

Increasing Productivity in Slurry Hydrogenation Processes

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Introduction

Hydrogenation in a batch three-phase slurry reactor is a classic and well-established technology and is often used in the manufacture of many specialty and fine chemical products. Commercial forces often demand productivity gains to make room for new product or to increase the capacity of existing products. Improving upon the fundamental chemistry such as finding new catalysts or developing new reaction pathways is a common method for increasing productivity. In addition, reactor and reaction engineering can also play an important role in improving productivity by increasing hydrogen mass transfer, removing solvents, intensifying the process into smaller reactors or changing reagent addition strategies.

Establishing the proper balance between competing rate processes is often the key to improving the productivity in a hydrogenation process. Heat transfer, mass transfer and kinetics can each create process limitations and opportunities for improvement. To increase reactor throughput, hydrogenation process equipment should be run at the limit of heat transfer, which is often the major constraint in a hydrogenation process. If possible the process temperature should be increased to increase the heat transfer driving force. Once heat transfer limitations are addressed, then mass transfer and kinetics should be matched to maximize the reactor rates and increase selectivity. The manipulation of reactor design, agitation intensity and reagent addition methods can improve process performance without changing the fundamental starting materials.

In this paper basic concepts in hydrogenation reactor engineering are developed and used to explore practical examples of productivity enhancement for a number of commercial industrial hydrogenation processes. Productivity improvements based on improving mass transfer, eliminating solvents, and converting a batch process to a semi-batch process are described.

1: Reactor Options

Two popular reactor configurations for slurry hydrogenation are illustrated in Figures 1.1 and 1.2. The traditional batch stirred tank design, Figure 1.1, is inexpensive, well known in the industry, easy to service and works well when operated in true batch mode, i.e., all the solvents and feeds are batch charged to the reactor. When delayed or semi-batch feeds are required, which subject the reactor to low liquid volumes, then the stirred tank reactor performance can be compromised. This occurs when the agitation system and heat transfer surfaces are not properly submerged for optimal operation. When large changes in liquid volume are required as in semi-batch processes, then the Buss Loop or Jet Loop reactor, Figure 1.2, can provide an improved alternative that allows for consistent heat and mass transfer under a wide range of liquid volumes.

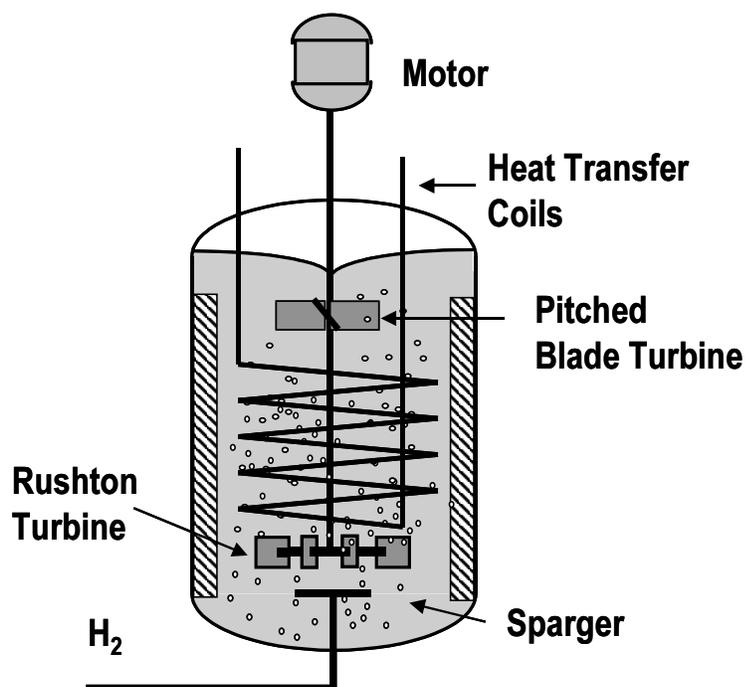


Figure 1.1: Conventional batch hydrogenation reactor system works well when heat transfer surfaces and impellers are properly submerged.

Increasing the heat transfer capacity of a stirred tank reactor often requires increasing the amount of heat transfer surfaces in the reactor such as cooling coils or steam tubes. When too many heat transfer surfaces are added in the reactor then the mixing and mass transfer in the reactor can be compromised. The heat transfer surfaces can restrict the free flow of liquid, which can limit mass transfer, and the proper flow across the heat transfer surfaces. Another option to increase heat transfer is the addition of a pump-around-loop, where an external heat exchanger is added to remove process heat. The contents of the reactor are drawn from the bottom the reactor into a recirculation pump which sends the reactor liquid through the heat exchanger and returns it to the top of the reactor. This configuration allows the heat exchanger and pump to be sized separately from the reactor agitation system and is often the best solution when retrofitting a stirred tank reactor for high heat transfer.

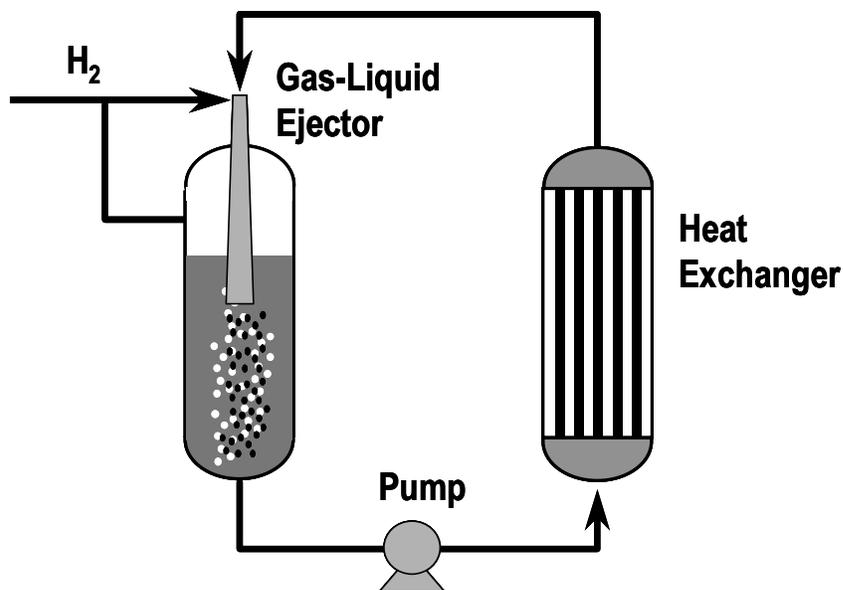


Figure 1.2: Buss Loop or Jet Loop hydrogenation reactor system works well under semi-batch operation where liquid volume change dramatically.

High heat transfer capability is available in commercial Biazzini stirred tank reactors, which use highly efficient curved plate heat exchangers rather than cooling coils [1]. The Biazzini reactor also can provide very high mass transfer by using a gas induction impeller that creates a highly dispersed gas and liquid phase. Like a stirred tank reactor with an external heat exchanger, the commercial Buss Loop or Jet Loop reactor systems can provide high levels of heat exchange while the gas liquid ejector can provide a high level of mass transfer [2].

2: Impact of Reaction Rates and Gas-Liquid Mass Transfer

The balance between reaction kinetics and gas-liquid mass transfer is often the key to insuring that a process has consistent performance. The following treatment of kinetics and mass transfer is simplified to illustrate the key principles required for effective reactor design and scale-up. Gas-liquid mass transfer depends strongly on thermodynamics, reactor and agitation design and can be represented by Equation 2.1. The mass transfer coefficient, ka , is a strong function of reactor design, agitation intensity and the physical properties of the reaction solution, Equation 3.1. The saturation concentration of hydrogen is a thermodynamic property of the solution. Hydrogen saturation concentration increases with increasing pressure and in organic solvent systems, increases with increasing temperature while in aqueous systems, generally decreases with increasing temperature.

Kinetic rate expressions can be very complex but batch hydrogenation processes can sometimes be approximated using Equation 2.2. This simplified rate expression contains the features that are of interest in a batch processes, the amount of catalyst, the hydrogen bulk concentration and the catalyst activity or rate constant.

$$Rate\left(\frac{gmole}{m^3s}\right) = kla\left(\frac{1}{s}\right) \cdot (C_{H_2,sat} - C_{H_2,bulk}) \quad \text{Eqn 2.1}$$

$$Rate\left(\frac{gmole}{m^3s}\right) = k_1\left(\frac{1}{wt\%s}\right) \cdot wt\% \cdot C_{H_2,bulk} \quad \text{Eqn 2.2}$$

where,

$kla\left(\frac{1}{s}\right)$ = Mass Transfer Coefficient

$C_{H_2,sat}$ = Hydrogen Saturation Concentration

$C_{H_2,bulk}$ = Hydrogen Bulk Concentration

$k_1\left(\frac{1}{wt\%s}\right)$ = Kinetic Rate Constant, Catalyst Activity

$wt\%$ = Weight% of Catalyst

The magnitude of the bulk hydrogen concentration dictates whether the reactor is operating under mass transfer or kinetic control and can be determined by equating Equation 2.1 and 2.2 and then solving for the bulk hydrogen concentration according to Equation 2.3.

$$C_{H_2,bulk} = \frac{kla \cdot C_{H_2,sat}}{k_1 \cdot wt\% + kla} \quad \text{Eqn 2.3}$$

Kinetic Control :

If $kla \gg k_1 \cdot wt\%$, then $C_{H_2,bulk} = C_{H_2,sat}$.

Mass Transfer Control :

If $k_1 \cdot wt\% \gg kla$, then $C_{H_2,bulk} = 0$.

Two important limiting cases are illustrated with Equation 2.3. When the mass transfer coefficient is very high relative to the numerical product of the kinetic rate constant and the amount of catalyst, then the reactor is under kinetic control and the bulk hydrogen concentration is equal to the hydrogen saturation concentration. On the other hand when the numerical product of the kinetic rate constant and the amount of catalyst is higher than the mass transfer coefficient, then the bulk hydrogen concentration approaches zero and the reactor is operating under mass transfer control. It should be noted that it is the numerical product of the catalyst rate constant and the amount of catalyst compared to the mass transfer coefficient that determines the bulk hydrogen concentration and the controlling mode of operation. For example, in laboratory studies, which attempt to generate exclusively kinetic rate information, the catalyst amount can always be adjusted in the experiment relative to the mass transfer to insure that the reactor is operating under kinetic control. Mass transfer coefficients can be easily measured for laboratory reactors using the batch absorption method [3].

Equation 2.3 can be combined with Equation 2.2 to obtain a rate expression for the hydrogenation process that does not explicitly use the bulk hydrogen concentration. This is shown in Equation 2.4.

$$Rate\left(\frac{gmole}{m^3s}\right) = k_1\left(\frac{1}{wt\%s}\right) \cdot wt\% \cdot \frac{kla \cdot C_{H_2,sat}}{k_1 \cdot wt\% + kla} \quad \text{Eqn 2.4}$$

Kinetic Control :

If $kla \gg k_1 \cdot wt\%$, then $Rate = k_1 \cdot wt\% \cdot C_{H_2,sat}$.

Mass Transfer Control :

If $k_1 \cdot wt\% \gg kla$, then $Rate = kla \cdot C_{H_2,sat}$.

Once again two limiting cases are illustrated. The kinetically controlled process has sufficient mass transfer to maintain the reactor near the bulk hydrogen saturation concentration with the rate proportional to the catalyst amount and activity. The mass transfer controlled process is independent of the amount or activity of the catalyst. In real industrial hydrogenation processes the overall process rate may be dominated by either mass transfer or kinetics but rarely to an extent where the bulk hydrogen concentration is zero. Typically reactors operate under a mixed control regime, which makes matching commercial reactor performance precisely with lab experiments difficult.

An industrial reactor's net productivity is determined by multiplying Equation 2.4 by the reactor volume and then simplifying the rate expression to obtain Equation 2.5.

$$RATE\left(\frac{gmole}{s}\right) = \frac{100\% \cdot \frac{k_1(V_{wt\%s}) \cdot m_{cat}(kg)}{\rho\left(\frac{kg}{m^3}\right)} \cdot [kla(V_s) \cdot V(m^3)]}{100\% \cdot \frac{k_1(V_{wt\%s}) \cdot m_{cat}(kg)}{\rho\left(\frac{kg}{m^3}\right)} + [kla(V_s) \cdot V(m^3)]} \cdot C_{H_2,sat} \quad \text{Eqn 2.5}$$

$V(m^3)$ = Reactor Liquid Volume

$m_{cat}(kg)$ = Total Mass of Catalyst

$\rho\left(\frac{kg}{m^3}\right)$ = Density of Liquid Phase

Equation 2.5 illustrates some very important principles in hydrogenation reactor engineering. First, the reactor productivity does not typically depend on the reactor volume, rather it depends on the total amount of catalyst that the reactor can handle. This is illustrated in Table 2.1, which shows the results of reactor productivity of specialty nitroaromatic compound. If the agitation and filtration system can handle a 2% catalyst charge then the reactor can be half of the size compared to a reactor that can only handle a 1% catalyst charge to achieve the same reactor productivity. Secondly, when a reactor volume is decreased to intensify the process, then the mass transfer rate must be increased accordingly so that the numerical product of the mass transfer coefficient and the reactor are constant. This is illustrated in the example in Table 2.1.

Table 2.1: Comparison of process requirements for different size reactors for the hydrogenation of a specialty nitroaromatic compound.		
	Current Process	Intensified Process
Liquid Reactor Volume	10 m ³	5 m ³
Substrate	6,000 kg	3,000 kg
Weight % Catalyst	1.0%	2.0%
Mass of Catalyst	100 kg	100 kg
Batch Time	120 min	60 min
Productivity	50 kg/min	50 kg/min
<i>kla</i>	0.05 s ⁻¹	0.10 s ⁻¹

In summary to maintain similar reactor productivity, as a reactor gets smaller, the mass transfer must be increased and the catalyst charge must be maintained. In addition, the heat transfer surfaces to achieve the reactor productivity must be compressed into the smaller reactor. For highly engineered specialty reactors such as the Buss Loop and the Biazzzi reactor this is achieved. These findings are general and the impact of catalyst charges on filtration must be included in analysis of process productivity.

Whether to add more catalyst or increase mass transfer to increase productivity depends on the magnitude of both the kinetics and mass transfer. The productivity profiles for the hydrogenation of a specialty nitroaromatic compound are summarized in Figure 2.1. If the catalyst charge is low then the reactor is dominated by kinetic control and increasing the mass transfer is not an effective way to increase reactor productivity. Likewise, if the mass transfer rate is low then the reactor is dominated by mass transfer control and increasing the catalyst charge is not cost effective. Understanding where the reaction is operating dictates the best strategy to increase reactor productivity. The same productivity can be achieved using low mass transfer and high catalyst charges or low catalyst charges and high mass transfer. Economics ultimately dictate which option is best.

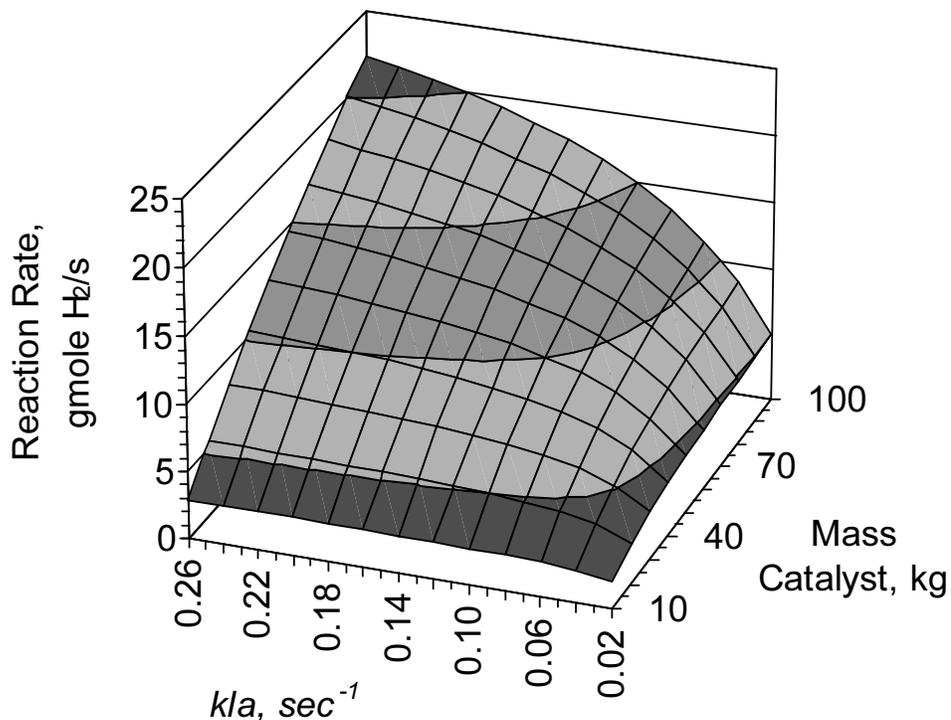


Figure 2.1: Impact of mass-transfer and catalyst charge on the average reaction rate of the hydrogenation of a specialty nitroaromatic compound in a 10 m³ liquid volume reactor, at 100°C and 15 barg, with an external heat exchanger.

3: Increasing Mass Transfer

The enhancement of mass transfer can be accomplished by manipulating a number of process and equipment factors including; the impeller design, the overall power/volume input to the reactor, the superficial gas velocity and the efficiency of reincorporating the headspace gas. For most hydrogenation processes using a stirred tank reactor, the overall mass transfer of hydrogen can be represented by Equation 3.1.

$$kla = \beta \cdot \left\{ \frac{P}{V} \right\}^a \cdot \{v_{gas}\}^b \quad \text{Eqn 3.1}$$

where,

β = Process coefficient which is primarily a function of the physical properties of the reactor fluid.

P/V = Power per unit of liquid volume input by the agitation system.

v_{gas} = superficial gas velocity = cross sectional area of the reactor divided by the actual hydrogen gas flow rate.

a, b = coefficients determined for the appropriate scale of the process. These values often lay between 0.3 and 0.7 depending upon the reactor configuration and size.

Based on Equation 3.1 and assuming that the physical properties of the process fluids are fixed, two conceptual approaches can be used to increase the mass transfer; increasing the power per unit volume in the reactor and increasing the gas superficial velocity. The power input to a reactor can be increased by using impellers that do not loose power under gassing conditions such as Smith-type turbines (concave blades) rather than Rushton turbines (flat blades) and increasing the impeller diameter and/or agitation rate. In addition, increasing the reactor length to diameter ratio, L/D, venting the reactor, using gas-inducing agitators, which reincorporate the headspace gases, can increase the superficial gas velocity.

A hydrogenation process is considered to be "dead-ended" when the process is run without continuous venting. Under constant pressure this can result in a situation where the pressure in the headspace of the reactor reaches the control set point but the flow, which depends directly on the reaction rate, is insufficient to saturate the liquid phase forcing the reaction rate to decline. This situation can be remedied by either venting the reactor which causes a sudden surge in the gas flow restoring mass transfer or by incorporating an impeller system that continuously remixes or reincorporates the headspace hydrogen back into the liquid phase. This effectively increases the overall gas superficial velocity even when the reaction rate is slow and increases the overall mass transfer rate. The presence of inert non-condensable gass such a carbon dioxide or nitrogen from the process chemistry or impure hydrogen can amplify this problem further.

A manufacturer of specialty chemicals was interested in expanding their operation and increasing productivity by a minimum factor of three. Currently they were hydrogenating a specialty aldehyde to its corresponding alcohol in a 3m³ conventional stirred tank hydrogenation reactor. Their plans were to install a new 9m³ hydrogenation reactor. Analysis of the process rates suggested that the process was operating below the hydrogen saturation concentration and that mass transfer improvement would help increase reaction rates. A series of small changes were made to the new reactor design to increase the mass transfer. These modifications are summarized in Table 3.1.

Table 3.1: Comparison of the impact of reactor and agitation design on Old and New Processes to manufacture a specialty alcohol.		
	Old Process	New Process
kg Catalyst/kg Feed	Same in both processes	
Reactor L/D of Liquid Phase	1.55	1.70
Reactor Diameter, m	1.42	1.98
Reactor Volume, m ³	3.0	9.0
Rotation Rate, rpm	155	84
Impellers	2	3
Liquid Surface Gas Induction	No	Yes
Average Superficial Gas Velocity, cm/s	0.4	0.6
Total Power Input by Impellers, P/V, kW/m ³	0.58	0.92
Estimated Mass Transfer Coefficient, <i>k_la</i> , sec ⁻¹	0.09	0.12
Estimated Gas Hold-up, volume%	5.6	7.4
Batch Time, hours	9.0	6.0
Relative Productivity of New Process (kg/day new process)/ (kg/day old process)	1.0	4.5

For pressure vessels, tall narrow reactors, i.e. high L/D ratios are less costly than reactor with the same volume but with lower L/D ratios. This is due to the decreased wall thickness that is required for narrower vessels. Using a reactor with a high L/D has the additional benefit of increasing the overall superficial velocity in the reactor but makes the problem of incorporating the head space gas much more difficult. To reduce the overall investment, a tall narrow reactor was chosen and to improve the headspace gas remixing, a modified impeller system was designed capable of efficient gas remixing.

The overall agitation power was increased by using a larger diameter impeller with a lower rotation rate. When the increase in power and the increase in superficial gas velocity were combined, the predicted mass transfer was increased by 33%. The improved mass transfer combined with the improved headspace remixing allowed the plant performance to exceed production requirements by 50%. In addition the process selectivity was also improved.

4: Reducing Solvent Load

One potential way to increase reactor productivity is to reduce or eliminate the solvents in a process. This literally expands the volume of the reactor available to make a product. Reducing solvent compositions will also have the advantage of reducing the demand on post reaction separations steps such as distillation and extraction. When necessary the reaction product of a hydrogenation can often be used as the solvent for the process. The chemistry may not allow the elimination of solvents but when possible the stepwise reduction of solvent concentration becomes a viable approach to enhancing process productivity. The impact of solvent on substrate and product solubility is obvious and can be characterized in simple laboratory tests. Less obvious is the impact of removing solvents on mass transfer, hydrogen solubility and mixing.

A producer of a specialty chemical required the hydrogenation or saturation of the aromatic ring in a compound containing an aromatic ring. In the original process the starting substrate was dissolved in a solvent making to make 55% (weight %) solution. The substrate and saturated product were liquids at process temperature so that the reduction of solvent seemed to be a viable option for productivity enhancement. The current process used a conventional reactor system as illustrated in Figure 1.1 and operated with a nominal mass transfer coefficient of 0.05 sec^{-1} . They wanted to understand the impact of removing solvent on overall reactor productivity.

The impact on solution physical properties was estimated using conventional thermodynamic models as the solvent/substrate compositions were changed. These results are summarized Figure 4.1 where the variables are normalized against their values at 55%. As the solvent concentration is reduced the viscosity and surface tension increased while the diffusivity of hydrogen decreased. Combined these changes in physical properties dramatically reduced the relative mass transfer rates represented by the variable β in Figure 4.1. Note that the variable β is the same variable shown previously in Equation 3.1. This suggests that even when the superficial gas velocities are similar and the power/volume is the same, the change in physical properties will have a dramatic and negative effect on the ability of this reactor design to deliver high mass transfer.

In Figure 4.2 the impact of the solvent/substrate composition on hydrogen solubility is shown. In this figure the hydrogen solubility at constant pressure was measured as the composition of the solvent/substrate was changed. Also illustrated in Figure 4.2 is the estimated bulk hydrogen concentration in the current reactor, indicated as the "low mass transfer reactor" and a newer proposed design indicated as the "high mass transfer reactor". These estimates of bulk hydrogen concentrations were obtained by combining a detailed kinetic model of the reaction, developed from laboratory experiments under kinetic control, with the mass transfer model in Equation 3.1 to create models similar to Equation 2.3.

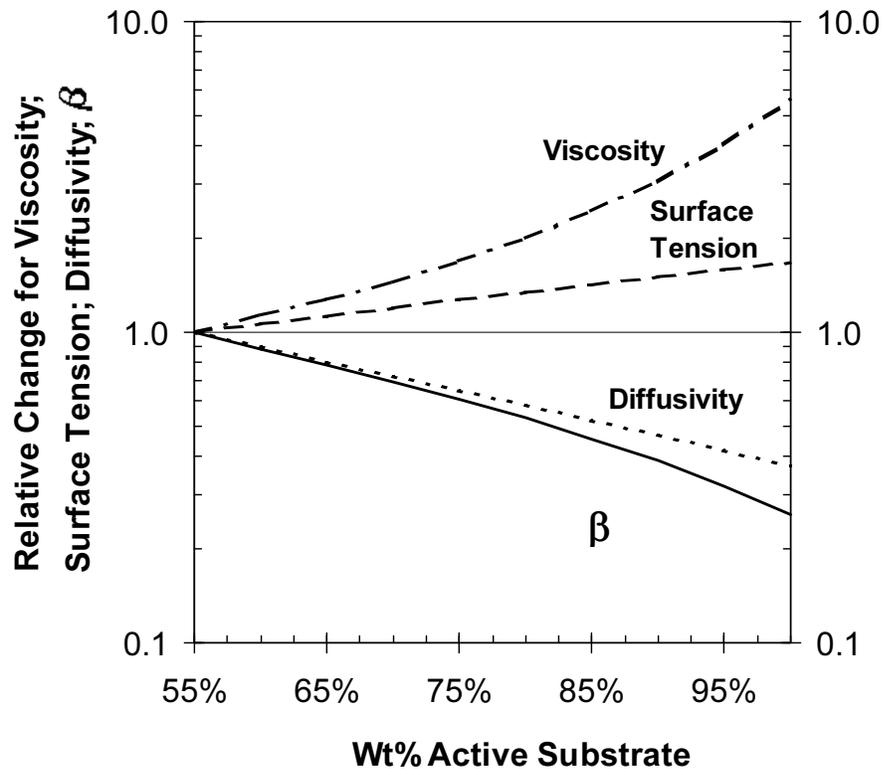


Figure 4.1: Impact of the solvent composition on solution physical properties and relative mass transfer rates. Variables values are compared to their values at 55%.

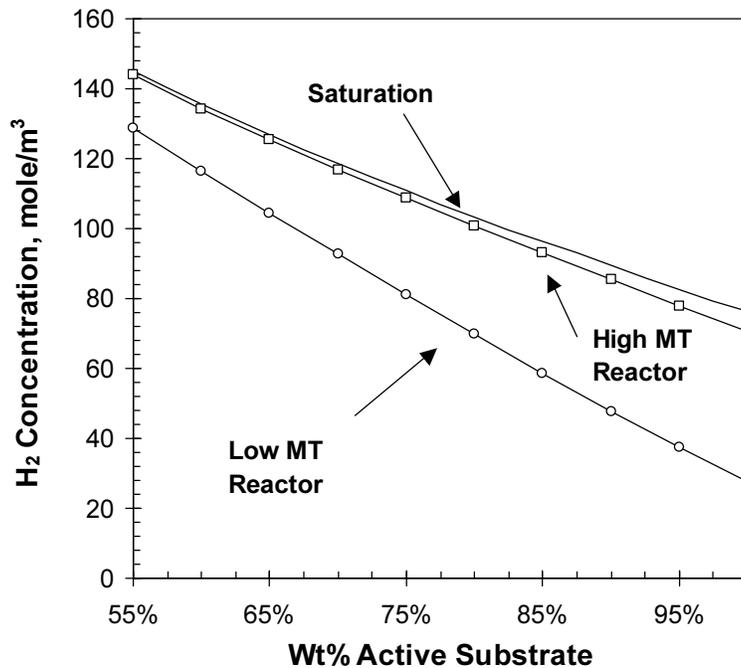


Figure 4.2: Impact of solvent composition on bulk hydrogen concentrations during hydrogenation in a high and low mass transfer reactor.

Figure 4.2 illustrates that the deviation of the bulk hydrogen concentration from the hydrogen saturation concentration is small for both the high and low mass transfer reactors at 55% substrate composition. However as solvent is removed from the process, the deviation of the hydrogen bulk concentration from the saturation concentration is much more dramatic with potentially more limiting processing consequences.

Kinetic and mass transfer models were combined to develop a picture of the overall process mass transfer rates, batch times and reactor productivity that would be possible for the existing low mass transfer reactor and the proposed high mass transfer reactor. These results are illustrated in Figures 4.3 and 4.4. In Figure 4.3 batch times for the low mass transfer reactor are shown to increase dramatically as the substrate/solvent composition is changed. This increase in batch time is caused by the reduced hydrogen solubility combined with the reduced effective mass transfer. This is then reflected by the decreasing productivity illustrated in Figure 4.4 for the low mass transfer reactor. Even though the reactor has increasingly more substrate, the reduced ability to transfer hydrogen has a net negative impact on productivity. On the other hand the high mass transfer reactor can provide the desired productivity benefit. The high mass transfer reactor also loses mass transfer effectiveness and hydrogen transfer efficiency as the solvent is reduced. However the relatively greater mass transfer compared to the original reactor allows increased reactor productivity as the substrate concentration is increased. These results were confirmed in lab experiments. Note however that at 55% substrate concentration there is little improvement in reactor productivity and the investment in a high mass transfer reactor or engineering modifications to make a high mass transfer reactor may not be justified.

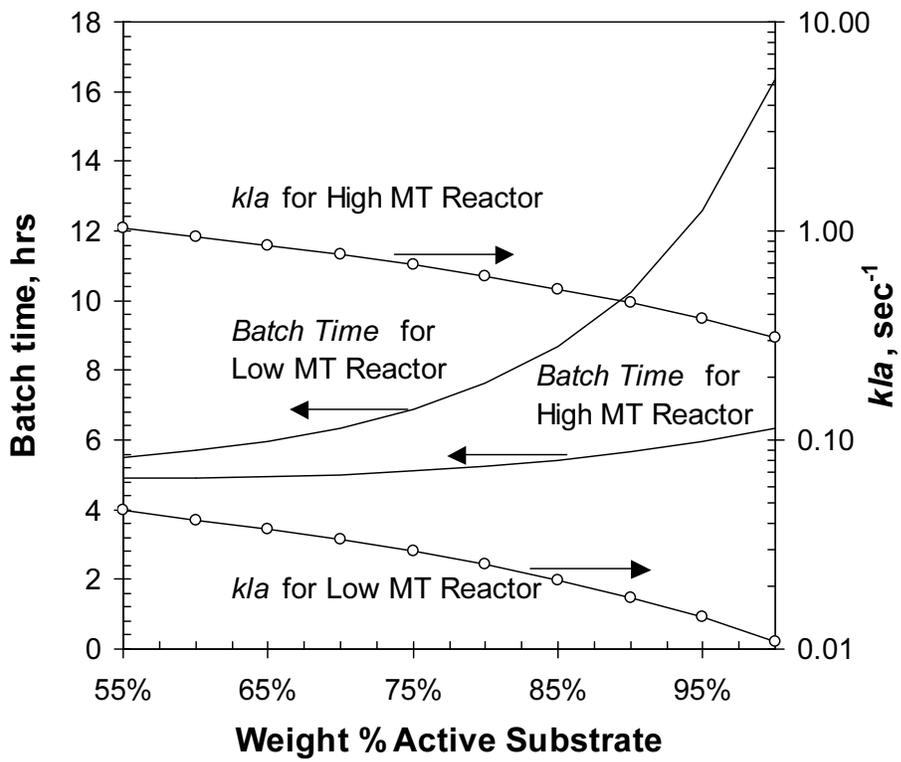


Figure 4.3: Impact of solvent/substrate composition on reactor batch time and mass transfer for a low and high mass transfer commercial reactor system. Temperature, catalyst composition and pressure are the same for both the high and low mass transfer reactors.

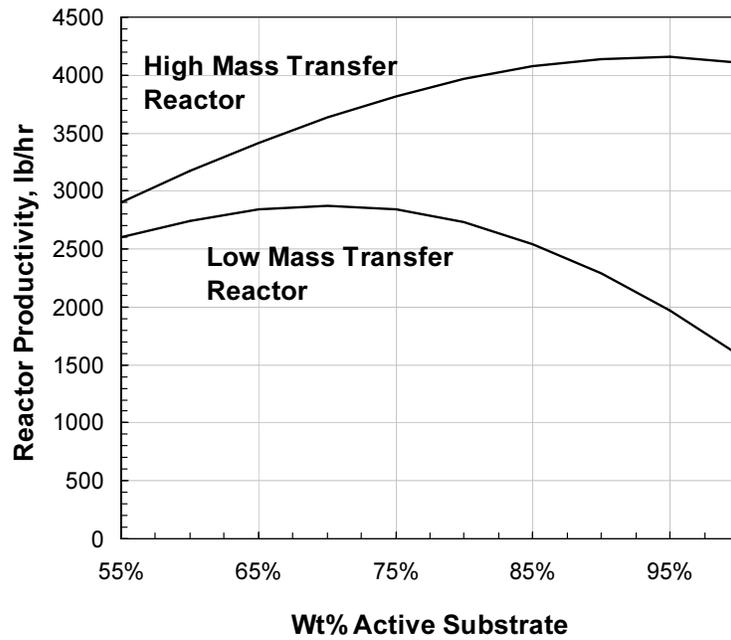


Figure 4.4: Impact of solvent/substrate composition on reactor productivity for a low and high mass transfer commercial reactor system. Temperature, catalyst composition and pressure are the same for both the high and low mass transfer reactors.

While the reduction of solvents may represent an obvious approach to increasing the productivity of a reactor, the influence of changing composition on the physical properties and hydrogen solubility on the process should be considered to understand the limits of this approach. At the same time the advantages of improved reactor designs and enhanced mass transfer can be accessed to determine the impact on process productivity and economics.

5: Converting from Batch to Semibatch

The most common hydrogenation process can be described as a process where the solvent, substrate, and catalyst are initially charged to a reactor while hydrogen is fed on demand using a pressure controller to maintain a constant pressure. To maintain the reaction heat evolution within the cooling capabilities of the reactor, the reaction rate is often reduced by reducing the availability of hydrogen. This is accomplished by reducing the pressure and agitation or by using reduced temperature. Reducing the temperature also reduces the kinetic rate constant. This situation can create hydrogen starvation or low bulk concentration during the reaction leading to catalyst deactivation and by-products. In addition, the design and selection of catalysts must be based on the ability of the catalyst to compete for hydrogen in the presence of high concentrations of a strongly adsorbing substrate. For this reason precious metal catalysts such as platinum and palladium which show high affinity for hydrogen are chosen over base metal catalysts such as nickel.

An alternative to the typical batch hydrogenation is the use of semi-batch hydrogenation where the substrate is fed over a period of time. This has a number of advantages over the former approach,

- The reactor can be operated at higher temperature facilitating heat transfer.
- The process can be operated at the highest possible mass transfer and pressure allowed by the process equipment in order to maximize selectivity and productivity.
- The process heat evolution and reaction rates can be controlled by controlling the substrate feed rate, allowing the process to meet the maximum cooling capability of the reactor.
- The concentration of substrate in the reactor can be kept to very low levels to alter the formation of reaction intermediates and to affect selectivity.
- Base metal catalysts can sometimes be used to replace precious metal catalysts.

The producer of a specialty primary amine was operating a conventional hydrogenation reactor illustrated in Figure 1.1. The corresponding nitrile feedstock was added batch wise with catalyst to the reactor, heated to 100°C, and allowed to react. The hydrogen was delivered on demand at 35 barg. A typical reaction batch profile is illustrated in Figure 5.1. The temperature and pressure had been optimized to keep the process within the cooling capacity of the reactor and to achieve a desired selectivity of the primary amine shown in Table 5.1.

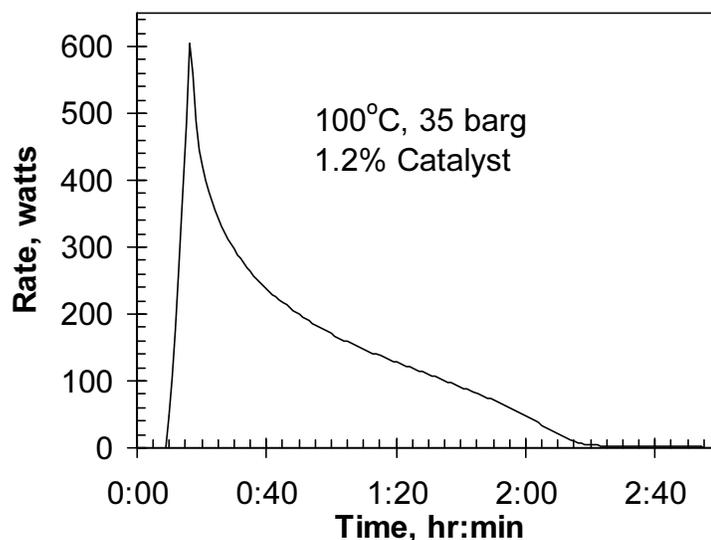


Figure 5.1: Exotherm profiles from a batch hydrogenation of a specialty nitrile measured in a 1.8-liter reaction calorimeter, RC1 HP-60 [4].

The same nitrile was fed in a semi-batch manner at 50 barg and 120°C into a liquid heal in the reactor that consisted of the amine and catalyst. The feed rate was adjusted in the laboratory experiment to determine the impact of feed rate on heat generation and to establish basic kinetic profiles. This experiment is illustrated in Figure 5.2. As shown, the reaction rate followed the feed rate until the highest feed rate, 7 gm/min, was imposed. At that time the reaction rate began to decline as the nitrile and possible intermediates accumulated.

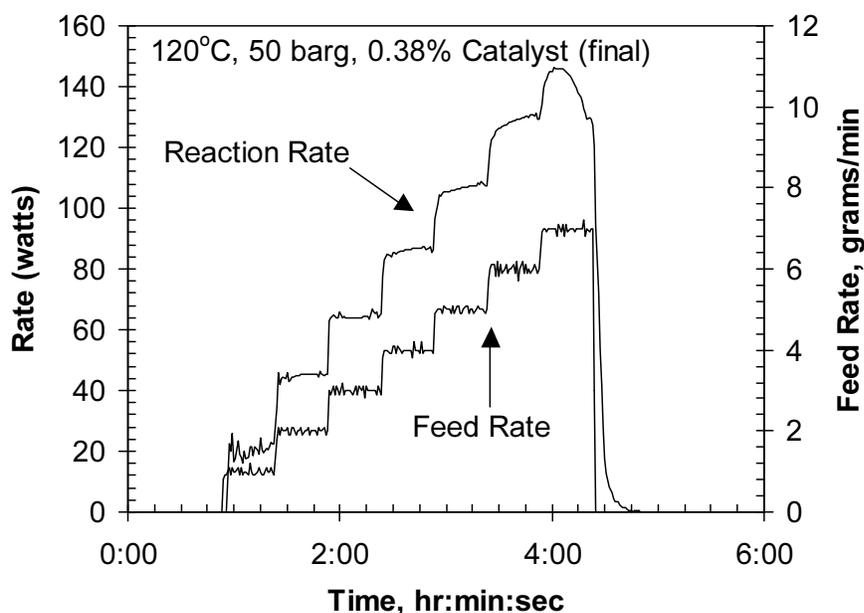


Figure 5.2: Exotherm profiles during semi-batch hydrogenation of a nitrile with a liquid heal of the corresponding amine (30% by volume based on the final liquid volume) measured in a 1.8 liter reaction calorimeter, RC1 HP-60 [4].

Batch data and additional semibatch experimental data were manipulated and normalized to the catalyst charge to calculate the rate vs concentration profiles illustrated in Figure 5.3. To develop the profiles in Figure 5.3, the accumulation of nitrile was estimated by subtracting the amount of nitrile that was added to the reactor from the amount that reacted according to the exotherm profiles. In this analysis all of the unreacted material was assumed to be the nitrile substrate. This is a simplification of the process chemistry yet is useful at this stage of process analysis.

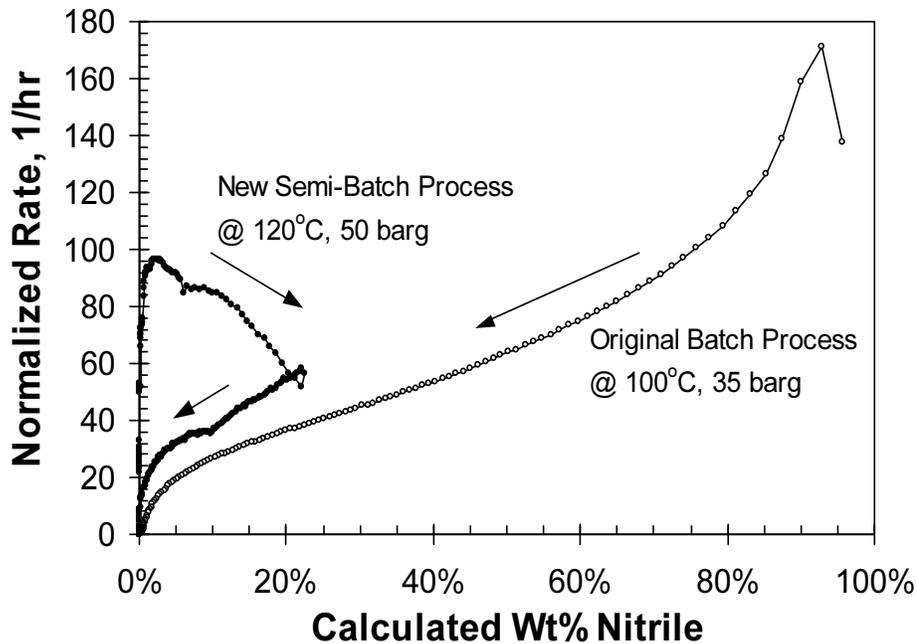


Figure 5.3: Normalized rate of reaction, kg nitrile reacted/(kg catalyst hour) as a function of the calculated nitrile concentration in the reactor under batch and semi-batch conditions.

The profiles in Figure 5.3 reveal an interesting observation. For the batch process the nitrile concentration starts at 100% and decreases to 0% by the end of the process. At low apparent concentrations of the nitrile, the reaction rates from the batch process are much lower when compared to the semi-batch operation. The semi-batch process, which starts out at very low nitrile compositions, yields a very high reaction rate. Based on the slope of the rate vs concentration profiles at low concentrations, the catalyst actually appears to be more than a 100 times more active during the semi-batch operation compared to the batch operation. As the semi-batch feed rate increases the reaction rate increase until the accumulation of high levels of nitrile begins. The rate then levels off and begins to decrease until the feed of fresh nitrile is terminated and the accumulated nitrile begins to react away. This apparent hysteresis of the rate curve in Figure 5.3 is a strong indication that intermediates have formed or that the catalyst activity has been compromised and demonstrate that the semi-batch process should be operated below the maximum rate to achieve the best process results.

Comparison of optimal processes for both the batch and semi-batch methods of operation are shown in Table 5.1. The semi-batch operation was operated below the point where the rate declined at low nitrile concentrations and yielded higher selectivity, higher productivity at higher temperatures when compared to the batch process. The semi-batch process also had a lower cooling requirement since the overall rate was constant for the entire process with a one hour feed addition time. It should be noted that the temperature of the semi-batch process was elevated not in improve reaction rates but to increase the heat removal

capabilities of the process thus allowing a high temperature difference between the cooling jacket and cooling coils, and the reactor. Increasing temperature was not possible for the batch process, which yielded increasingly lower yields with increasing temperature.

Table 5.1: Comparison of process approaches to increase reactor productivity.			
	Original Plant Process	Lab 2 liter	Buss Loop Reactor 300 liters
Process Class	Batch	Semibatch	Semibatch
Temperature	100°C	140°C	140°C
Pressure	35 barg	50 barg	50 barg
kla, sec^{-1}	unknown	0.40	1.0
Net Reaction Time, hrs	2.2	1.0	1.0
Maximum Heat Duty on Reactor kwatts/kg	0.70*	0.50	0.50
Productivity, kg Product/ (kg Catalyst hr)	30.0	50.0	50.0
Primary Amine	92.0 %	99.17 %	99.32 %
Nitrile	0.50 %	0.05 %	0.05 %
Secondary Amine	2.39 %	0.05 %	0.16 %
Other By-products	5.11 %	0.73 %	0.47 %

Based on the laboratory findings, the semi-batch process was scaled-up to a Buss Loop reactor as illustrated in Figure 1.2. The process performance is summarized in Table 5.1. The scaled process yielded virtually identical yield and selectivity when compared to the lab studies confirming the process analysis. The Buss loop reactor was chosen as the best reactor for scale-up since by its unique design, it is capable of having 100% of its maximum the heat transfer and mass transfer capability over a wide range of liquid volumes. For comparison a traditional stirred tank reactor such as that illustrated in Figure 1.1 does not perform well at low liquid volumes. Low liquid volume in a stirred tank reactor often leads to poor mixing, mass transfer and heat transfer as the cooling coils and impellers are not submerged for efficient operation.

Traditional batch hydrogenation processes have a number of limitations, which can be overcome by converting the process to a semi-batch hydrogenation process. Improvements in productivity, heat transfer, selectivity, and catalyst performance can be realized. The proper design of a process requires the consideration of how materials are combined and in what order they are combined. The semi-batch approach can provide an additional control technique to greatly enhance hydrogenation processes.

Conclusions

The ways to improve the productivity of a chemical process are as numerous as the number of creative minds set to the task. However a number of practical and standard approaches to improve productivity can be applied to batch slurry hydrogenation reactor systems.

To intensify a process, using a smaller reactor to achieve the same productivity as a large reactor, the gas-liquid mass transfer in a reactor must be increased and the catalyst charge must be maintained. In addition, the heat transfer surfaces to achieve the reactor productivity must be compressed into the smaller reactor. For highly engineered specialty reactors such as the Buss Loop and the Biazzi reactor this is achieved.

While the reduction of solvents may represent an obvious approach to increasing the productivity of a reactor, the influence of changing composition on the physical properties and hydrogen solubility on the process should be considered to understand the limits of this approach. At the same time the advantages of improved reactor designs and enhanced mass transfer can be accessed to determine the impact on process productivity and economics. Increasing mass transfer by increasing the power per unit volume, the superficial gas velocity and the ability of a reactor to reincorporate the headspace gas can provide a simple strategy to increase reactor productivity.

Traditional batch hydrogenation processes have a number of limitations, which can be overcome by converting the process to a semi-batch hydrogenation process. Improvements in productivity, heat transfer, selectivity, and catalyst performance can be realized. The proper design of a process requires the consideration of how materials are combined and in what order they are combined. The semi-batch approach can provide an additional control technique to greatly enhance hydrogenation processes.

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