the effect of the impeller geometry in the reaction, there are some articles dealing with the effect of the agitation speed. Zajcew [1960] observed that the concentrations of trans-isomers among the products in hydrogenation of fatty oil decreased with increased agitation speed, and explained the results by the differences in the hydrogen concentration on the catalyst surface. Eldib and Albright [1957] also reported that the formation of the trans-oleic acid was favored at a lower agitation speed in the hydrogenation of linoleic acid.

In this study, the effects of the impeller characteristics on the reaction rate, selectivity, and product distribution in aniline hydrogenation on Ru/C catalyst were examined in an attempt to obtain useful design data for the selection of the impeller system in a large-scale reactor. The reaction experiments were performed with a laboratory reactor and the type of the impeller, combination of impellers, and direction of impeller rotation were varied to find how the impeller geometry affects the hydrogenation reaction.

EXPERIMENTAL

The hydrogenation reaction was carried out with a 2 L high pressure reactor made of stainless steel, whose schematic diagram is shown in Fig. 1. The reaction temperature was controlled by using a heating block attached on the reactor wall and a cooling coil inside the reactor. The hydrogen gas was bubbled through a sparger installed at the bottom of the reactor and its input rate was controlled by a pressure regulator at the rate of hydrogen consumption in the reactor (dead-end type operation). The amount of hydrogen

†To whom correspondence should be addressed.
E-mail: yhp427@chollian.net
‡This paper is dedicated to Professor Baik-Hyon Ha on the occasion of his retirement from Hanyang University.

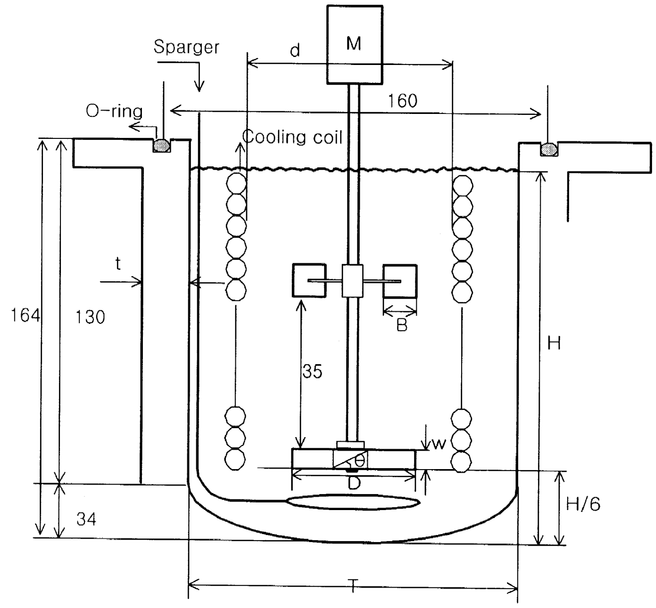
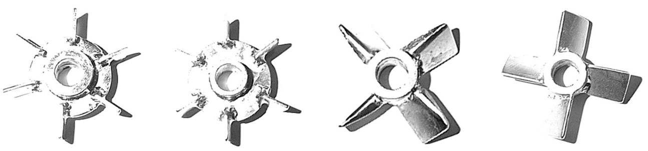


Fig. 1. Schematic diagram of the reactor.

D/T=0.5	B: Width of the blade
H: Liquid death=106	t: Reactor thickness=11
H/T=1.3	T: Reactor diameter=120
D: Impeller diameter	d: Inside diameter of cooling coil
W: Impeller height=D/8	



Impeller type	DT-w	DT-n	PBT-f	PBT-s
Number of blades (ea)	6	6	4	4
Impeller diameter (mm)	62	60	60	60
Impeller height (mm)	19	19	19	19
Blade width (mm)	16	15	20	20
Blade angle (degree)	90	90	71.5	71.5

Fig. 2. The shape and dimension of the impellers used in the reaction experiment.

consumed during the reactor was monitored by means of a mass flow meter.

Agitation in the reactor was performed by dual impellers installed on the shaft of a magnetic drive. The agitation speed of the stirrer could be varied up to 1,800 rpm and its pumping direction could be changed by shifting the rotating direction of the motor. The shapes and dimensions of the impellers used in the experiment are shown in Fig. 2. These impellers include disk turbines (DT) invoking a radial flow and pitched blade turbines (PBT) generating an axial flow. Of the two kinds of disk turbines used, one (DT-w) had wider blades and a larger disk than the other (DT-n). In the case of pitched blade turbines (PBT), one (PBT-s) had flat blades, while the other (PBT-f) had folded blades; this is believed to have the effect of intensifying the axial flow. Various kinds of dual impellers were used in the experiments to examine the effects of impeller geometry in

Fig. 3. A glass reactor used to measure the depth of vortex.

the reaction. When the same types of impellers were installed, the impellers fell into four cases: [DT-w+DT-w], [DT-n+DT-n], [PBT-f+PBT-f], [PBT-s+PBT-s]. (The first word in the parentheses indicates the upper impeller and the next one indicates the lower impeller.) When impellers of a different type were combined, two kinds of impellers were tested: [DT-w+PBT-f], [PBT-f+DT-w].

The effects of the impeller characteristics on the flow pattern in the reactor were visually examined by using a glass vessel (Fig. 3). The vessel that had the same shape and dimension with the autoclave was fitted to the reactor head, and was filled with water for agitation experiments.

Hydrogenation reaction was performed over Ru/C catalyst (5 wt% on carbon) at 170 °C and 50 bar of hydrogen pressure. The catalyst loading was 1 wt% of the reactant. The reaction products were regularly sampled through a dip tube of the reactor for analysis. GC/MS (Fisons MD800, Column: HP-5) was used for the identification of reaction products and GC (HP-6890 plus, Column: HP-5) was used in the quantitative analysis. Conversion and selectivity were calculated as follows.

$$\text{Conversion (\%)} = \frac{\text{mole of aniline reacted}}{\text{mole of aniline feed}} \times 100$$
$$= (1 - \text{mole fraction of aniline unreacted}) \times 100$$

$$\text{CHA Selectivity (\%)} = \frac{\text{mole of CHA produced}}{\text{mole of aniline reacted}} \times 100$$
$$= \frac{\text{mole fraction of CHA}}{\text{sum of mole fractions of the products}} \times 100$$

RESULTS AND DISCUSSION

1. Basic Reaction Characteristics

In the hydrogenation of aniline, cyclohexylamine (CHA) was produced along with dicyclohexylamine (DCHA) and cyclohexane (CH), but cyclohexanol observed in other work [Greenfield, 1964] was not obtained. The changes in the product distribution with time are shownin Fig. 4. After the reaction started, the amount of CHA product increased with a steep decrease of aniline while the yields of DCHA and CH steadily increased.

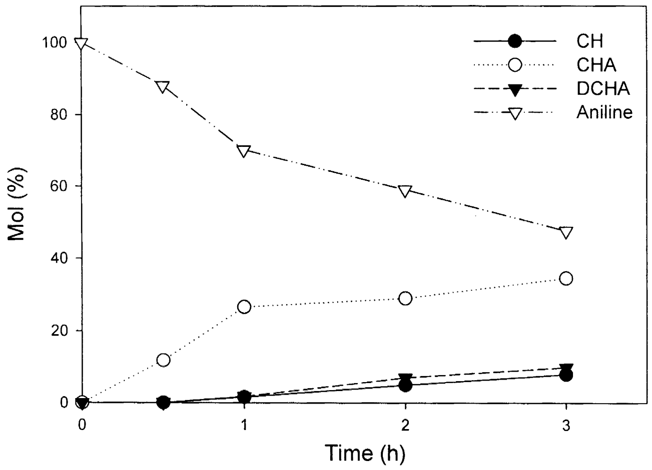


Fig. 4. The reaction profile of aniline hydrogenation (170 °C, 50 bar, 300 rpm, upward-flow, impeller: [PBT-f+PBT-f]).

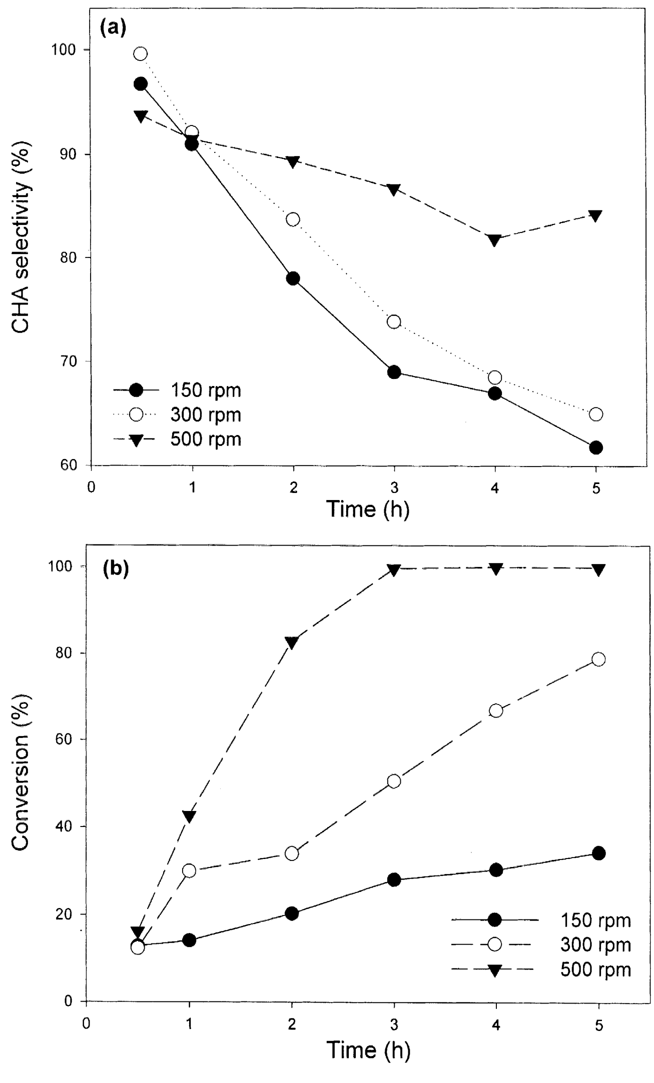


Fig. 5. The effect of agitation speed on the CHA selectivity and aniline conversion (upward-flow, impeller: [PBT-s+PBT-s]).

The conditions of the reaction experiments to examine the effect of impeller characteristics were determined experimentally. Agitation speed, an important process parameter influencing the hydrogenation reaction, was varied from 150 rpm to 500 rpm, and the results of reaction are given in Fig. 5. At the speed of 150 rpm, only 30% of reactant was converted in 5 hours of reaction, while 100% conversion was obtained in 3 hours at 500 rpm. The selectivities to CHA were also higher at 500 rpm than other cases. These results show that the agitation speed of 500 rpm is preferable for the best result of reaction, but it is not easy to obtain such a high impeller speed in the industrial reactors. In the following experiments, the agitation speed of 300 rpm was used to observe more clearly the differences in the reaction behavior according to the impeller geometry. And a temperature of 170 °C and pressure of 50 bar were used in all the experiments for studying the effects of impellers.

2. Effects of Impeller Types

The effects of impeller characteristics in the hydrogenation were studied by examining the changes in the selectivity to the major

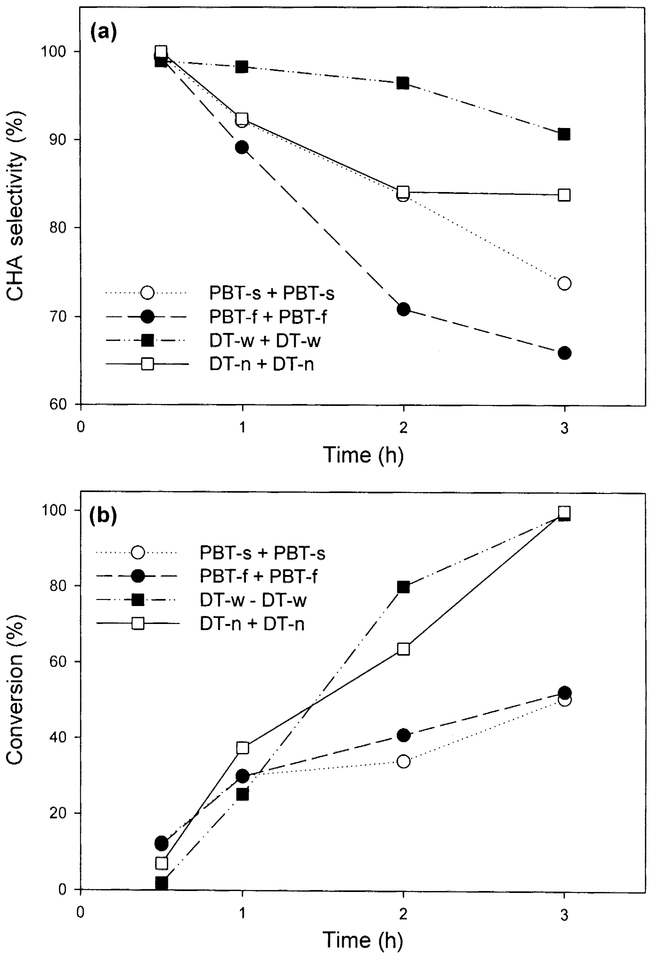


Fig. 6. The effect of impeller type on the CHA selectivity and aniline conversion (upward-flow, 300 rpm).

product (CHA) and the rates of aniline conversion. First, the effects of the impeller type on the reaction were investigated by using dual impellers of the same type and the corresponding results are shown in Fig. 6. Near 100% conversion of aniline was obtained in 3 hours of reaction with impellers of DT type, while impellers of PBT type gave only 50% conversion in 3 hours of reaction. Whereas the DT-w impeller gave CHA selectivity of over 90%, the PBT-f impeller gave selectivities of less than 70%. The superiority of the DT impellers in hydrogenation can be understood in the light of a previous finding [Nagata, 1975] that the disk turbine impeller is effective for gas dispersion in gas-liquid reaction. It is considered that the DT impeller facilitates hydrogen dissolution into the liquid to give a higher reaction rate in aniline hydrogenation.

Regarding the shape of the impeller, the DT-w impeller with wider blades showed a similar reaction rate with the DT-n impeller with narrow blades. When the performance of the PBT impellers was compared, the PBT-f impeller with folded blades also gave similar rate with the straight-bladed PBT-s impeller. These results suggest that the shape of the impeller did not affect the reaction rate significantly at the given reaction conditions, which is in contrast to the case of the impeller type.

The reaction performance of each impeller was compared with the depth of the vortex formed by the impellers to find the relation between hydrogenation and vortex formation. Table 1 shows the changes in the vortex depth with the impeller type. Disk turbines giving higher reaction rates produced deeper vortices than the pitched blade turbines, while no definite relation was found between the selectivity and the vortex depth. The linear relationship between the reaction rate and the vortex depth could be understood considering the previous report [Nagata, 1975] that the hydrogen incorporation from the gas phase was enhanced by the vortex. Disk turbines producing a deeper vortex seem to have provided higher concentration of hydrogen in the reaction mixture leading to a higher rate of aniline hydrogenation.

3. Effects of Impeller Combination

Next, reaction experiments with two different impellers installed on the stirrer shaft were performed and the results are shown in Fig. 7. (These results correspond to the data points with the legend of 'upward flow' in Fig. 7) When PBT-f was installed at the upper position and DT-w was installed at the lower position ([PBT-f+DT-w]), the reaction rate was a little higher than that with the impellers installed the other way around ([DT-w+PBT-f]). However, the selectivity was maintained over 93% in both cases. When these results are compared with the previous ones in Fig. 6, both the [PBT-f+DT-w] and [DT-w+DT-w] impellers gave 100% conversion of aniline in 3 hours. The product selectivity with impellers of [PBT-f+PBT-f] type was also comparable to that of [DT-w+DT-w] impellers. But the performance of [PBT-f+DT-w] impellers was much better than that of [PBT-f+PBT-f]. It was notable that the selectivity to CHA decreased with time when two impellers of the same type were used, while the selectivity was maintained constant when two different impellers were used. These results indicate that [PBT-f+DT-w] impellers give better performance in hydrogenation than other impellers studied, which agrees with the view of Oldshue [1980].

Table 1. Changes in the vortex depth with impeller type

Impeller type			Vortex depth (mm)	Flow direction
Upper position		Lower position		
DT-w	+	DT-w	42	Upward pumping
DT-n	+	DT-n	42	
PBT-f	+	PBT-f	32	
PBT-s	+	PBT-s	28	

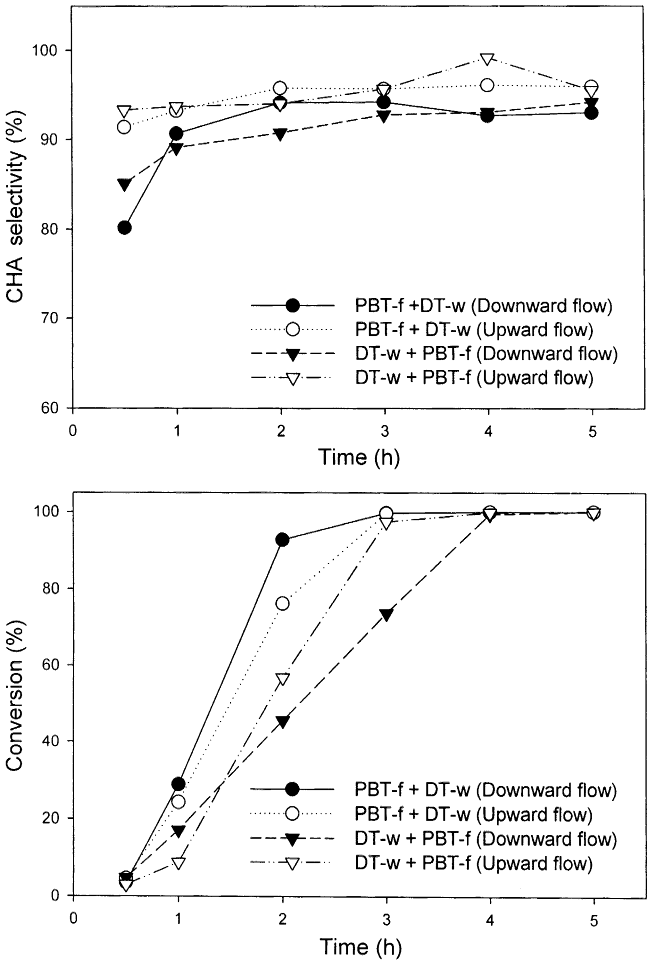


Fig. 7. The effect of impeller combination on the CHA selectivity and aniline conversion.

4. Effects of Direction of Impeller Rotation

Fig. 7 also shows the changes in the CHA selectivity and aniline conversion according to the change in the direction of impeller rotation. The direction of impeller rotation determines the direction of pumping fluid in the reactor. With the change in the flow direction from upward to downward the rate of reaction with [PBT-f+DT-w] impellers increased up to 20%, while the selectivity to CHA decreased by 3-10%. In the case of [DT-w+PBT-f] impellers, the reaction rate decreased up to 25% and the CHA selectivity decreased by 4-7% with the same change in the flow direction. It is noteworthy that the reaction result became different with the change in the direction of impeller rotation even when the impellers were not changed. With a stirrer consisting of axial- and radial-flow impellers like [PBT-f+DT-w], the change in the direction of impeller rotation seemed to affect the flow pattern in the reactor to result in

Table 2. Changes in the product distribution with conversion[a]

Agitation speed (rpm)	Reaction time (h)	Conversion (%)	Selectivity (%)		
			CH	CHA	DCHA
300	1	29.9	5.2	89.1	5.7
	2	41.0	12.1	70.9	17.1
	3	52.4	15.2	66.0	18.9
500	1	50.1	0.2	92.2	7.6
	2	97.5	0.4	94.6	5.1
	3	100	0.3	93.9	5.7

[a]Impeller: PBT-f+PBT-f

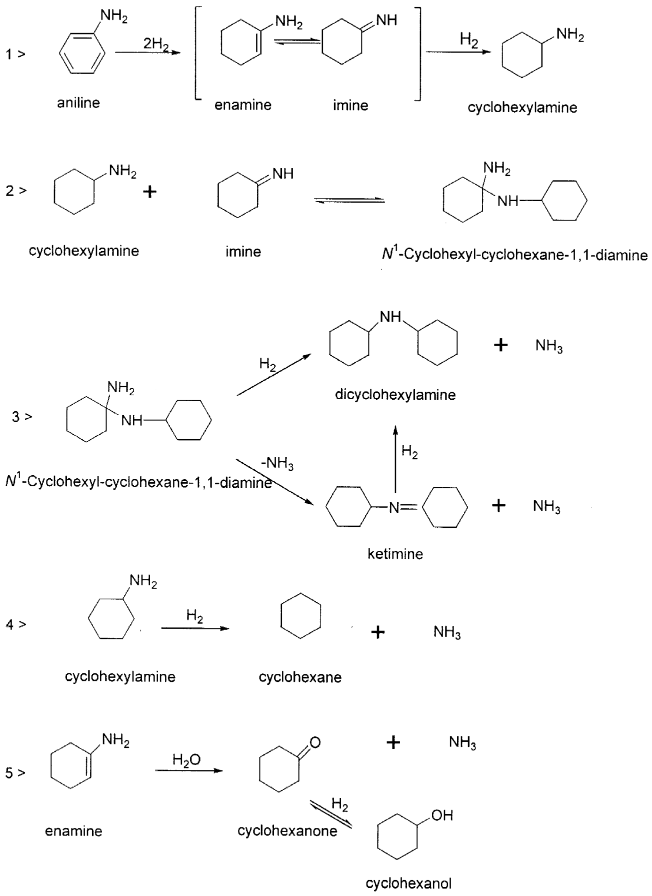
a different distribution of hydrogen concentration in the reactor leading to a different reaction rate.

5. Effects of Impeller Characteristics on Product Distribution

The results on the product distribution were examined in depth to find out how agitation parameters affect the reaction mechanism of aniline hydrogenation (see Table 2). When the agitation speed was 300 rpm in the hydrogenation reaction, the byproducts (DCHA and CH) were produced in large amounts and their yields increased with conversion. On the other hand, when agitation speed was 500 rpm, the yields of DCHA and CH were much lower and remained constant. At the speed of 300 rpm the hydrogen concentration in the solution is considered to have been lower than that at 500 rpm (which is evidenced by the lower rate of aniline conversion in Table 2) and the yields to the byproducts became higher. These observations suggest that the side reactions to the byproducts become significant when the hydrogen concentration in the reaction mixture is low.

Other results on the product distribution obtained at different agitation conditions are also shown in Table 3. Here, the reaction results were compared at a similar conversion of aniline to avoid the effect of the conversion on the selectivity. When [PBT-s+PBT-s] impellers were used in the reaction, large amounts of DCHA and CH were produced at 300 rpm, while the yields of the byproducts were low at both 300 rpm and 500 rpm with [DT-w+PBT-f] impellers. In addition, the impellers of the type [DT-n+DT-n] gave lower yields of byproducts and CH/DCHA ratio than the [PBT-s+PBT-s] impellers. These results clearly show the significant effect of the agitation parameters on the formation of byproducts.

These changes in the product distribution with varied agitation parameters can be understood in the light of the reaction mechanism (Scheme 1) of aniline hydrogenation which have been suggested by several authors [Greenfield, 1964; Nishimura et al., 1966; Sven and Skanberg, 1988]. Aniline with three double bonds is hydrogenated to cyclohexylamine (CHA) rate via either enamine or imine. CHA can be converted to DCHA through a condensation reaction between CHA and imine, which is insensitive to the hydrogen concentration. Cyclohexane (CH) is also obtained through hydrogenolysis of cyclohexylamine, which proceeds at a rate slower than reduction of the double bonds of aniline. When agitation is good and hydrogen concentration in the ligand is high, hydrogenation reaction toward CHA seems to dominate the whole reaction and further conversion of CHA to DCHA and CH is minimized. Conversely, when the hydrogen supply is insufficient due to the slower agitation, the reaction to CHA becomes slower and the conversion of CHA to DCHA or CH becomes apparent, so that the fraction of



Scheme 1. Reaction mechanism of aniline hydrogenation [Greenfield, 1964].

Table 3. Effects of mixing on the product distribution at similar conversion

Agitation parameter		Conversion (%)	Selectivity (%)			Reaction time (h)	Impeller condition
			CH	CHA	DCHA		
Agitation speed (rpm)	300	50.6	16.8	73.8	9.4	3	PBT-s+PBT-s
	500	42.7	0.9	92.1	7.0	1	
	300	56.8	0.4	94.0	5.6	2	DT-w+PBT-f
	500	60.5	0.7	94.2	5.1	1	
Impeller type	DT-n+DT-n	37.5	1.3	92.4	6.3	1	300 rpm
	PBT-s+PBT-s	34.1	14.1	83.7	2.2	2	

the byproducts becomes larger. In addition, the overall selectivity to CHA decreases with time and the consumption of CHA in those side reactions becomes larger. It seems that the relative rates of double bond reduction, condensation and hydrogenolysis change with the mixing condition to result in a different product distribution in aniline hydrogenation. The observations from this work suggest that the mass transfer of hydrogen gas in the reaction mixture seems to control the reaction rate and selectivity, even though there are the many other effects of agitation such as catalyst suspension and blending.

CONCLUSIONS

Various types of impellers were tested by lab-scale reaction experiments in an effort to obtain a design guide for industrial reactors. The reaction employed was aniline hydrogenation over Ru/C catalyst where cyclohexylamine (CHA) was obtained along with dicyclohexylamine (DCHA) and cyclohexane (CH). The following conclusions were obtained.

1. When the same dual impellers were used in agitation, disk turbines (DT), showed a higher selectivity to CHA and reaction rate than pitched blade turbines (PBT). The selectivity to CHA gradually decreased with the use of same dual impellers.

2. When a combination of PBT and DT impellers was employed, high reaction rate and good selectivities were observed as in the case of the dual DT impellers, and CHA selectivity was maintained constant at a high value.

3. Shifting the direction of impeller rotation resulted in a different reactor performance, which seems to be due to the different flow patterns generated by the impeller.

4. Product distribution from aniline hydrogenation varied with the type of impellers and impeller speed. Agitation parameter seems to affect the hydrogen concentration in the reaction mixture, changing the relative rates of double bond reduction, condensation and hydrogenolysis which occur during hydrogenation of aniline.

5. These results show that the lab-scale reaction experiment can be used in obtaining design data which would be helpful in selecting the optimum impeller for the industrial reactors.

REFERENCES

David, S. D. and John, C. F., "Dimensional Analysis for Fluid Agitation Systems," *Chem. Eng.*, 139 (Jan. 5, 1976).

David, S. D. and Richard, W. H., "Fundamentals of Agitation," *Chem. Eng.*, 93 (Feb. 2, 1976).

Eldib, I. A. and Albright, L. F., "Effect of Operating Variables on the Reaction in the Hydrogenation of Cottonseed Oil," *Ind. Eng. Chem.*, **49**, 825 (1957).

Greenfield, H., "Hydrogenation of Aniline to Cyclohexylamine with Platinum Metal Catalyst," *J. Org. Chem.*, **29**, 3082 (1964).

Kaufman, P., "New Hydrogenation Technology: Improvements in Product Yield and Uniformity - Reductions in Reaction Time and Catalyst Costs," Proceedings from AchemAsia, Beijing, China (1998).

Jo, M. C., Song, S. H., Noh, B. I. and Kim, J. H., "Investigation of Feed-pipe Backmixing in an Agitated Vessel," *Korean J. Chem. Eng.*, **13**, 337 (1996).

Lewis, E. G., Terry, L. H. and John, G. F., "How to Select the Optimum Turbine Agitator," *Chem. Eng.*, 110 (Dec. 8, 1975).

Lewis, E. G., Jerry, R. M. and Phillip, L. F., "Selecting Agitator Systems to Suspend Solids in Liquids," *Chem. Eng.*, 114 (May 24, 1976).

Lu, W. M., Wu, H. Z. and Chou, C. Y., "Effect of Impeller Blade Number on K_{La} in Mechanically Agitated Vessels," *Korean J. Chem. Eng.*, **16**, 703 (1999).

Nagata, S., "Mixing, Principles and Application," Kodansha Ltd., 407 (1975).

Nishimura, S., Tetsuo, S. and Tomoyoshi, H., "The Ruthenium Catalyzed Hydrogenation of Aromatic Amines Promoted by Lithium Hydroxide," *Bul. Chem. Soc. Jap.*, **39**, 329 (1966).

Oldshue, J. Y., "Mixing in Hydrogenation Processes," *Chem. Eng. Prog.*, 60 (June, 1980).

Richard, W. H. and Lewis, E. G., "How to Select Turbine Agitators for Dispersing Gas into Liquids," *Chem. Eng.*, 141 (July 19, 1976).

Sven, H. and Skanberg, US patent 4,779,990 (1988).

Van't Riet, K., Boom, J. M. and Smith, J. M., "Power Consumption, Impeller Coalescence and Recirculation in Aerated Vessels," *Trans IChemE*, **54**, 124 (1976)

Zajcew, M., "Reaction Selectivity in the Hydrogenation of Fatty Oils," *J. Am. Oil Chem. Soc.*, **37**, 11 (1960).