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A Comparative Mass Transfer Study in the Reductive N-Alkylation of Aromatic Nitro Compounds

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I. INTRODUCTION

For decades, serious equipment alternatives have been designed and have become commercially available to address the opportunities recognized in three-phased reactions. These opportunities arise from the limitations of the conventional stirred tank in terms of mass and heat transfer requirements, as well as the recognized difficulties associated with the scale-up of such equipment.

Earlier publications [1,2] have already shown that notable rate improvements are achievable with the Buss-Loop system when compared to the customary stirred-tank reactor. The reactions studied for these comparisons were the catalytic reduction of aromatic nitro compounds, the hydrogenation of unsaturated fatty acids, and the carbonylation of several amines and some others. More recent publications [4,5] compare engineering design information. Our brief study is based on a comparison of reaction rate data from plant and laboratory size stirred-tank reactors and from a pilot plant Buss-Loop reactor. These data were obtained on the catalytic N-alkylation reaction of an aromatic amine.

This reaction or reactions differ from above-mentioned chemistry because they encompass several steps that must occur in the proper sequence and require separate operating conditions, which reflect on greatly different heats of reaction. Several means exist to carry out this rather complex sequence, as is shown in the patent literature. The conditions used in the experiments described were essentially those in reference 3. The chemistry involved is shown in Figure 6.1, where 4-nitrodiphenylamine is hydrogenated to form

STEP 1



STEP 2

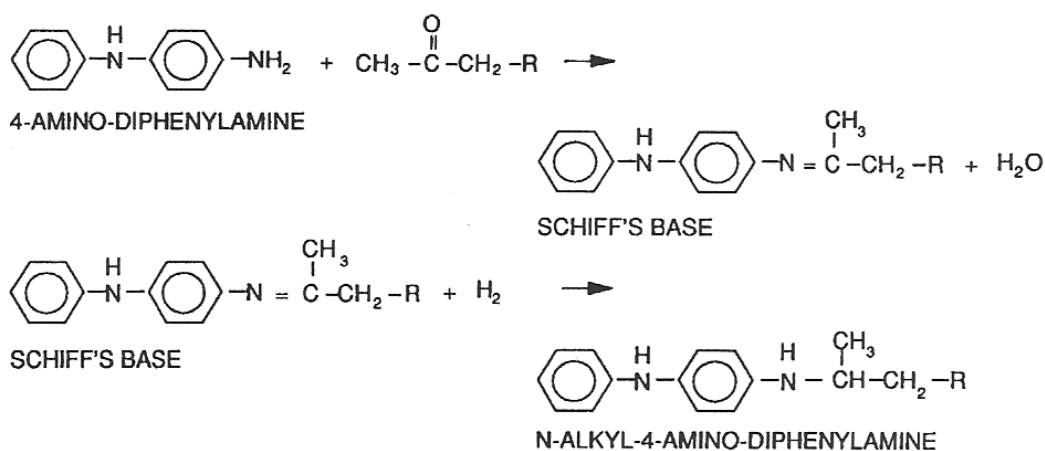


Figure 6.1 Principal chemistry of catalytic reductive alkylation.

4-aminodiphenylamine in the first step. In the second and third steps the Schiff base is generated which, during the hydrogenation, splits off water and converts the intermediate to the mono-*N*-alkyl-4-aminodiphenylamine.

Those familiar with this chemistry recognize that the reaction temperature and the hydrogen pressure for the first step must stay relatively low, not only to avoid hydrogenation of the aromatic ring, but also to permit the control of a very exothermic reaction, the reduction of the aromatic nitro group. The Buss-Loop reactor facilitates—as has already been recognized—an effective means for the very critical removal of heat with the external heat exchanger, but it also assures the best possible intimate contact of the three phases, which is kinetically needed for the constant regeneration of active hydrogen on the catalyst.

During the second step, an acidic catalyst is needed to form the Schiff base and to encourage the equilibrium, which in turn

is brought out of balance during the hydrogenation to the product. Since the second and third steps are far slower and less exothermic when compared with the nitro reduction step, the reaction temperature is raised while observing the limits for the undesirable saturation of the aromatic rings. And, with thorough mixing available, the benefits of a higher hydrogen concentration (higher pressure) are applied.

From a chemist's point of view, one should expect from the use of a Buss-Loop reactor benefits similar to those shown for the other perhaps less complex reactions mentioned; but these assumptions had to be confirmed.

II. EXPERIMENTAL

To reduce the difficulties with other variables (e.g., raw materials), a rather large quantity of commercially manufactured 4-nitrodiphenylamine was isolated and blended. Similarly, a whole catalyst shipment

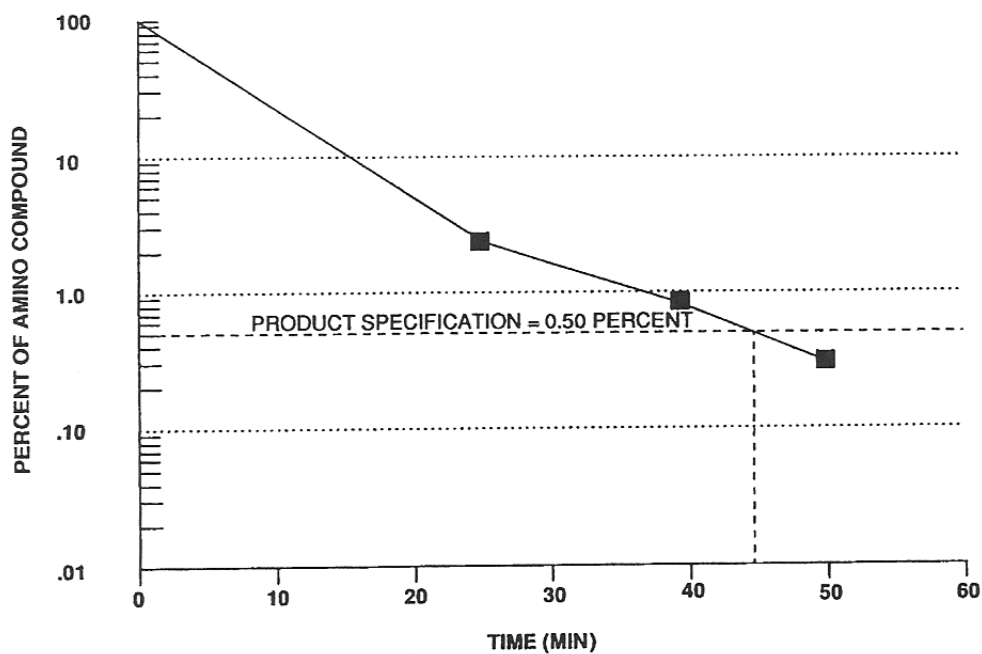


Figure 6.2 Percent of amino compound versus time.

was separated and shipped to the different test sites; the same was done for the ketone used. Last, only compressed electrolytic hydrogen was utilized at all locations.

For the initial step, the hydrogenation of the nitro group, the flow of hydrogen was observed as pressure drop per unit time. To measure the rates of the reaction during the reductive alkylation steps, a standardized analytical procedure was agreed upon, samples were exchanged, and the data confirmed. A semilogarithmic scale was used on several samples taken throughout the reaction, and the analytical results were plotted against the time at which the sample had been taken. This permitted the projection of an end point of the reaction as long as the rate followed a typical first-order reaction plot (see Fig. 6.2).

The initial experiments with a stirred reactor were carried out on plant scale with a charge of catalyst low enough to permit the observation of a measurable decline in rate after several runs. The same conditions and catalyst charge were then used in a 1-liter reactor autoclave. The pilot plant experiments were carried out in a 50-liter Buss-Loop reactor.

III. RESULTS AND DISCUSSION

The reference tests were carried out in a plant autoclave, using a catalyst charge of 0.65 wt %, and gave a total time cycle of 128 ± 12 minutes. The corresponding Buss-Loop reactor cycles at an identical catalyst charge were 64 ± 6 minutes. This is an improvement in rate of about 100%. Needless to say, a faster reaction rate offers an opportunity to better the overall production rate, provided all other operational steps can be adjusted proportionally. An alternative consists in lowering the catalyst charge, provided the minimum charge has not already been reached. Therefore, a series of experiments in this direction was carried out. All results are summarized in Table 6.1.

Figure 6.3 is a simplified drawing of the basic elements of a stirred-tank reactor, including the customary cooling coils and heating jacket, as well as a cutaway drawing of a typical Buss-Loop reactor from earlier publications [5]. As pointed out elsewhere [5], the available heat exchange area in a stirred-tank reactor is limited. The heat exchange unit in the Buss-Loop reactor is external and offers opportunities in simplicity and size.

In the loop reactor, the bulk of the turbulent mixing occurs in the nozzle, which acts as an eductor, making intimate mixing of the three phases possible. This is where the chemical reaction occurs, while the body of the reactor functions as a reservoir for

Table 6.1 Experimental Data on Catalytic Reductive Alkylation

Run number	Industrial plant		50-Liter Buss loop			1-Liter lab-stirred tank		
	Catalyst (wt %)	Run time (min)	Run number	Catalyst (wt %)	Run time (min)	Run number	Catalyst (wt %)	Run time (min)
48	0.53	130	26	0.53	65		0.65	55
49	0.65	110	27	0.65	57		0.65	68
50	0.65	145	28	0.65	70		0.65	59
51	0.65	115					0.65	70
53	0.65	125		Average 64			0.65	90
	Average 128							Average 68
			13	0.4	86			
			23	0.4	100			
			24	0.4	136			
			25	0.4	141			
			Average 116					

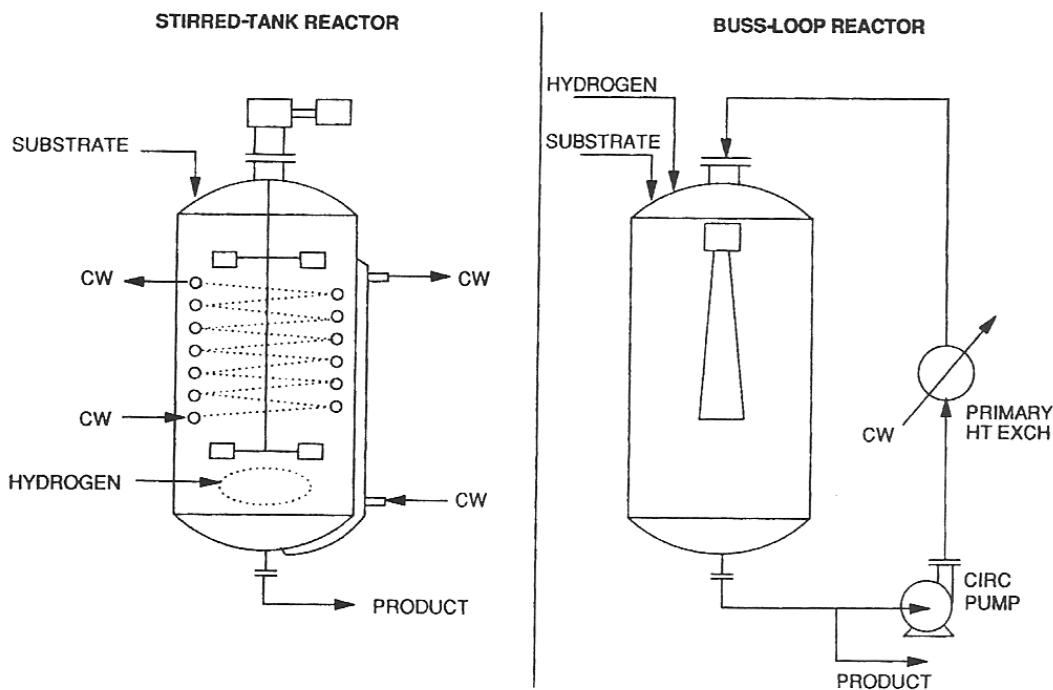


Figure 6.3 Stirred-tank and Buss-loop reactors.

the critical circulating pump. From Figure 6.3 it is understandable that such a unit tolerates a relative wide margin for the charged volume without a change in the efficiency of either the mass transfer or the heat transfer of the system. This observation is supported by a very satisfactory scale-up history of plant designs of Buss-Loop reactors by Herzog and Hart in the United States and Buss AG worldwide.

V. CONCLUSIONS

1. The Buss-Loop reactor showed the expected rate improvement for the catalytic *N*-alkylation reaction.
2. Prediction of large-scale Buss-Loop reactor performance based on laboratory autoclave tests is possible due to optimized mixing in both systems. This has not been possible with stirred-tank reactors.
3. The configuration of the Buss-Loop reactor allows for unlimited heat transfer, and the degree of gas/liquid/catalyst mixing is not sensitive to charge volume.

REFERENCES

1. Leuteritz, G. M., Reimann, P., and Vergeres, P., *Hydrochem. Process*, June 1976.
 2. Malone, R. J., *Chem. Eng. Prog.*, 76:6 (1980).
 3. Summers, C. G., U.S. Patent 3,576,767 (April 1971); H. Merten et al., U.S. Patent 4,900,868 (February 1990).
 4. Von Dierendonck, L. L., and Leuteritz, G. M., in *6th European Conference on Mixing*, May 1988.
 5. Concordia, J. J., *Chem. Eng. Prog.*, 86, 50-54 (1990).
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