Adiabatic Ammonia Synthesis Converter

During the last three years of operation, this two-stage design has been proven to be economically attractive to operate, as well as safe to load, unload, operate, and control.

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The basic function of an ammonia synthesis converter is to bring a hydrogen- and nitrogen-rich gas stream into contact with a promoted iron catalyst for several seconds at elevated temperatures and pressures. When this is done, part of the hydrogen and nitrogen is converted to ammonia. In most modern plants, the synthesis is carried out at pressures between 2,000-and 5,000 lb./sq. in. gauge and at temperatures between 700- and 1,000°F.

There are several basic design requirements of a converter system. It must hold the pressure, it must control the temperature, and because the reaction is highly exothermic, and because lower outlet temperatures favor higher equilibrium conversion, heat must be removed from the reacting gas at some intermediate point or points. The materials of construction must withstand the attack of hydrogen and nitrogen, and the converter must operate safely under the varying conditions normally encountered in an industrial plant.

This article describes how these requirements were met in the 1,000 ton/day ammonia plant designed and built by C F Braun & Co. for Arco Chemical Co. at Fort Madison, Iowa.

Desirable Features

First, let us consider some features which we believe are desirable in an ammonia synthesis converter.

Simplicity – Although obviously desirable because of the severe conditions and the requirements for temperature control, simplicity is difficult to achieve.

Small Openings – A way of loading catalyst by gravity through a small top opening and removing it by gravity through a small bottom opening, without using a removable basket, would avoid the necessity of providing a full diameter opening in the pressure shell, and the cost of a structure or mobile crane for basket handling.

High Lvel heat Recovery – As in any process, the higher the level at which the heat of reaction is recovered, the more efficient the process can be, whether the heat is used to preheat feed, preheat boiler feed water, generate steam, or supply other heat requirements.

Indirect Heat Removal – Catalyst is used more efficiently if all the gas passes through all the catalyst, and intermediate heat removal is by indirect exchange rather than by quench with cold feed gas which has bypassed part of the catalyst.

Separate Exchangers – If feed-effluent exchangers are separate from the catalytic reactors, routine maintenance work on the exchangers can be performed by normal procedures. Also, the exchanger diameter can then be optimized independently of the catalytic reactor diameter. The optimum feed-effluent exchanger diameter is generally less than one-half the optimum catalytic reactor diameter.

Reduced Pressure Shell Temperature – The lower the temperature of the gas to which the pressure shell is exposed, the less expensive the material of construction can be.

Minimum Refractory Lining – If the use of refractory linings inside the reactor to protect materials of construction can be avoided, or at least minimized, then the risk of refractory failure, and resultant hot spots, is avoided or reduced.

Optimum Pressure Drop – Pressure drops through the catalyst should be high enough to ensure good distribution, but not so high as to consume excessive power.

Operating Stability – The reactor system should be safe and stable in the face of operating upsets and variations in operating conditions.

Most modern converter designs provide some of these features, but no previous designs that we know of provide all of them. The design described in this article, does.

Adiabatic Catalyst Beds

Returning to the first desirable feature, simplicity, let us consider one of the simplest of catalyst bed configurations; the fixed adiabatic downflow bed. As a specific example, consider a bed operating at 200 atm. under steady-state

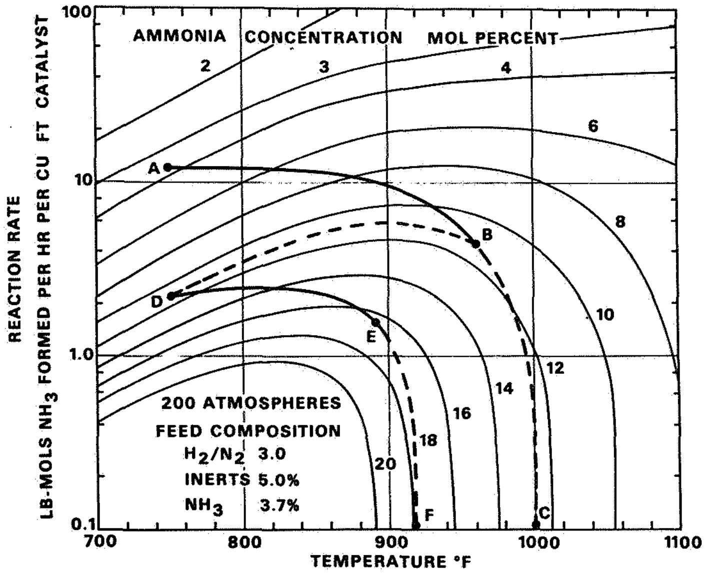


Figure 1. Ammonia synthesis reaction rate.

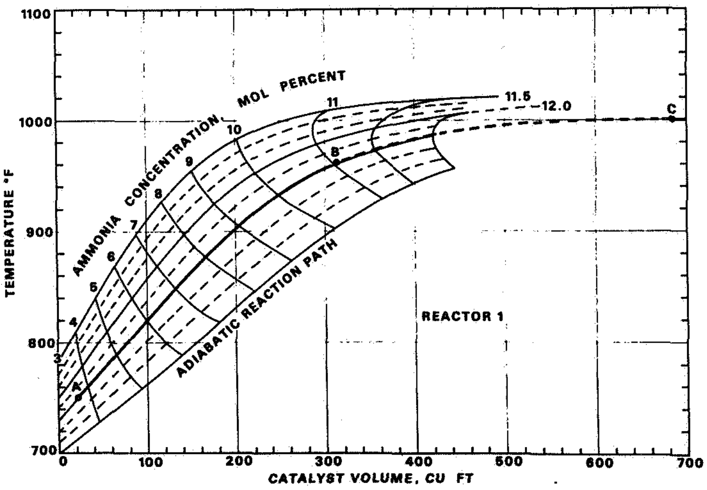


Figure 2. Ammonia synthesis/adiabatic reaction paths.

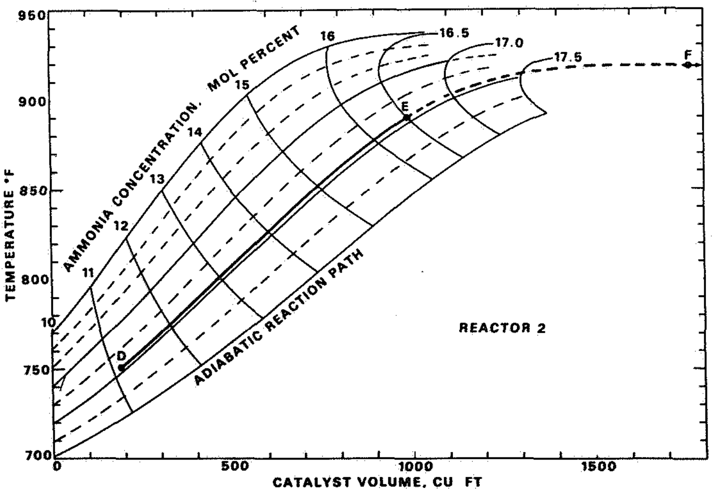


Figure 3. Ammonia synthesis/adiabatic reaction rate.

conditions with a feed consisting of a 3:1 mixture of hydrogen and nitrogen containing 5% inerts and 3.7% ammonia. For a reactor operating under these conditions with a given catalyst, the reaction rate at any point in the bed can be expressed as a function of temperature and ammonia concentration. Such a function is shown graphically in Figure 1 for a typical catalyst.

In this figure we see that for each ammonia concentration there is a temperature at which the reaction rate is maximum, but for each ammonia concentration, temperature can vary from the maximum over a wide range without a drastic reduction in reaction rate. At an ammonia concentration of 10%, for example, the reaction rate is over 90% of the maximum between about 850- and 950°F, a range of 100°F. Thus precise control of temperature is not critical to the operation of the reactor.

If the feed enters the catalyst at a temperature of 750°F, then the catalyst inlet condition is represented by point A. As the gas proceeds through the catalyst, reaction conditions can be computed thermodynamically to follow path ABC. At point C, the mixture asymptotically approaches equilibrium. Because of the very low reaction rate near point C, a very large catalyst volume would be required to reach this point.

To exceed the 12.6% ammonia concentration of point C, it is necessary to remove heat at some intermediate point in the catalyst bed. In the example shown, when the gas reaches the condition of point B, heat is removed to cool the gas from 960°F to 750°F, as indicated by point D. From this point, the reaction again proceeds adiabatically along the path DEF. In our example, the final catalyst outlet condition is represented by point E at a concentration of 16.5% ammonia and a temperature of 890°F.

Using the same information, another plot which is useful in tracing the reaction path in an adiabatic bed is shown in Figure 2. Here, for a feedrate of 17 million std. cu. ft./hr., temperature is plotted vs. catalyst volume for each of several adiabatic reaction paths. Also shown are lines of constant ammonia concentration. Points A, B, and C represent the same adiabatic reaction path as the corresponding points in Figure 1. For a given catalyst volume, this plot allows us to easily visualize the effect of variations in inlet temperature, inlet ammonia concentration, catalyst activity, or space velocity.

Figure 3 shows a similar plot, except for a higher range of ammonia concentrations. The reaction path represented by points D, E, and F represent the same path as for the corresponding points in Figure 1.

Still another plot of the same information is shown in Figure 4. Here the same reaction paths are shown as plots of mol percent ammonia vs. temperature. The equilibrium ammonia concentration is also plotted against temperature at 200 atm. and several lower pressures.

Mechanical Design

Now let us consider the mechanical design of such reactors. An important practical problem is protection of the pressure shell from the reaction conditions. Materials are available which will withstand the full temperature, pressure, and composition of the reaction mixture, but to build the pressure shell of such materials would be very costly. On the other hand, it is possible to design the reactor so that the pressure shell is isolated from the reaction temperature by means of a cold feed gas passage between the pressure shell and the catalyst container,

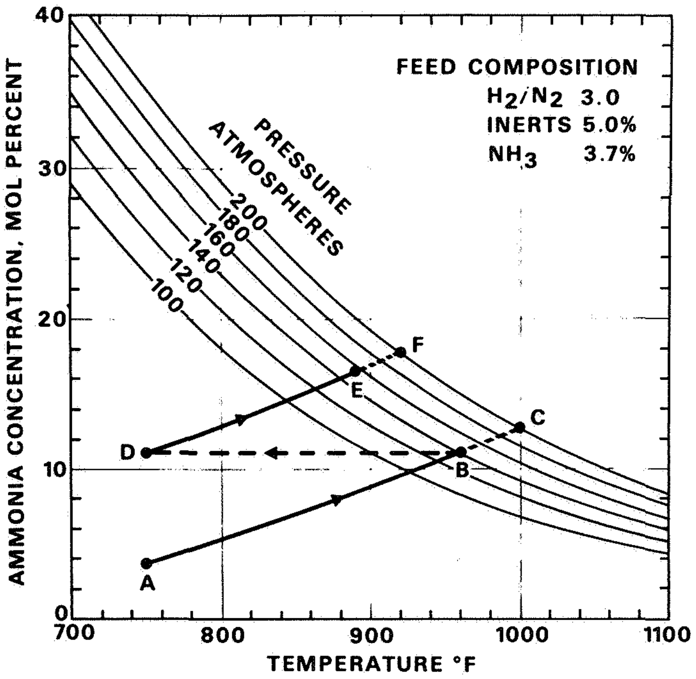


Figure 4. Ammonia synthesis equilibrium conditions.

possibly in combination with a layer of internal insulation. But such a design would be complex and costly. An intermediate possibility is suggested by a review of metallurgical requirements at various temperatures and partial pressures of hydrogen and nitrogen.

At the full reaction temperature of 900- to 1,000°F. at least the inside surfaces of the vessel would have to be made of materials such as 304 stainless steel or Inconel. Also, lower allowable stresses would require considerably thicker walls. If, however, the gas to which the pressure shell is exposed could be limited to a maximum design temperature of 800°F, then alloy steel containing 2¼- or 3% chromium and 1% molybdenun can be used. Having good mechanical strength, these materials can be used for the pressure shell safely and at moderate cost.

A reactor design which limits the shell temperature to the lower range is shown schematically in Figure 5. The catalyst is held in a simple cylindrical container inside the pressure shell. The 750°F feed gas enters through an annulus surrounding the bottom outlet nozzle, and then passes through a narrow annulus between the catalyst container and the pressure shell, protecting the shell from the higher reaction temperatures. At the top of the reactor, the feed gas passes over the edge of the catalyst container and enters the open top. It then flows downward through the catalyst, reacts adiabatically, and leaves the reactor through a bottom outlet nozzle.

A small opening is provided in the top of the reactor for access and for loading the catalyst. To remove the catalyst, the bottom connection is removed and the catalyst is dumped by gravity.

Arco Chemical Design

For the Arco Chemical plant, studies led to the use of two such reactors in series in a synthesis loop shown schematically on Figure 6. Design operating conditions are roughly those shown in the examples on Figures 1 through 4.

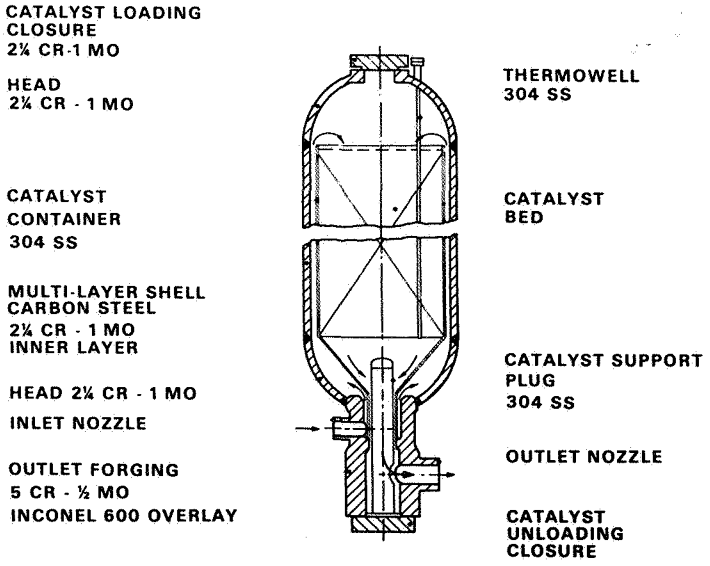


Figure 5. C F Braun adiabatic ammonia synthesis converter.

Heat removed between the two beds is used to heat the feed to the first bed. Heat is recovered from the effluent of the second reactor, first by generation of 1,500 lb./sq. in. gauge stream, and then by lower level heating of the feed to the first reactor. Following heat recovery, the reactor effluent is cooled and chilled to condense ammonia product.

To ensure good gas distribution in this, the first commercial reactor of its kind, the design was conservatively based on a velocity, pressure drop, and catalyst particle size comparable to those demonstrated in other types of downflow ammonia converters. Also, a healthy allowance for catalyst breakage and fouling was included. On this basis, the particle size was 6- to 10 mm. and the design pressure drop through the two catalyst beds was 95 lb./sq. in. Studies indicate, however, that the economics can be improved somewhat by going to shorter, fatter cylindrical beds, or spherical beds with less pressure

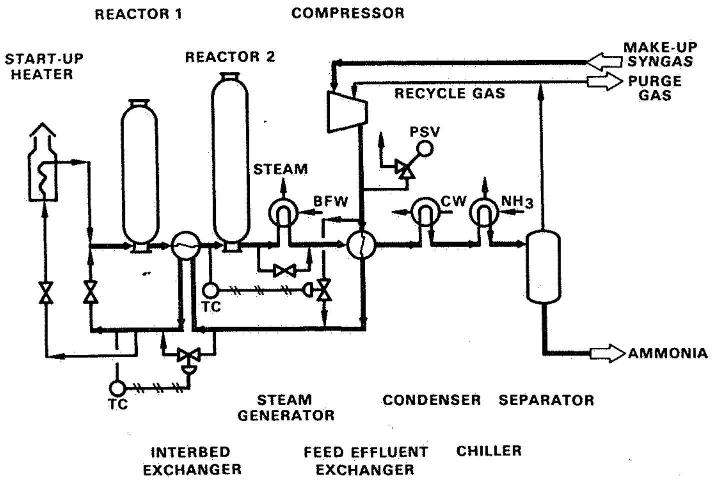
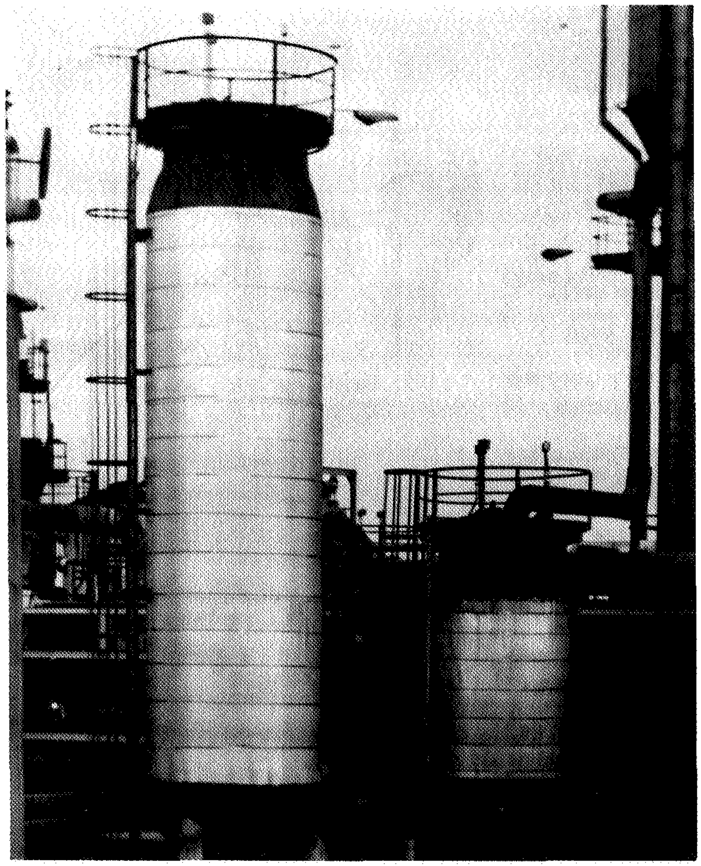


Figure 6. Ammonia synthesis loop.



Synthesis reactor vessels in Arco ammonia plant—first stage to the right, second stage to the left.

drop and smaller catalyst particles – which would allow some reduction in catalyst volume. Operating experience at Arco Chemical, to be discussed later, indicates that performance would be equally good.

An alternative design considered was a cold quench system, where the first reactor effluent is cooled by mixing with some of the cold feed gas taken directly from the compressor discharge. This would have eliminated the interbed exchanger. On the other hand, however, it would have added a high temperature feed-effluent exchanger, reduced the steam generation by about 50%, and increased the recycle rate by about 10%, based on the same total catalyst volume and approach to equilibrium.

Another alternative considered was a hot quench system where the first reactor effluent is cooled by adding feed gas taken from a point downstream of the feed-effluent exchanger. This also would have eliminated the interbed exchanger, added a high temperature feed-effluent exchanger, reduced the steam generation by 10% and increased the recycle rate by 30%, again based on the same total catalyst volume and approach to equilibrium. The indirect heat exchanger was clearly more economic.

Safety

The converter system had to be designed to operate safely not only at design conditions, but at many other conditions to which it will be exposed during start ups, shutdowns, upsets, and other conditions different from design. Protection against excessive pressure is provided in a straightforward way with a relief valve located at the discharge of the makeup-recycle compressor.

For protection against excessive temperatures, the design temperature of the pressure shell of both reactors is 780°F. The temperature of the inlet gas, after passing through the inlet annulus, is normally 755°F in both reactors, providing a normal safety margin of 25°F. The design of the outlet connection of the first reactor is adequate for 1,000°F, a margin of 40°F over the normal outlet temperature of 960°F.

In designing for higher temperatures caused by abnormal conditions, one consideration was that the catalyst volume was conservatively based on aged catalyst. Fresh catalyst would have about 40% greater activity. Might not this lead to an excessive temperature rise? Referring again to Figure 2, for a catalyst 40% more active, and assuming that the full loop pressure could be maintained, the outlet conditions could be carried to a point equivalent to 40% more catalyst, where the temperature is seen to be quite close to the equilibrium temperature of 1,000°F, corresponding to infinite catalyst volume. While such a condition would shorten catalyst life, it is not hazardous. In actual operation, however, the makeup compressor could not supply the additional feed gas corresponding to the higher conversion, so the pressure, conversion, and temperature rise would balance out at lower values. A final adjustment of inlet temperature would bring the outlet temperature to a normal operating level.

A condition equivalent to more active catalyst is that of an inadvertent reduction in circulation. In that case, of course, the reduction in pressure would not be automatic. To adjust the first reactor outlet temperature from the 1,000°F level to a more desirable level would require that an operator adjust to some combination of lower pressure and lower inlet temperature.

Analysis of Figures 2 and 3 reveals that the outlet temperature responds to adjustments in inlet temperature roughly according to a 1:1 ratio. It also shows that variations in inlet ammonia concentration normally expected do not create any serious difficulties in controlling the reactor temperatures within a safe and stable range.

By analyzing a wide variety of abnormal conditions with the aid of such charts, it was predicted that the two-stage adiabatic synthesis converter would be at least as safe and stable and as easily controlled as other types considered. An important factor in this stability is the combination of the high temperature and close approach to equilibrium at the reactor outlet, which tends to stabilize conditions at that point.

Operating Experience

The reactors were installed and loaded with CCI C-73 catalyst in March 1969. The catalyst was not prereduced. Because the startup schedule was limited by work in other areas, the loading proceeded intermittently over a ten day period, at the end of which the reactors were closed and ready for initial operation. By working continuously, it is estimated that the same loading could be accomplished in about four days or less.

The loading procedure was essentially the same as that used for the shift converters and methanator. The catalyst was screened into a metal loading bucket which held the contents of one drum. The loading bucket was then lowered through the top opening into the vessel, where a man emptied the bucket and spread the catalyst to ensure against catalyst classification. The man was protected by a continuous air supply, a dust mask, a lifeline attached to a harness, a rope ladder, and another man in constant attendance at the vessel opening. The screening proved to be precautionary only, as less than a 0.5 percent fines were separated.

The catalyst was reduced in June 1969. Because the supply of makeup gas was interrupted by some mechanical problems upstream of the synthesis loop, the reduction was stretched out over nine days from the lighting of the startup heater to the first production of anhydrous ammonia product. Analysis of the reduction experience indicates that if the makeup gas interruptions had not occurred, the reduction could have been accomplished within five days or less.

The plant has now been in operation for thee years. No mechanical problems have originated with the reactors, but one problem which originated in the reactor effluent waste heat boiler caused a serious upset in the second reactor. This occurred during the three months following initial operation. A leak developed in the tube seal welds of the waste heat boiler. Referring to Figure 5, water from this leak backed up into the bottom cone of the second reactor during a shutdown. The water damaged the catalyst in the bottom cone and apparently caused some cracks in the catalyst support plug and in the catalyst container near the seam weld at the top of the cone. In September 1969, the catalyst in the second reactor was removed, the exchanger was repaired, the support plug was replaced, and a liner section was welded over the cracked area of the cone weld.

The catalyst removal was accomplished by removing the bottom flange and catalyst support plug, jetting the caked catalyst out of the bottom cone with water, then allowing the rest of the catalyst to flow freely through the opening. The catalyst that flowed out of the reactor was hosed down to control the heat of oxidation. It took 8 hr. from the time the bottom flange was opened until all the catalyst was emptied from the reactor.

The reloading took 20 hr. The restart, including reduction of the new catalyst, from the time of heater lightoff to ammonia production, was completed in 30 hr. Additional repairs were necessary later on to finally eliminate the water leakage, but revised operating procedures prevented any further water backup into the reactor. The replacement catalyst in the second reactor and the initial charge in the first reactor are still in service.

The reactors operated at production rates as high as 115% of design two years after startup. Now, after three years, they operate at 105% of design production with a pressure still 200 lb./sq. in. below design, and a pressure drop through the two reactors 25 lb./sq. in below design.

Referring to Figure 6 again, control of reactor temperatures has been particularly easy. It has proven unnecessary to exceed 760°F during any mode of operation.

The self-limiting characteristics of the outlet temperature have also been proven in operation. The highest outlet temperature measured has been 1,000°F at the outlet of the first reactor. This was reached momentarily on two occasions when operation was resumed after a short interruption with the reactors still hot. In these instances, circulation was restarted at an unnecessarily low rate – about 20% of design. Reactor outlet temperatures are now held at design levels or lower during hot restarts by resuming circulation at a higher initial rate.

After a short shutdown, the reactor can be restarted almost instantaneously without lighting the startup heater if the catalyst has not cooled below about 700°F. This does not occur until about 24 hr. after a shutdown.

Restart time from a cold condition is limited only by the rate at which the equipment can be warmed up safely. It takes about 6 hr. from introduction of gas into the loop to production of ammonia.

In Summary

A two-stage adiabatic ammonia synthesis converter, which provides the nine desirable features outlined at the beginning of this article, has been designed, installed, and operated successfully for three years. It is economically attractive and it has proven to be simple, convenient, and safe to load, unload, operate, and control. Certain features of the design are the subject of patent applications.

Acknowledgement

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