Investigation of a Complex Reaction Network: I. Experiments in a High-Pressure Trickle-Bed Reactor

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A high-pressure trickle-bed reactor was used to achieve high productivity and selectivity for the manufacture of a key herbicide intermediate (α-aminomethyl-2-furanmethanol (amino alcohol, AA) from α-nitromethyl-2-furanmethanol (nitro alcohol, NA). Raney Nickel catalysts of varying activity were prescreened for suitability in trickle-bed operation. The effect of operating parameters such as reactant feed concentration, liquid mass velocity, and temperature on the yield of amino alcohol (AA) for RNi-a are discussed. The superiority of trickle-bed reactors over others such as semibatch and batch slurry systems is demonstrated. The AA yield increases with decrease in feed reactant concentration and liquid mass velocity, as well as with lowering of the operating temperature. A maximum product yield of 90.1% was obtained at 8.3 wt. % feed concentration of nitroalcohol (NA), while at the highest feed concentration of 40 wt. % NA, the maximum product yield was 58%. The volumetric productivity of AA was significantly higher at higher reactant feed concentrations, even though the yield was lower under these conditions. The operating temperature was also an important parameter, with a lower temperature being preferable for trickle-bed experiments. Bed dilution with inert fines improved catalyst utilization and increased the AA yield and productivity in the laboratory-scale trickle-bed reactor.

Introduction

The choice of a particular reactor for a new process is governed by the reaction chemistry, conversion and selectivity requirement, and by heat- and mass-transfer considerations. In many applications, due to the complexity of the reaction scheme, the choice of the reactor is not as obvious as it is for simple reaction schemes. This warrants a thorough laboratory-scale investigation of relevant reactions before the final choice and design of the commercial-scale reactor is undertaken. Traditionally, trickle-bed reactors have been used primarily in hydrotreating and hydrodesulfurization applications in the petroleum industry, whereas slurry reactors have been preferred in the chemical industry for continuous or batch hydrogenation, oxidation, halogenation and several biochemical processes. Despite the complexity of many of these reactions, the laboratory-scale studies reported in the open literature on three-phase reactors in general, and on trickle beds

in particular, have been limited to simpler reactions such as hydrogenation of alpha-methylstyrene (Morita and Smith, 1978) or hydrogenation of crontonaldehyde (Sedriks and Kenney, 1973), with few exceptions such as hydrogenation of nitrobenzene (Chaudhari et al., 1993) and nitrotoluene (Hatziantoniou et al., 1986).

Laboratory-scale slurry reaction studies, on the other hand, are done routinely for process development and in many cases have been directly translated to commercial (slurry) reactors without thorough analysis of the optimal reactor configuration for the complex reactions involved in the process. The formation of byproducts and kinetics of side reactions have been often ignored in these studies. The few kinetic studies that have been reported for multiple reactions in trickle beds have relied on lumped rate constants (Satterfield, 1975), making it difficult to study the influence of operating param-

eters on the yield of individual reactions. The issue of byproduct formation and the effect of the type of multiphase reactor (and pertinent operating parameters) on the side reactions has also not been thoroughly investigated. Investigation of reactions in trickle beds beyond the realm of petroleum processing is itself very limited.

This work focuses on studying an industrially relevant reaction network for production of a herbicide intermediate (Aryl amino-alcohol, α-aminomethyl-2-furanmethanol). This intermediate, α-aminomethyl-2-furanmethanol [referred to here as "Aryl aminoalcohol" (AA)], which is a key ingredient in the manufacture of a new herbicide safener [3-dichloroacetyl-5-(2-furanyl)-2,2-dimethyloxazolidine], is produced by catalytic reduction of the corresponding α-nitromethyl-2-furanmethanol [referred to here as "Aryl nitroalcohol" (NA)] using hydrogen on a Raney Ni catalyst. The caveat in this reaction system is that the reactant is unstable under reaction conditions and decomposes while the exothermic reaction is in progress. The product, being basic in nature, catalyzes this decomposition and reacts with the decomposition products to form other undesired byproducts. Some of these products are identifiable and quantifiable while others, particularly the polymeric products, are not amenable to quantitative analysis at present. A high yield (over 90%) of the desired product AA was demonstrated experimentally in a mechanically agitated slurry reactor operated in a semibatch operating mode [with very low liquid reactant feed rate (< 0.5 mL/min)] with low reactant concentration (Gaede et al., 1993; Chou, 1995). However, this (semibatch) process is not suitable to meet the projected demand if operated in a large-scale unit. A reactor with higher volumetric productivity and selectivity is needed.

An important consideration in this process is prevention or minimization of the homogeneous decomposition of the reactant (NA), which is catalyzed by the desired product (AA). Another goal is to suppress multiple side reactions of the decomposition products with the intermediate and product of the main reaction, which results in undesired byproducts. The desired candidate reactor should be able to consume the reactant before it decomposes homogeneously by providing a large catalyst to liquid volume ratio (that is low liquid holdup) and a high pressure of hydrogen needed to promote the desired catalytic hydrogenation and to suppress the decomposition of reactant and other side reactions. All of these objectives can be more readily accomplished in a continuous flow packed-bed (trickle-bed) reactor with gas-liquid cocurrent downflow than in a stirred autoclave.

The advantages of a trickle bed over the suspended catalyst mixed slurry system operated in either continuous mode or semi-batch mode are numerous. A packed bed provides a much higher catalyst to liquid volume ratio, which promotes the desired catalytic reaction. Higher pressure can be achieved in a packed bed more readily than in a mechanically agitated slurry system where problems arise in sealing the rotating shaft of the agitator. A slurry system cannot be operated continuously, as in a continuous flow stirred tank reactor (CSTR), at high reactant conversions, because it would enhance undesired byproduct formation catalyzed homogeneously by the reaction products due to low catalyst to liquid ratio (high liquid holdup). A slurry system operated in a semi-batch mode requires very low product concentration to suppress homogeneous reactions as opposed to that attain-

able in a packed bed where much higher product concentrations should be achievable due to higher catalyst to liquid ratio.

The first part of this study discusses experimental investigation of the effect of operating parameters on yield and productivity in a high-pressure trickled-bed reactor. Attempts at obtaining intrinsic and apparent kinetics are also presented and their inadequacy to give kinetic information is discussed. The use of laboratory trickle-bed data for obtaining apparent kinetic information using a proposed mechanism and a reactor model are discussed in the sequel to this article. A simplified model is fitted to the data to examine whether such an approach could be used in complex reaction systems where intrinsic and apparent kinetic data are not obtainable by conventional means. This approach underscores the importance of laboratory trickle-bed work in such complex systems as a requirement before scale-up and design of commercial-scale reactors can be undertaken.

Reaction Network

The reaction network shown in Figure 1 represents the main reaction, as well as the numerous side reactions that are occurring in this reaction system. AA is produced by catalytic reduction of NA with hydrogen on a Raney-Nickel catalyst. The main reaction is a two step process in which the NA is converted to a hydroxyamine (B) intermediate and then further hydrogenated to AA (Chou, 1995). The NA simultaneously decomposes to furfural (F) and nitromethane (NM). NM can in turn be hydrogenated to aminomethane, which reacts with furfural to give methyl-furylmethylamine. The decomposition product of NA (furfural, F) also reacts with the intermediate and product of the main reaction to give undesired nitrone and reduced nitrone (which, in turn, can slowly convert back to the desired amino-alcohol). The decomposition is catalyzed by basic compounds such as the product and
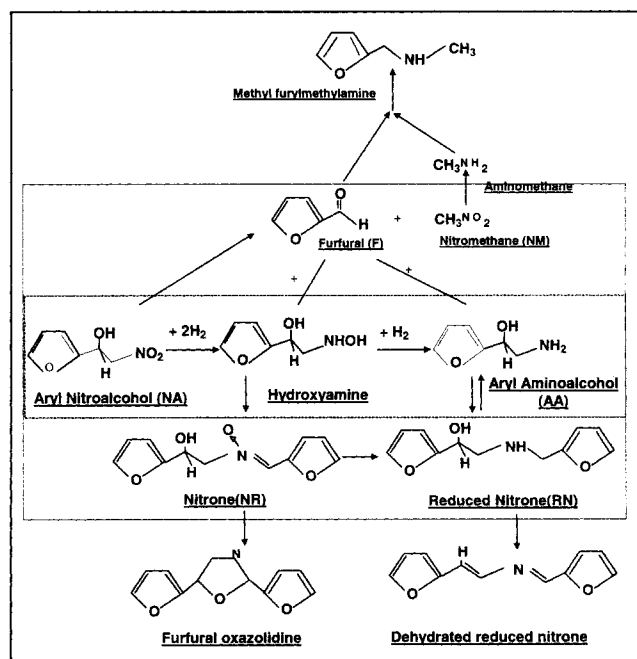

Figure 1. Key features of the reaction network.

is promoted by high temperature. The reduced nitrone can further give dehydration products, while the nitrone forms oxazolidines, both of which can react further to form oligomeric and polymeric components. Of all the species present in the reaction scheme, compounds other than those involved in the main reaction and primary side reactions such as reactant decomposition, and nitrone and reduced nitrone formation, are such that either their amounts are not significant enough or they are not detectable by the present analytical method. Hence, these species are not considered in analysis and discussion of the obtained results. The network of reactions considered here is thus a simplified version chosen to reflect only the main reaction and significant side reactions, involving only those species which can be quantitatively estimated.

Experimental System

As the first step, it was necessary to evaluate the activity of the catalyst (in powder and particle form) and find the suitable size and activity of particles to be used in the trickle-bed reactor. For this purpose, a high-pressure autoclave was set up in such a manner that it could be run as slurry or a basket reactor system in a batch, semi-batch, or continuous mode. This was followed by investigating the reaction in a high-pressure trickle-bed setup using the catalyst of the chosen size and activity. The construction and operational details of the two systems used in this study are described here (the autoclave and the trickle-bed system).

Autoclave system

The high-pressure autoclave reactor used is essentially a 1-L three-phase stirred-tank reactor which can be operated either with a slurry of powdered catalyst in liquid or with catalyst particles enclosed in a wire mesh basket. The reactor contents can be heated or cooled by means of internal coils and an external jacket. This setup can be operated in batch or semi-batch mode with a very wide operating range in terms of temperature (10–600°C) and pressure (0–2,000 psig) (1–138 atm). The liquid feed can be pumped from the batch feed tank to the autoclave by a high-pressure pump. The gas is introduced into the head space from a high-pressure gas cylinder and then bubbled through the hollow shaft of a six bladed disk turbine by impeller induced suction. The agitator rotates at the center of the reactor (at 100–2,000 rpm), while keeping the circular basket fixed around the impeller blades (when the basket reactor configuration is used). The process and instrumentation diagram for the autoclave setup is shown in Figure 2. The batch mode experiments for both the slurry and basket reactor were performed at 450 psig (31.6 atm) and 37°C as recommended in the previous studies (Chou, 1995).

Trickle-bed reactor system

The high-pressure trickle-bed reactor facility (Al-Dahhan, 1993) used in this study consists primarily of a packed-bed reactor, a gas-liquid separator, and a gas and liquid delivery system. The reactor is designed to handle high pressure (up to 69 atm, ~1,000 psig) and temperature (up to 100°C) in both downflow and upflow mode of operation. The reactor is also equipped with a jacket for cooling or heating as re-
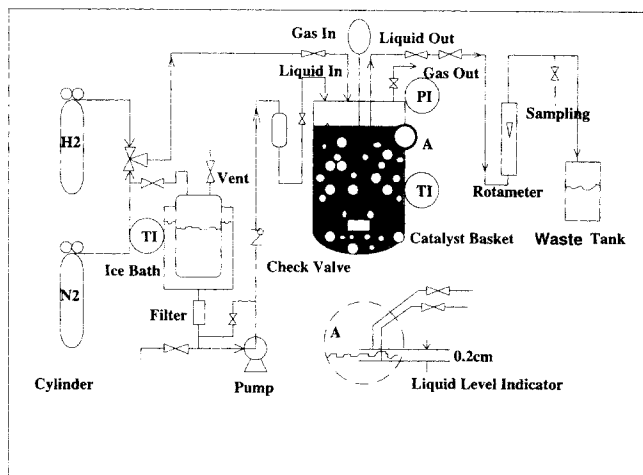

Figure 2. Autoclave reactor and instrumentation diagram.

quired. The facility as well as the reactor and separator are shown in Figures 3a and 3b. The feed liquid is pumped by a precalibrated high-pressure pump (via a damping system) to the distributor at the top of the reactor (Figure 3b). The gas (pure hydrogen, industrial grade) is fed to the reactor after bubbling through saturators (containing the solvent) to minimize evaporation of the solvent in the reactor. The distributor ensures uniform gas and liquid distribution at the inlet to the reactor. The exit gas and liquid streams are split in the gas-liquid separator below the reactor. An automatic liquid level controller ensures constant level in the separator and avoids any pressure fluctuations in the reactor. Liquid samples are collected from the separator and analyzed by GC with programmed temperature control. Raney Nickel catalyst particles are packed into the trickle-bed reactor, which is previously filled with water to avoid accidental exposure of the pyrophoric catalyst to air. The packing structure of the reactor is shown in Figure 3b.

Results and Discussion

Catalyst identification for trickle-bed reactor experiments

Catalyst in the form of powder, crushed particles, and whole particles was tested using slurry and basket reactors. The experiments were performed with the purpose of obtaining intrinsic and apparent kinetics, as well as to determine the suitability of catalysts for trickle-bed operation. All the experiments were performed in either semi-batch or batch mode for both slurry and basket reactors at a pressure of 450 psig (3.1 MPa). The following catalyst sizes and types were tested:
- Powder catalyst (RNi): mean size 38 μm.
- Fine particle catalyst (RNi-a): mean size 0.79 mm (1/32 in).
- Whole particle catalyst (RNi-b): mean size 2.6 mm and surface area 32 m^2/g.
- Crushed catalyst (RNi-b crushed): mean size ~40 μm with maximum size 75 μm.

Even at high catalyst loading (up to 85 grams) and low reactant feed concentration, no significant product was observed for whole particle catalysts in both the batch and semi-batch modes of operation in the autoclave reactor. The
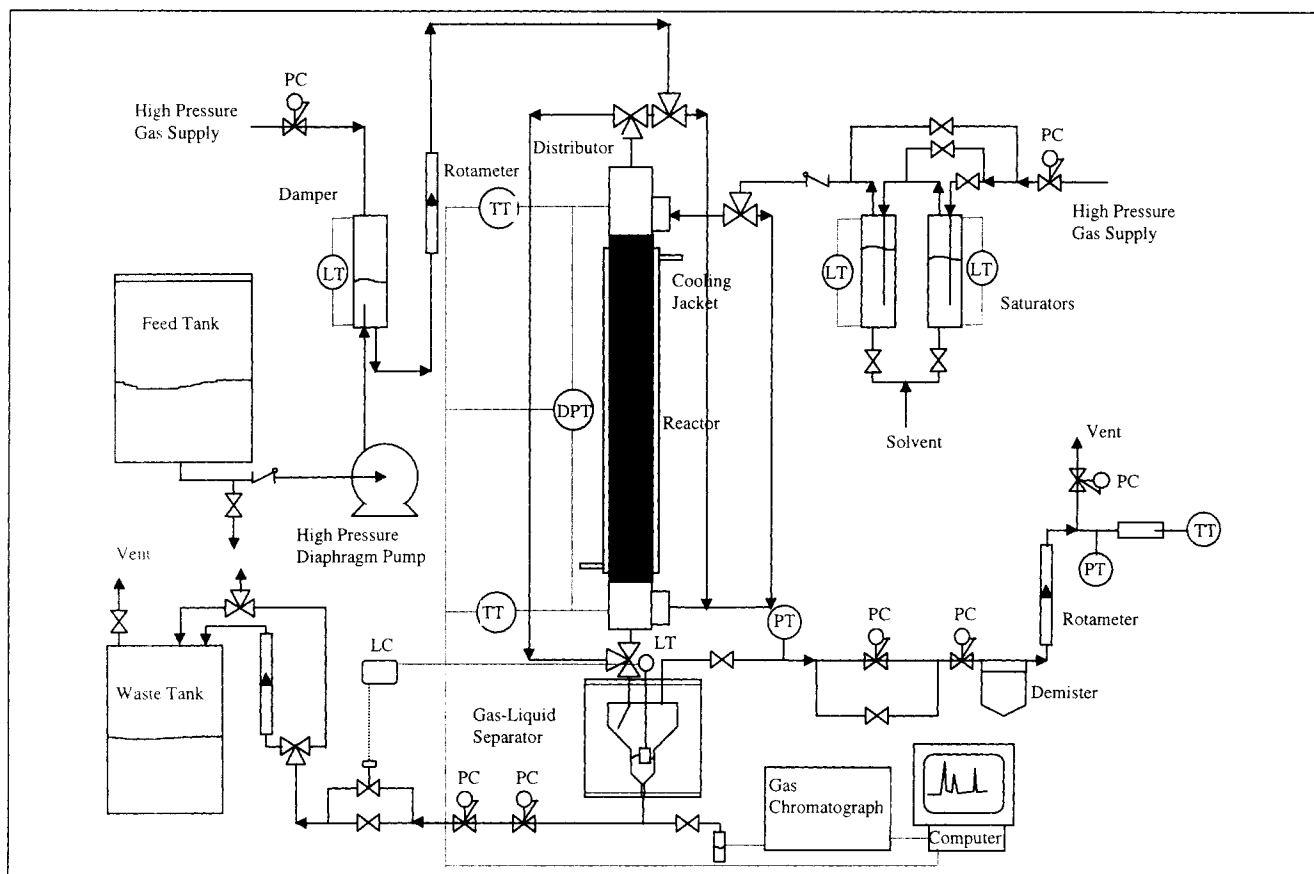
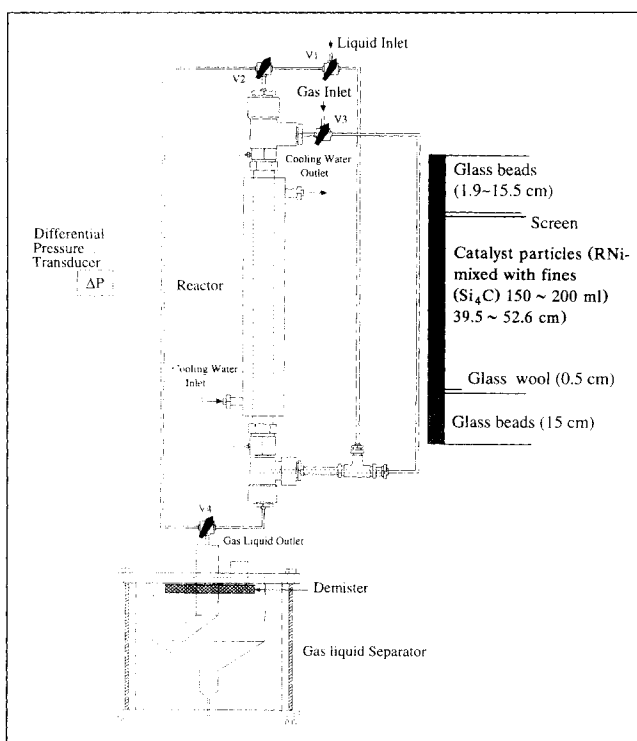**Figure 3a. High-pressure trickle-bed setup.**

Figure 3b. High-pressure trickle-bed reactor and gas-liquid separator setup.

Bed dimensions H = 59.0 cm I.D. = 2.2 cm.

crushed catalyst tests showed some conversion and yield of desired product at low reactant concentrations, but not enough to obtain reliable kinetic information. (Further experimental details are presented in the second part of this article). When the activity of the catalyst is low and the catalyst to liquid volume ratio is low, the reactant (NA) decomposes homogeneously to furfural (F) and NM. The product AA catalyzes this decomposition. When this occurs, byproducts (reduced nitrone (RN) and nitrone (NR)) are produced from the reaction of F with the intermediate B and product AA, respectively. Therefore, catalyst activity and size as well as the catalyst to liquid volume ratio are critical in achieving high conversion and selectivity. Based on the crushed catalyst tests, two sizes of catalysts (RNi-a with a mean size of 0.79 mm and RNi-b with 2.6 mm) were found to be suitable to be used in trickle-bed reactor experiments.

In order to assess the feasibility of using a trickle-bed reactor for manufacturing AA, several experiments were conducted in the high-pressure trickle-bed reactor facility described in the previous section. All the experiments were performed with a prewetted bed to avoid possible hydrodynamic hysteresis effects on the observed performance (Kan and Greenfield, 1978). The two sizes of catalyst (Raney Nickel) used in trickle-bed studies were 2.6 mm (RNi-b) and 0.79 mm (RNi-a). The liquid reactant used was *Technical grade* NA (only ∼ 80% of which is active reactant), which was diluted with methanol to the desired feed concentration. The wt. % reported in the results represents the percentage of the *Technical grade* reactant used in the feed, whereas the molar con-

Table 1. Gas and Liquid Mass Velocities in Trickle-Bed Experiments

Superficial Gas Velocity, U_G(cm/s)	2.98
Superficial Gas Mass Velocity, G(kg/m^{2}s)(lb/ft^{2}h)	0.039 (28.8)
Superficial Liquid Velocity, U_L (cm/s)	0.01–1.37
Superficial Liquid Mass Velocity, L (kg/m$^2\cdot$s) (lb/ft$\cdot^2$ h)	0.08–11 (58.9–8,103)

centrations reported in all figures reflect the actual reactant concentration. Pure hydrogen (industrial grade) was used as the gas phase and the reaction pressure was maintained at 200 psig (14.6 atm). The reactor temperature was controlled by water circulated in the jacket to achieve an exit temperature of $40\pm1°C$ with the feed temperature at $20\pm1°C$. Liquid samples were drawn from the gas-liquid separator after ensuring that steady state was reached at each liquid-flow rate (about 25 – 45 min.). The ranges of operating conditions investigated are presented in Tables 1 and 2.

Several key factors affecting the performance in trickle-bed experiments such as catalyst particle size, reactant feed concentration, liquid mass velocity, operating temperature, and bed dilution with fines were investigated. The observed effects of these parameters are not typical of simple reaction systems and are elaborated upon in the subsequent discussion.

Catalyst comparison in trickle-bed reactor

The catalyst particles studied earlier in the batch experiments (RNi-b, mean size = 2.6 mm) were used in the first set of experiments (Table 2) conducted in the trickle-bed reac-
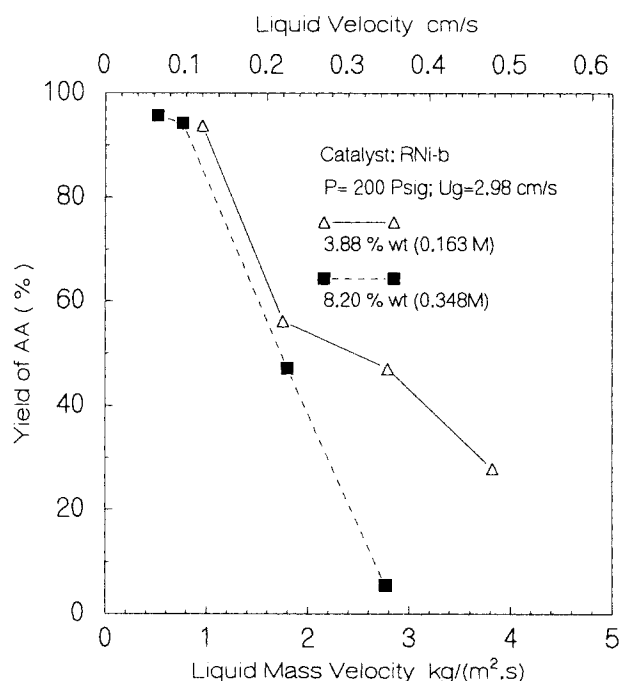

Figure 4. Effect of feed concentration on the yield of the product (AA) with RNi-b catalyst in a trickle-bed reactor.

tor. For this catalyst, it was observed that although a high product yield (above 90%) was obtained at lower liquid mass velocity (high space time), the yield dropped considerably with increased liquid mass velocity (lower space time) (Figure 4). The reactant feed concentrations investigated with this catalyst were chosen to be low (3.9% and 8.2 wt.%) to minimize

Table 2. Operating Conditions for Trickle-Bed Runs

Pres. (psig)*	Temp. Feed/Exit (°C)	Feed Conc. wt. % (mol/L)	Catalyst Type (mm)	Max. Yield (Y) AA (%) (Liq. Flow, WHSV)**
200	Feed 20 ± 1, Exit 40 ± 1	3.88% (0.163)	RNi-b (2.6)	93.7 (1.50)
200	Feed 20 ± 1, Exit 40 ± 1	8.20% (0.349)	RNi-b (2.6)	95.7 (0.79)
200	Feed 20 ± 1, Exit 40 ± 1	8.31% (0.357)	RNi-a (0.79)	90.1 (3.21)
200	Feed 20 ± 1, Exit 40 ± 1	11.0% (0.476)	RNi-a (0.79)	86.2 (1.32)
200	Feed 20 ± 1, Exit 40 ± 1	14.72% (0.651)	RNi-a (0.79)	84.1 (1.31)
200	Feed 20 ± 1, Exit 40 ± 1	20.00% (0.894)	RNi-a (0.79)	74.1 (1.32)
200	Feed 20 ± 1, Exit 40 ± 1	29.95% (1.375)	RNi-a (0.79)	71.1 (0.67)
200	Feed 20 ± 1, Exit 40 ± 1	39.99% (1.896)	RNi-a (0.79)	58.9 (0.66)
200	Feed 20 ± 1, Exit 40 ± 1	29.95% (1.27)	RNi-a (0.79) + fines (0.2)	66.0 (0.91)
200	Feed 20 ± 1, Exit 12 ± 1	21.3% (0.888)	RNi-a (0.79)	93.9 (3.55)

*SI conversion: kPa = psig × 6.89
**Since the catalyst amount differed in each run, the mass velocities are reported per unit mass of catalyst. WHSV refers to m^3/s/kg·cat and not m^3/h/kg cat as commonly used.

byproduct formation. In order to investigate higher feed concentrations up to the desired maximum feed concentration of 40.0 wt. %, a catalyst with smaller particle size (RNi-a, mean size = 0.79 mm) was tested. The activity of this catalyst (RNi-a) was found to be significantly higher (about 4 times) than the previously used catalyst (RNi-b). This means that four times the liquid mass velocity (and, hence, productivity) can be achieved using the RNi-a catalyst than with the RNi-b catalyst without sacrificing the yield (Table 2, rows 2 and 3). This catalyst size (0.79 mm (1/32 in.)) may be considered suitable for the commercial trickle-bed process. Further decrease in catalyst size may increase activity, but at the cost of higher-pressure drop ($\Delta P/Z = 0.1$ atm/m for 0.8 mm particles, while $\Delta P/Z = 0.15$ atm/m for 0.4 mm as calculated using a typical pressure drop correlation (Ellman et al., 1988)).

Effect of feed concentration of NA on yield of AA

In order to get higher reactor volumetric productivity, high reactant feed concentration and high liquid flow rate are typically used in trickle-bed reactors for conventional simple reaction systems. However, in this reaction system, this does not guarantee a high yield due to the numerous side reactions taking place. Experiments with different feed concentrations of NA were designed to get the relation between reactant feed concentration and the yield of AA. For all the cases the yield of AA decreased with increasing feed concentration of NA (wt. % Tech. grade in solvent) from 8.2% (0.349 mol/L) to 40% (1.896 mol/L), as shown in Figure 5. For the low feed concentration cases (below 15.0 wt.%), it was possible to reach more than 80% yield (Figure 5) at the low liquid-flow rates investigated (limited to 2 mL/min by the pump capacity). However, the yield did not reach 90% when the feed concentration was higher than 15.0% (by weight) in this range of operating temperatures ($20 \pm 1°C$ feed and $40 \pm 1°C$ exit).
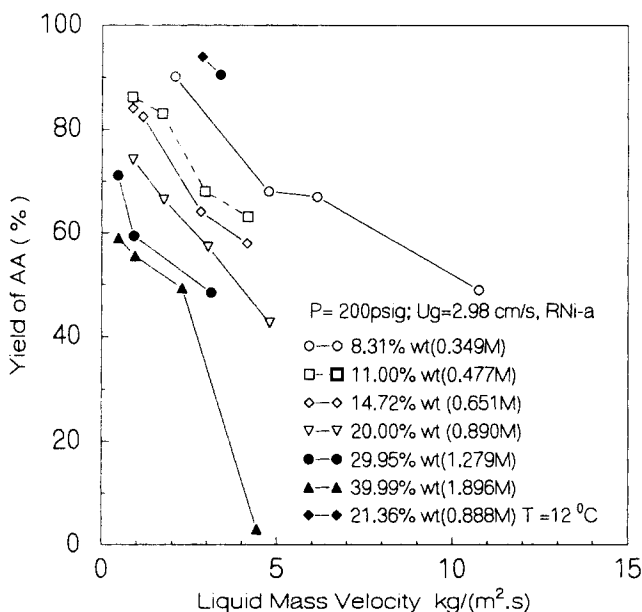

Figure 5. Effect of feed concentration on the yield of the product (AA) with RNi-a catalyst in a trickle-bed reactor.

This strong dependence of the yield on the feed concentration is due to the nature of the side reactions occurring in this system. The higher the reactant (NA) feed concentration, the higher are the concentrations of its homogeneous decomposition products F and NM, and, hence, the higher the side reactions between these and the intermediate and product (AA) of the main reaction. Thus, higher feed concentration does not reflect in higher rates and, hence, higher yields. In fact, it enhances contacting between the product and the reactant, and further decomposition and byproduct formation. It must be noted that the product yield in all trickle-bed runs was still significantly higher than that observed in the batch reactor experiments for which no yield was observed for particles (in the basket) and low yield was observed for the crushed catalyst. In the autoclave system, the complete mixing between the reactant and all the products enhanced the side reactions, thus reducing the yield. The high catalyst to liquid volume ratio in the trickle-bed reactor enhanced the main reaction and was also successful in reducing the reactant decomposition and subsequent side reactions by minimizing the contact between the liquid reactant and product (which catalyzes the reactant decomposition).

Effect of feed flow rate of NA on yield of AA

The liquid hourly space velocity (LHSV, (h^{-1}), defined as liquid-flow rate per hour per unit volume of catalyst) is a very important parameter for scale-up of trickle-bed reactors. The range of liquid-flow rates [2 mL/min (0.085 $kg \cdot m^{-2} \cdot s^{-1}$) to 70 mL/min (3.0 $kg \cdot m^{-2} \cdot s^{-1}$)] examined in trickle-bed experiments was governed by pump capacity. For all the cases studied, the yield of AA decreased with the increase in liquid feed flow rate (decrease in space time) and this effect of liquid mass velocity is shown in Figures 4 and 5 for both catalysts RNi-b and RNi-a. This observation is akin to the conventional single reaction schemes in literature studies mentioned earlier. The higher reactant feed concentration (above 15% by weight) runs would give a better yield at high space time (which were not investigated in this study due to the limited range of flow rates delivered by the pump). This would be at the cost of incomplete catalyst wetting and, hence, under-utilization of the trickle bed (Al-Dahhan and Dudukovic, 1996) and a potential for temperature runaway due to low radial thermal conductivity.

Productivity of the trickle-bed reactor

Reactor volumetric productivity (VP, defined as kmol of product produced per unit time per unit reactor volume) calculated under different reaction conditions is a function of operating conditions (feed flow rate, feed concentration and reaction temperature), as well as that of the catalyst activity. The productivity of RNi-b was found to be significantly lower than the productivity obtained with RNi-a as mentioned earlier (lowest points in Figure 6). For each catalyst, the productivity increases with increased flow rate and feed concentration even though the product yield drops. For example, a higher feed concentration gives higher productivity even when the yield is low (Figure 6, 40.0% feed concentration data). However, this may not be the optimum operating condition if the downstream separation cost of the product is high. It might be better to choose a lower feed concentration (and
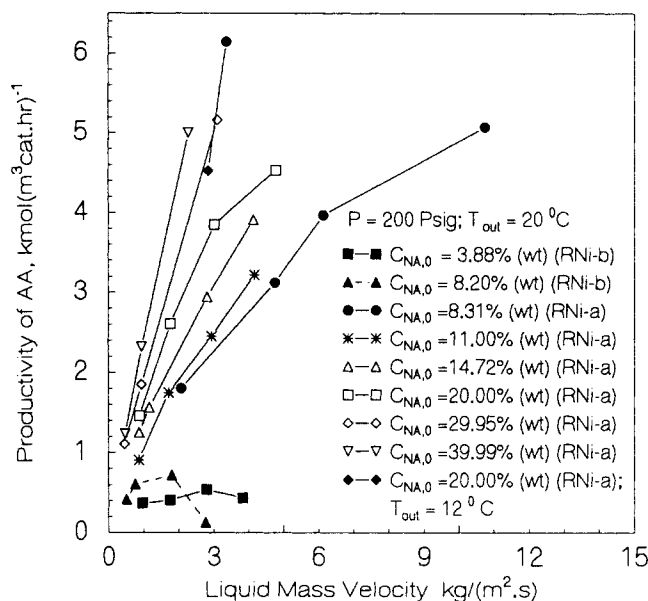
Figure 6. Effect of feed concentration, particle size and temperature on the productivity of AA.

Figure 7. Effect of reaction temperature on the yield of product (AA) in trickle-bed reactor with RNi-a (feed concentration = 21.36 wt %).

higher yield), even if the productivity is lower than that obtained at higher feed concentration (Figures 5 and 6, where yield and productivity show opposite trends with liquid flow rate). The productivity at lower operating temperature was seen to be much higher than that obtained at the same flow rates at the higher temperature (Figure 6) due to the higher yield of AA.

Effect of operating temperature on the yield of AA

Most of the trickle-bed reactor runs were conducted at the temperature of $20 \pm$ °C at the inlet (feed) and 40 ± 1°C at the exit. A temperature range of 30 to 35°C was recommended from previous semi-batch experiments (Chou, 1995). A lower reaction temperature was seen to yield more intermediate formation and polymeric byproduct formation in the semi-batch experiments of Chou (1995). We observed that side reactions, such as decomposition of the reactant, are significant at the recommended temperature when a higher reactant feed concentration is used, and yields over 90.0% are never reached. In order to suppress the homogeneous decomposition of reactant, one test run was conducted at a much lower temperature (20 ± 1°C feed and 12 ± 1°C exit). It was observed that the product yield can easily exceed 90.0% even at 21.36 wt. % (0.886 mol/lit.) feed concentration of NA (Figure 7). This is much higher than the yield ($\sim 60\%$) reached at the same feed concentration at higher reaction temperature (Figure 7). Consequently, the volumetric productivity achieved is also higher than that for any of the runs conducted at high temperature (Figure 6). Thus, it is clear that the effect of operating temperature on the yield of the desired product AA is significant even for the more active catalyst (RNi-a). Lower temperature is therefore preferable to get higher yield and better productivity in a trickle-bed reactor.

Another important consideration in designing and operating an industrial trickle-bed reactor is whether it can be operated adiabatically. For this purpose, the adiabatic tempera-
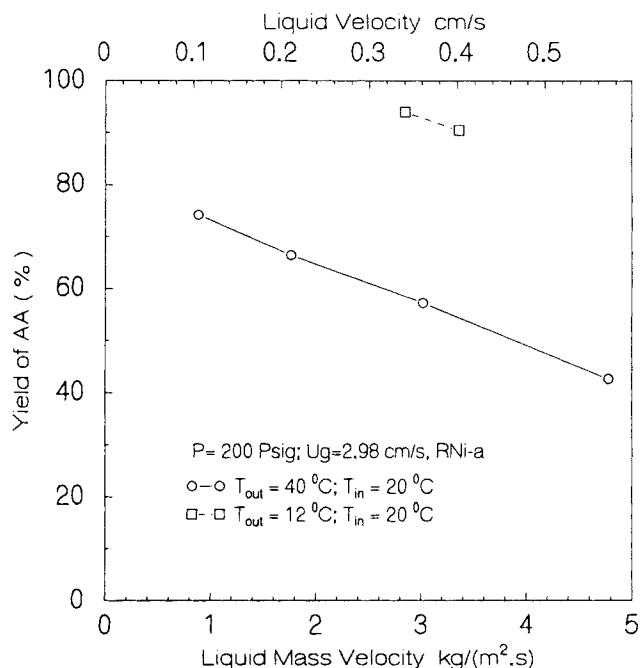
ture rise was calculated for the highest yield and feed concentration examined. The heat of reaction for the main reaction (NA conversion to AA) is -5.272×10^5 J/mol. The maximum adiabatic temperature rise for this reaction neglecting any evaporation is as

$$(\Delta T)_{Ad} = \frac{(-\Delta H)_R C_{A0} Y}{\rho_L C_{Pl} \left(1 + \dfrac{GC_{Pg}}{LC_{Pl}}\right)} = 346°C \qquad (1)$$

This rise in temperature is too high to operate the trickle-bed reactor adiabatically. The use of some means of heat removal is inevitable. This can include a volatile solvent, which by evaporation can pick up the heat of reaction. The solvent can be condensed at the exit and recycled back to the system for heat removal. If this is not possible, multitubular trickle beds with external cooling are needed to accomplish the desired heat removal. The other factor that is important in the reaction scheme is that there are numerous side reactions for which the heats of reaction are unknown (such as nitrone and reduced nitrone formation and formation of their polymeric products). The only other reaction for which the heat of reaction data is available is the homogeneous decomposition of the reactant NA to F and NM. This is an endothermic reaction for which the heat of reaction is $+1.25 \times 10^5$ J/mol. This must be taken into account when the heat removal system is designed for the large-scale reactor. If heat removal is not efficient, large temperature rise due to the heat of the main reaction will enhance the side reaction, that is, decomposition of the reactant. Although this side reaction will absorb some of the heat produced by the main reaction, its progress will reduce the yield of the desired product. Good heat re-

moval is crucial to the large-scale reactor since an adiabatic reactor may result in a very poor yield and a significant rise in temperature. However, the adiabatic reactor may be feasible with a properly chosen solvent, which would pick up the heat of the main reaction by evaporation.

Effect of fines (Silicon Carbide, Si_4C) on the yield of AA

As seen from the experimental results in Figures 4 and 5, a lower liquid-flow rate leads to a higher yield of the desired product AA due to the increased space time. However, lower liquid flow also possibly results in nonuniform liquid distribution, which leads to incomplete catalyst utilization in the trickle bed. Introduction of inert fine particles (that is, Si_4C) mixed with the catalytic packing renders the liquid distribution more uniform by smoothening the porosity distribution, which leads to higher contacting efficiency of liquid and catalyst particles, and improves the yield of the desired product (Al-Dahhan, 1993; Al-Dahhan and Dudukovic, 1996; Wu et al., 1996). Comparison of yield obtained with and without fines in the trickle bed is shown in Figure 8. It is clear from the figure that addition of fines to the bed of catalyst particles improves the yield of the desired product at all liquid mass velocities except at the lowest one. Improved liquid-solid contacting should result in improved yield of AA, which is produced by a catalytic reaction. However, fines significantly increase liquid holdup also, which in turn results in increased residence times. Increased liquid residence time favors homogeneous reactions to byproducts, and this may explain the lack of improvement in the yield at the very lowest liquid mass velocity.

It should be noted that fines are used only to improve the liquid distribution in a laboratory-scale trickle-bed and decouple the hydrodynamics of the laboratory reactor from the

actual kinetics. Once scale-up of the reactor based on equal liquid hourly space velocity (equal space time) is done, liquid velocities in the commercial reactor will be higher than in the laboratory scale and good catalyst irrigation will be achievable without the use of fines (Al-Dahhan and Dudukovic, 1996).

Catalyst deactivation

The Raney Nickel catalyst (RNi-a) has been demonstrated to be a good candidate to be used in a commercial trickle-bed reactor. It is known from previous studies (Chou, 1995) that excessive accumulation of intermediate during reaction results in its polymerization, which eventually leads to catalyst deactivation and yield loss (Chou, 1995). During the present study, no loss of activity was observed and data from initial runs were reproduced after using the catalyst for several hours. By washing the catalyst in solvent after each run for a long time and then storing the catalyst in solvent under high nitrogen pressure [400 psig (2.8 MPa)], a fairly constant catalyst activity was maintained for at least 3 to 4 runs. However, activity was lost when the packing was stored in water or kept under low nitrogen pressure [50 ~ 150 psig (0.3 ~ 1.0 MPa)]. The above is probably due to the use of solvent at high pressure, which keeps the polymeric byproducts from depositing in the pores of the catalyst by dissolving most of them at the pressure under which the catalyst is stored (twice that of reaction pressure). This prevents drying and deposition of the products onto the catalyst surface, while nitrogen prevents any possibility of further hydrogenation of the byproducts.

Conclusions

Raney Nickel catalyst (RNi-a) with the mean size of 0.79 mm (1/32 in.) was found to have the desired activity to promote the reaction for feeds with high reactant concentration, and gives higher yield and productivity than the catalyst with mean size of 2.6 mm (RNi-b). Liquid trickling flow pattern is preferable to get the desired yield of product AA, since it favors high ratio of catalyst to liquid volume (which was confirmed by low yields in basket and slurry reaction tests).

For a given catalyst and operating pressure, the yield of AA is a function of temperature, liquid flow rate (or space time), and feed concentration. The yield always improved by decreasing the feed concentration of NA and by decreasing feed-flow rate (increasing space time), as well as by lowering the reaction temperature. All of these approaches prevent the decomposition of NA and reduce contact between NA and AA. Reactor productivity of AA is a complex function of the feed concentration, feed flow, and temperature. A lower operating temperature is desirable to get a good yield and good productivity. (This is different from that of semi-batch operating mode where optimum temperature is 30 ~ 35°C.) The highly exothermic main reaction and endothermic side reaction complicate the heat effect estimation and necessitate design of an effective heat removal system.

The use of bed dilution with fines demonstrated that the laboratory trickle-bed was underutilized. The data from beds diluted with fines give a better estimate of the utilization and the yield obtainable in a commercial-scale unit. Finding a set of optimum operating parameters for this complex reaction
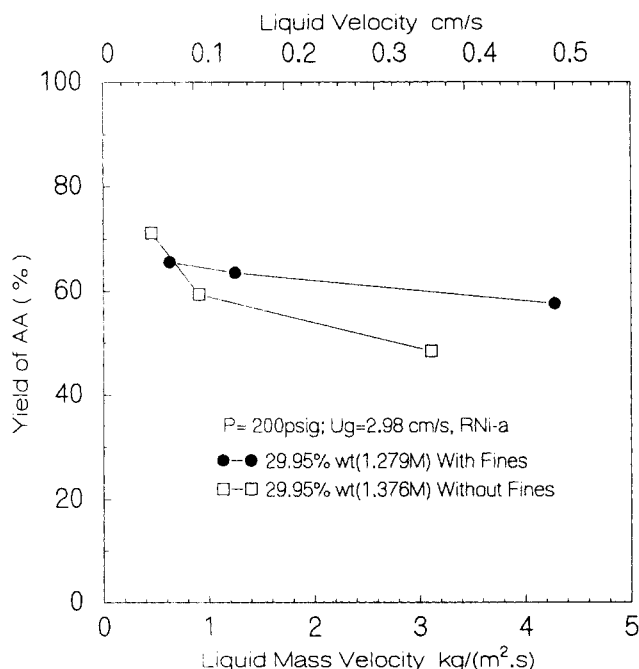
Figure 8. Comparison of reaction yield in trickle-bed with and without fines.

system is a daunting task in comparison to simpler systems. Comprehensive experimentation and simulation are needed in understanding and designing these systems. This study represents a start in the right direction.

Acknowledgment

Notation

AA = amino alcohol (α-aminomethyl-2-furanmethanol)
$C_{A,0}$ = feed concentration, mol/L
C_P = concentration of AA (Product), mol/L
C_{PG} = gas heat capacity.
C_{PL} = liquid heat capacity.
G = superficial gas mass velocity, kg/m^2
ΔH_{vb} = enthalpy of vaporization at T_b, kJ/mol
ΔH_R = heat of reaction, kJ/mol
NA = nitro alcohol (α-nitromethyl-2-furanmethanol)
NM = nitro-methane
NR = nitrone
P = operating pressure, psig (MPa)
ΔP = pressure drop, atm/m
Q = volumetric feed rate (m^3/h), (mL/min)
RN = reduced nitrone
T = temperature, °C
T_{in} = feed temperature, °C
T_{out} = exit temperature, °C
$(\Delta T)_{ad}$ = adiabatic temperature rise, °C
U_G = superficial gas velocity, cm/s
U_L = superficial liquid velocity, cm/s
V_{cat} = packing volume of catalyst, mL
VP = productivity of AA, P [kmol/m^{3}cat) · h] = [Q(m^3/h) × C_{A0}(kmol/m^3) × Y]/V_{cat}(m^3)
     = {[Q(mL/min) × C_{A0}(mol/L) × Y]/V_{cat}(mL)} × 60 kmol · m^{-3} cat · h)
$WHSV$ = weight hourly space velocity, m^3/s/kg · cat
Y = yield of desired product AA, yield = (C_p/$C_{A,0}$)×100
Z = length of catalyst packing, cm
ρ_L = density of liquid flow, kg/m^3

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