Debottlenecking the Ammonia Synthesis Reactor System with the aid of Attainable Region Theory

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Abstract

Attainable Region theory is used to define the bounds of the operating region where an improvement in the productivity of ammonia is realised. An iso-productivity plot is used in conjunction with the results obtained from the attainable region to define a region of increased productivity. The objective is to determine the operating conditions under which the existing reactor system can handle increased productivity. This system consisted of a single reactor and a feed-product heat exchanger. The reactor system was modelled using the modified Temkin reaction scheme. A counter-intuitive result showed that an increased production rate of ammonia is associated with a decrease in conversion. Analysis of the results showed that a 10% increase in feed flow rate could possibly result in a 9% increase in productivity. It was found that the only way to increase the productivity of an existing reactor is to decrease the residence time. The results also showed that increasing the temperature need only be considered when implementing large increases in feed flow.

Keywords: Attainable Region, Ammonia synthesis, optimisation, productivity, debottlenecking

1 INTRODUCTION

The use of Attainable Region Theory, as a synthesis tool, has become well-established in recent years. The Attainable Region as developed by Horn (1964) is defined by Hildebrandt and Glasser (1990) as “the set of all outlet variables which can be reached by any possible steady-state reactor system from a given feed”. By examining the extreme regions (boundaries) of these geometrical constructions it is possible to determine the limitations of a given system (Feinberg, 1999). This theory has also been extended to distillation separation processes (Kauchali, 2000) since the Attainable Region (AR) is simply an optimisation method and hence can be applied to a large variety of problems.

The geometric nature of this theory makes it relatively easy to work with once the AR is plotted. Much work has gone into developing methods that allow finding the AR to be accurate and rigorous (Feinberg, 2000a, 2000b). Comparison of the AR with Pontryagin’s maximum principle carried out by McGregor et al (1999) has allowed some insight into determining the boundary of the AR. Abraham and Feinberg (2004) have shown promising developments in AR plot determination by building the region from the outside while Kauchali et al (2002) have proposed techniques for building the AR from the inside. These methods allow the AR to be used more efficiently increasing its scope as an optimisation tool.

The focus of AR theory has been mainly as an aid to design methods, especially for reactors, allowing the designer a broader appreciation of all the options available. The work presented in this article explores the use of AR theory as a debottlenecking tool as opposed to a design tool and shows the benefits of this alternative use. In order to fully grasp the potential of this concept it is necessary to highlight the difference between initial design procedures and debottlenecking procedures.

The object of the work presented is to determine whether or not it is possible to increase the productivity or production rate of ammonia in the reactor. The production rate (productivity) is simply the flow rate of ammonia leaving the reactor. A bounded region of increased productivity is obtained to identify the scope for improvement. The bounded region of interest is formed by the AR on one side and the Iso-productivity curve for a design optimum on the other. It is also essential to examine the possible degrees of freedom that may be manipulated in order to remain in the region of increased productivity. This will help to identify the variables that can be adjusted. It was found that of all variables available temperature and flow rate were the most useful options.

The work presented in this article is broken down in the following manner. Section 2 gives a brief background of the problem at hand. Section 3 shows the modified Temkin equation that was used to the model the reaction kinetics. Section 4 shows the difference between design and debottlenecking procedures with the aid of a simple example. Section 5 explains the concept of productivity by deriving the relevant equations and introduces the concept of iso-productivity curves. Section 6 explores the attainable region of the single reactor system incorporating the iso-productivity curve and explains the bounds on productivity that are created by incorporating these two plots. Section 7 shows the results obtained by increasing the temperatures and flow rates going into the reactor. These results are discussed in Section 8. The article is concluded in Section 9 with brief comments and conclusions.

2 PROBLEM STATEMENT

The unique aspect of this problem is that it is to be carried out on the existing ammonia synthesis process that does not allow for inside re-arrangement and addition of reactor beds. The system is highly integrated with very few degrees of freedom. Determining the limitations of the existing reactor will enable a comprehensive investigation into the scope for improvement as far as productivity is concerned. The reactor system was modelled as a single reactor with a feed-product heat exchanger. The system is shown in Figure 1.

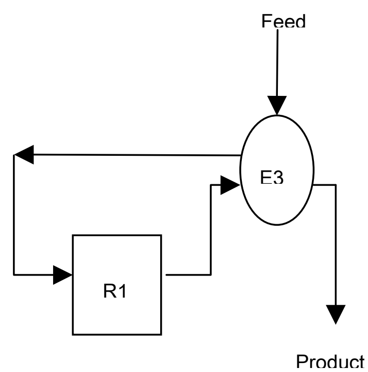

Figure 1: Schematic representation of Simplified Reactor System

3 KINETIC MODEL

The reaction kinetics used to model the reactor are derived from the modified Temkin model as shown below (Equation 1).

$$r = M \frac{k_{*} {P_{N_2}}^{1-\alpha}\left(1 - \frac{{P_{NH_3}}^{2}}{K_P P_{N_2} P_{H_2}^{3}}\right)}{\left(\frac{1}{P_{H_2}} + \frac{{P_{NH_3}}^{2}}{K_P P_{N_2} P_{H_2}^{3}}\right)^{\alpha}\left(1 + \frac{l}{P_{H_2}}\right)^{1-\alpha}} \quad \ldots(1)$$

Where r is the rate of reaction [mol/ hr. m^3]

P is the partial pressure of the component specified by the subscript [atm]

K_p is the equilibrium constant

k_{*}, α and *l* are parameters specific to the catalyst used.

M is a correction factor based on empirical calculations to fit plant data

4 DESIGN AND DEBOTTLENECKING

As mentioned earlier, one can only truly understand the importance of this work once the difference between designing a plant and debottlenecking one has been made clear. In an attempt to assist the reader the following example is considered.

In order to design a reactor one has to take note of such factors as equilibrium characteristics of the reaction, the optimum temperatures and pressures and possibly the most suitable catalyst to use. All these factors must be carefully weighed to ensure that the end result is a reactor that meets the desired specifications with respect to productivity, efficiency and economic feasibility.

Typically a designer would start by investigating the equilibrium data for the reaction of interest. Figure 2 shows one such plot. Adiabatic profiles for two different initial conditions i.e. inlet temperature are also plotted on Figure 2. It is clear that 'Option 1' provides a greater conversion while starting at a lower initial temperature. Although this may seem favourable one often finds that this comes at the expense of excessive reactor volumes as well as large catalyst amounts. In order to obtain the adiabatic profile 'Option 2' a reactor volume of 10 m^3 was specified which achieved a final conversion of 0.136 of nitrogen. The adiabatic profile 'Option 1' achieves a conversion of 0.287 but has a reactor volume of 380 m^3.

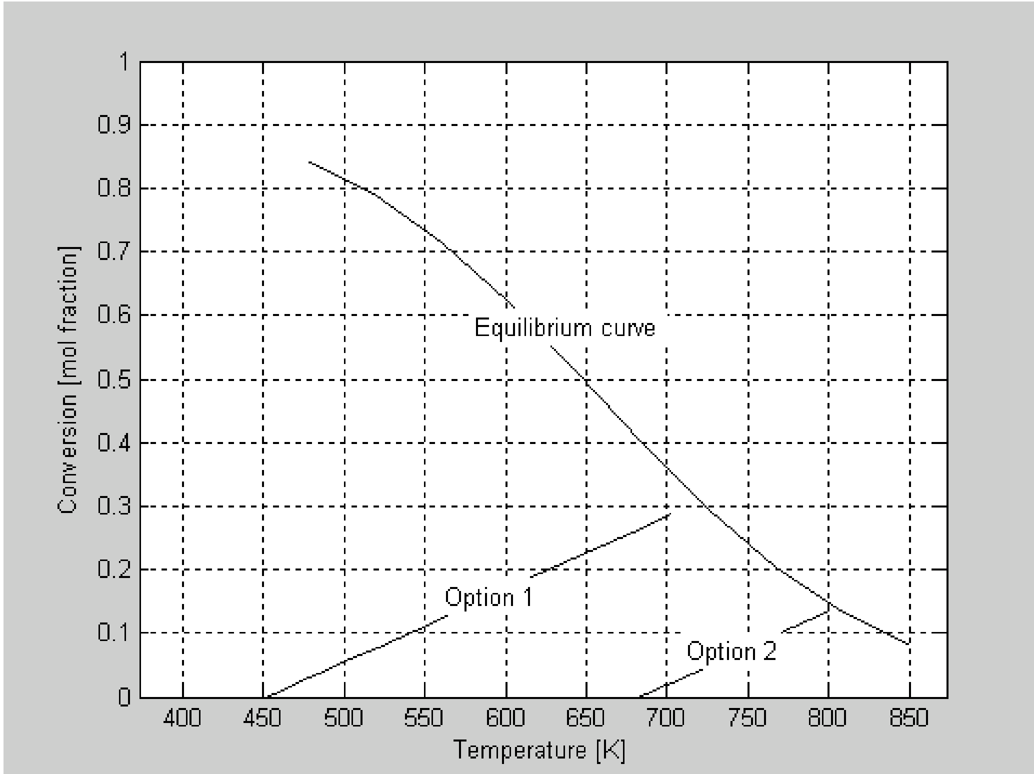

Figure 2: Equilibrium curve and adiabatic profiles for ammonia reactor

The conversion is doubled but the reactor volume is increased by a factor of 38. ‘Option 2’, though achieving a lower overall conversion, is a more desirable reactor system with respect to residence time and cost. The designer is in a position to choose which system is most favourable with respect to economics and productivity. The designer is allowed to vary amounts of catalyst and general reactor configuration until an optimal system is obtained. However the process of debottlenecking is very different. When undertaking a debottlenecking exercise one attempts to determine the limiting process on the system whether it be a reactor, a separator or other unit operations. To find the bottleneck it is necessary to determine the part of the plant that cannot accommodate increased capacity, which then determines the rate of production of the plant i.e. is the limiting factor of the process. Steps are then taken to ensure that the bottleneck is operated in an optimal way so as the meet the demands of the plant.

In the case of the ammonia plant the possible bottlenecks are the separators, the compressors and the reactor. The most obvious place to start investigating is the reactor since it is here that the product is made. If it is not possible to produce enough product in the reactor then it is trivial to investigate options on the rest of the plant. To facilitate an understanding of the type of changes that must be considered it is first necessary to discuss the concept of productivity.

5 Iso-Productivity Plots

How can the production of ammonia be increased without changing the mass of catalyst? It is necessary to obtain a relationship between productivity and the amount of catalyst in order to proceed. To derive this expression consider Equations 2 and 3.

$$P = x \cdot \dot{m} \qquad \ldots(2)$$

Where P is the production rate of ammonia

x is the conversion with respect to nitrogen
$\dot{m}$ is the mole flow rate of nitrogen into the reactor

$$\tau = \frac{V_{cat}}{Q} \quad \ldots(3)$$

Where τ is the residence time
V_{cat} is the amount of catalyst
Q is the volumetric flow rate of nitrogen into the reactor

With the aid of simple substitution and the relationship mole = volume x molar density, equations 2 and 3 can be combined as shown below. Equation 2 becomes

$$P = x \cdot \rho \cdot Q \quad \ldots(4)$$

Where ρ is the molar density of the nitrogen in the incoming stream which is assumed to be constant over the range of conditions considered.

Equation 3 can be re-written as

$$Q = \frac{V_{cat}}{\tau} \quad \ldots(5)$$

Rearranging Equation 4 and equating with Equation 5 and rewriting with respect to τ results in

$$\tau = \frac{V_{cat} \cdot x \cdot \rho}{P} \quad \ldots(6)$$

Plotting τ versus x yields a straight line with gradient $\frac{V_{cat} \cdot \rho}{P}$, provided a constant production rate is achieved since catalyst volume is constant. It is for this reason that these contours are referred to as iso-productivity curves. Conventional methods prefer to plot extent, ϵ, rather than *x*. To incorporate this convention a slight modification is made to Equation 6.

Noting that the extent of reaction is

$$\boldsymbol{\varepsilon} = 1 - x \quad \ldots(7)$$

Rewriting for *x* and substituting into Equation 6 yields

$$\tau = \frac{V_{cat} \cdot \rho \cdot (1-\varepsilon)}{P} \quad \ldots(8)$$

Further simplification produces Equation 9

$$\tau = \frac{V_{cat} \cdot \rho}{P} - \frac{V_{cat} \cdot \rho \cdot \varepsilon}{P} \quad \ldots(9)$$

The slope of Equation 9 is simply the negative of the slope of Equation 6. Figure 3 shows typical iso-productivity curves that can be achieved for reversible, exothermic reactions in general. The nature of the gradient term means that increasing the production rate means decreasing the slope as illustrated in Figure 3.

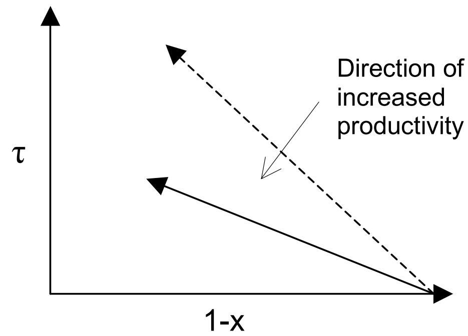

Figure 3: Iso-productivity curves

Notice that in an initial design flowsheet the production rate is set to ensure that market demands are satisfied during the operation of the plant. The optimisation is set for this production rate which sets the lower bound on how much should be produced.

6 BOUNDS ON PRODUCTIVITY

A brute force method of obtaining the AR for a single adiabatic ammonia reactor is to plot the adiabatic conversion along the reactor bed as a function of residence time for various inlet temperatures. This is shown in Figure 4.

The resulting residence time-conversion plots were convexified which allowed the envelope of the attainable region to be determined. Figure 4 shows the attainable region that was obtained. The curves shown represent the adiabatic profiles obtained for various inlet temperatures while setting the reactor volume at 30 m^3. The envelope is obtained by joining the outer lying points of each adiabatic profile. Points that lie outside the envelope cannot be achieved using the single reactor. It is of interest to note that for the higher temperatures the adiabatic profiles tend to asymptote to a constant value. The reason for this is that at higher temperatures equilibrium is reached quickly and a smaller residence time is required to obtain equilibrium.

Figure 4 also shows the iso-productivity curve that was plotted for a reactor with inlet temperature set at 350°C and reactor volume of 20 m^3 as indicated by ‘A’.

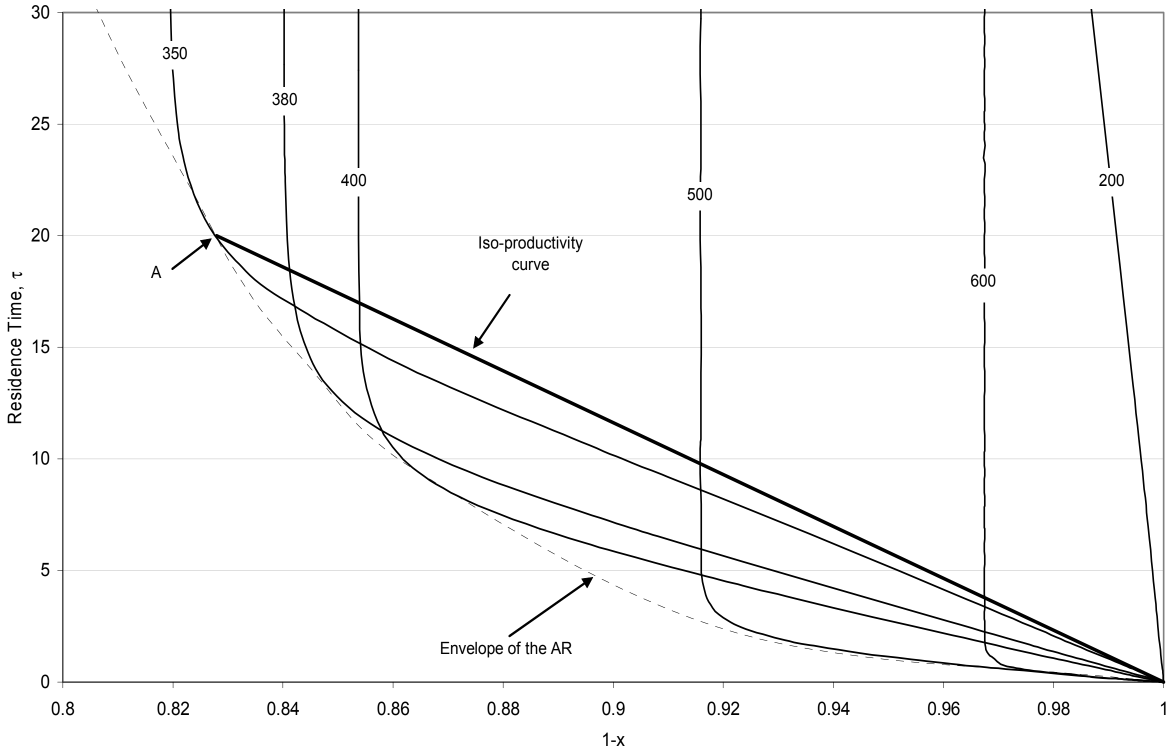

Figure 4: AR for single ammonia reactor showing adiabatic profiles for various temperatures [°C], the envelope of the AR and an Iso-productivity curve

Figure 5 highlights the region enclosed by the iso-productivity curve and the envelope of the attainable region. This area is referred to as the region of increased productivity. As explained in Section 5 in order to increase the productivity of the reactor it is necessary to decrease the slope of the iso-productivity curve. This would mean moving into the region shown. Moving past the envelope would be impossible since all points outside the envelope are not attainable. Moving above the iso-productivity curve is the equivalent to decreasing the production rate since one could only do so by increasing the slope of the curve. Incorporating the iso-productivity curve and the attainable region is useful since it helps to hone in on the possible solution by eliminating non-optimal solutions.

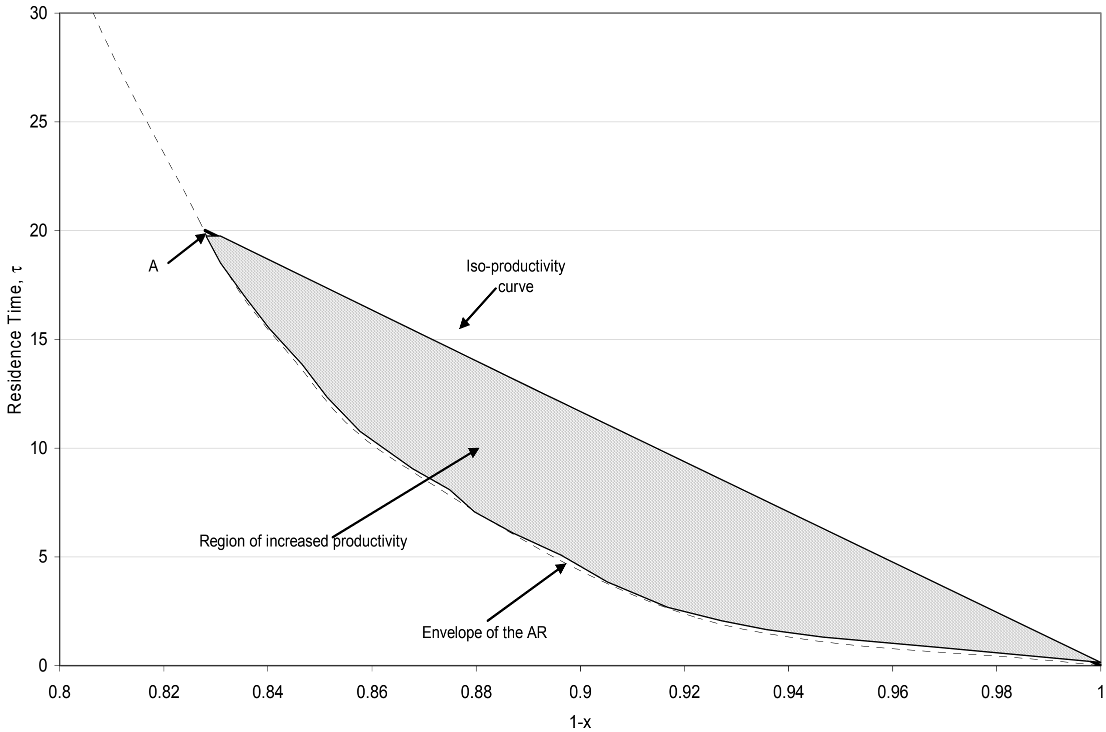

Figure 5: The Region of increased productivity

The current system ends at the point labelled ‘A’ (Figure 5). It is of interest that all the adiabatic profiles that lie within the region of increased productivity are in fact higher temperature profiles. This indicates that increasing the productivity may require the inlet temperature to the reactor to be increased.

Careful inspection of Figure 5 reveals that in order to achieve higher production rates i.e. to move into the desired region it is necessary to decrease the residence time, τ, and also decrease the conversion. The latter point seems to be very much against normal optimisation procedure but this will be further explained in Section 7.

Since the reactor volume cannot be changed the only way to decrease the residence time is to increase the flow rate to the reactor. Of course this may have repercussions as far as the downstream or for that matter upstream processes are concerned, but for the purpose of this article it is necessary only to determine whether or not or not the reactor is a bottleneck so these repercussions, though noted, will not be fully explored.

7 INCREASING THE FLOW RATE AND TEMPERATURE

To determine the extent to which the flow rate into the reactor can be increased a flow rate factor was incorporated into the reactor program allowing the factorial increase to be specified. Figure 6 shows the plot of conversion versus flow increase factor. The curve obtained when the inlet temperature was set at 350°C shows the highest conversion than that of the 370°C and 400°C curves. The reason for this is clear from Figure 4 where point ‘A’, which represents the operating conditions for the 350°C curve, clearly shows the highest conversion possible in the region of increased productivity. This also ties up with the equilibrium plot shown in Figure 2 where it is clear that higher inlet temperatures result in smaller overall conversions.

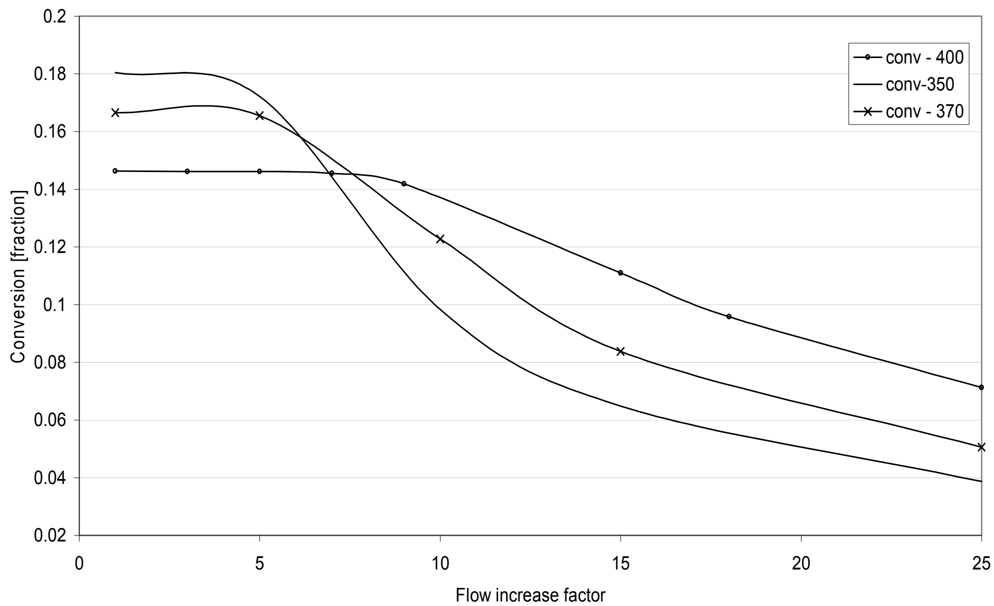

Figure 6: Comparison of Conversion vs Flow increase factor for various Temperatures [°C]

The percentage increase of ammonia leaving the reactor, considered as a measure of the productivity, was then plotted against the flow increase factor as shown in Figure 7.

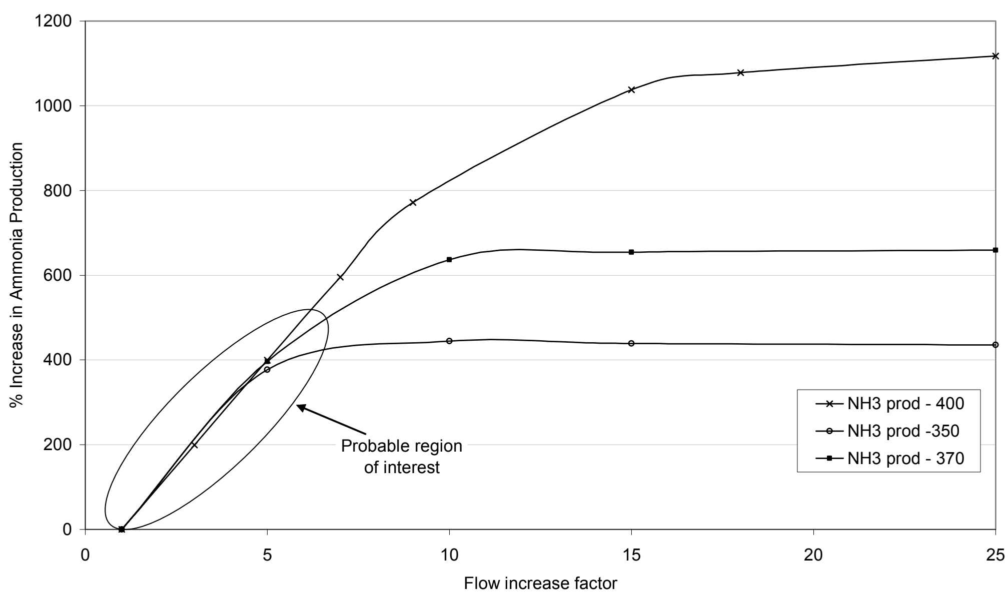

Figure 7: Comparison of % Increase in Ammonia Production Rate for various Temperatures [°C]

It is interesting to note that even though the conversion in the reactor is dropping, as shown in Figure 6, the flow rate of ammonia leaving the reactor increases. This justifies the discussion in Section 6 that decreasing the conversion allows for higher productivity.

Figure 7 shows the effect of increasing the feed flow rate by as much as 25 times. It is obviously impractical and highly unlikely for one to contemplate a flow increase of this magnitude considering the impact it would have on the rest of the plant. The reason that this graph is shown is that it highlights a rather interesting characteristic of the AR-Iso-productivity plot shown in Figure 4. Note the approximately linear nature of the adiabatic profiles before they hit the envelope of the AR. In order to increase the productivity of the reactor it has been shown that it is essential that the slope of the Iso-productivity curve be decreased.

Consider the case where the iso-productivity curve lies on the linear portion of the corresponding temperature adiabatic profile i.e. they are co-linear to the straight portion of the adiabatic profile. Further increase of the productivity would no longer be possible since one is not able to decrease the slope of the iso-productivity plot while ensuring that the iso-productivity curve and the corresponding adiabatic profile intersect. To further increase the production rate one would then have to consider a temperature increase. Figure 7 shows that when the curve for an inlet of 370°C tends to a constant the 400°C curve continues to increase. It is of interest that the adiabatic profile stops being linear near the envelope of the AR. This confirms the theory that the optimal operation is achieved at the envelope.

Figure 7 also shows that for small flow increase factors (up to 5) the three curves are more or less equivalent, yet this is the steepest portion of the curve. This would indicate that flow rate has a bigger effect on the productivity than temperature does. This only changes as the various adiabatic profiles approach the limiting conditions explained above.

The area labelled 'Probable Region of Interest' is highlighted to show the typical magnitude of increase that a plant would consider implementing. It is this region that was used to determine the extent of improvement that might be achieved using this method. The results are highlighted in Section 9.

8 DISCUSSION

It is clear from Figure 7 that the reactor is not the bottleneck in the system since it is capable of handling increased capacity. Further investigation will have to be undertaken to find the bottleneck. The method of incorporating the AR and iso-productivity plots helps to focus on the possible solution though it does not provide a way of determining the best solution within the Region of increased productivity. In Figure 7 it appears that the increase in the rate of production is limited i.e. does not increase indefinitely. If the only goal was to make as much ammonia as possible then one could very easily operate at that point were the curves become constant i.e. along the envelope of the AR. However this is rarely the case so the best solution can only be obtained once the rest of the plant has been thoroughly analysed. However it must be noted that bounds where the one can search for the best solution have been found relative to the rest of the plant.

9 CONCLUSION

Debottlenecking the ammonia synthesis loop was carried out with focus on the reactor system. It is shown that conventional optimisation techniques such as altering reactor volumes and configuration and increasing conversion cannot be employed. The reason for this is that these changes cause the system to operate outside the region of increased productivity. In order to determine the changes that were required to make the system more productive the AR and iso-productivity plots were combined which gave rise to the region of increased productivity. To operate within this region the residence time and conversion had to be decreased. It was found that increasing the temperature and flow rate entering the reactor would result in increased productivity. It was also found that adiabatic profiles that lay within the region were all higher temperature profiles, which indicated that a temperature increase might also be necessary. Analysis of the results showed that a 10% increase in feed flow rate resulted in a 9% increase in productivity for all three temperature curves as shown in Figure 7. Increasing the temperature need only be considered when implementing large increases in feed flow. This method will also prove useful when dealing with aging catalysts as it provides a guideline for changes that are to be implemented to ensure a constant production rate.

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