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UREA PLANTS FOR THE 21ST CENTURY

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Overview

As global industry is changing to respond to the ever increasing difficulty of economic and environmental challenges, the design and operation of urea plants must also react to the changing market to become more economical, energy efficient and environmentally clean. Technologies for the production of urea, originally developed by Urea Technologies, Incorporated (UTI), and now being offered by Monsanto Enviro-Chem Systems, Inc. (MEC), have resulted in considerable improvements to the design of commercial urea plants.

Urea plants providing improved economics are currently available. In the early days of urea manufacture, corrosion problems were at the forefront of operations. To battle this problem, reactors were frequently lined with expensive materials such as silver, zirconium, lead or titanium. For example, Dupont, unable to find a desirable corrosion resistant alloy for its first urea plant at Belle, West Virginia in 1930, lined its two foot diameter and 20 foot long reactor with silver.

The Heat Recycle Urea Process (HRUP), originally introduced to the Fertilizer Industry by UTI in 1977, significantly reduces corrosion in the reactor, heat exchangers and other process equipment. In HRUP designs, the only low carbon stainless steel material required is for the reactor liner and internals. All of the heat exchangers are of conventional mechanical design using type 316 or 304L stainless steel materials. The corrosion problem is practically eliminated due to the relatively high NH₃ to CO₂ mole ratio throughout the process. In fact, the useful life of metal parts in contact with the HRUP process solution have gradually improved to the point that corrosion in the reactor, heat exchangers and piping materials has been practically eliminated.

The mechanical design of high pressure pumps required to recycle the unconverted material back to the reactor has also substantially improved, eliminating frequent pump failures. Expensive vertical structures are no longer necessary as the urea synthesis unit is extended horizontally, eliminating the need for high and costly structures. The reactor and other pieces of heavy equipment are self supporting on foundations. These mechanical and structural improvements increase the on-stream time and operability while decreasing the overall project cost.

Other options for economical, efficient urea plant design include modularized, skid mounted urea plants up to 600 T/D, which offer substantial savings in construction costs and delivery time as well as an improvement in quality control of the constructed plant. Each module is sized to fit on a truck or a ship for easy transport. Two complete urea synthesis units utilizing this modularized concept have been built in North America and shipped to Africa.

Efficient and economical MEC designed urea plants are possible today by achieving high conversion in the reactor along with computerized process control optimization. An isothermal, countercurrent reactor with an open ended internal coil significantly improves conversion of carbamate to urea. Conversion values up to 77% are achieved in existing UTI installations.

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The Isothermal Urea Reactor (refer to Figure 1)

Reactor efficiency is the most important factor governing the economics of a urea plant. The higher the reactor efficiency, the higher the conversion of CO_2 to urea per reactor pass at a given NH_3/CO_2 and $\text{H}_2\text{O}/\text{CO}_2$ mole ratio, and consequently the lower the overall plant investment cost and utility consumption.

The proprietary isothermal urea reactor design available from MEC, balances the heat throughput of the reactor and optimizes feed rates, thereby maximizing conversion. This design minimizes energy consumption downstream of the reactor and maximizes plant efficiency, making the overall investment economically justifiable.

A very consistent actual relationship between reactor conversion, NH_3/CO_2 mole ratio, $\text{H}_2\text{O}/\text{CO}_2$ mole ratio and reactor temperature exists and was determined by UTI after years of practical experience. This relationship of reactor efficiency determines the economics of the urea plant and can be used in evaluating existing conventional reactor installations.

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The operational efficiency of the urea reactor can be calculated either by determining the actual urea production rate, the high pressure NH_3 reactor feed, the high pressure CO_2 reactor feed, the high pressure carbamate recycle solution reactor feed and its composition, or by analyzing the reactor effluent before any decomposition or stripping of the reactor effluent is performed.

In practice, a great difference in reactor efficiency exists at constant temperature. This mainly depends upon reactor internals and upon the extent of counter-current heat exchange inside the reactor between the exothermic reaction of NH_3 and CO_2 to carbamate, and the endothermic conversion of carbamate to urea and water. For instance, a conventional reactor originally installed in a horizontal position within a urea plant in the USA in 1962, provided with efficient internal trays and receiving the feeds at one of its ends, yielded a conversion per pass of total CO_2 to urea of 49% when operating at a NH_3/CO_2 mole ratio of 3:1 and at a $\text{H}_2\text{O}/\text{CO}_2$ mole ratio of 0.4:1 at 186°C . The back calculated efficiency of this reactor was low, mainly as a consequence of poor mixing and poor absorption of gaseous reactants by the liquid phase.

Several months later the above same reactor was re-installed into a vertical position to receive the feeds at its bottom end without any modifications to its internals, and it yielded a conversion per pass of 58.66% under the same operating conditions as above. This modification increased the efficiency, as seen by the increased conversion.

Years later, a vertical UTI reactor provided with an internal coil for counter-current heat exchange and with efficient trays at 193°C yielded a total CO_2 conversion to urea of 75% at an NH_3/CO_2 mole ratio of 4.2:1 and at a $\text{H}_2\text{O}/\text{CO}_2$ mole ratio of 0.7:1. As seen by this data, the isothermal UTI reactor far outperformed the conventional design and maximized reactor conversion.

High conversion substantially reduces the size of associated equipment in the carbamate decomposition (or stripping) and absorption sections required to recycle the unconverted carbamate back to the reactor, and it reduces the plant investment cost and the utility consumption.

MEC/UTI counter-current isothermal reactors have been in continuous operation for more than 15 years with excellent results and with no corrosion of their internals. The design operating conditions of the reactor which eliminate corrosion make the long term economics very appealing. For comparison, in the lifetime of an urea plant, a conventional reactor will be repaired every few years and replaced at least once due to high corrosion.

In this same time frame, the originally installed MEC isothermal urea reactor will still be operating and have shown virtually no corrosion, eliminating costs related to reactor repair and replacement.

Heat Recovery (refer to Figure 2)

Large amounts of heat are generated with the urea process. Instead of being irreversibly and uneconomically rejected to cooling water, heat generated within the MEC/UTI urea process is re-utilized internally for decomposition of unconverted carbamate, reactor feed preheating and urea product concentration. The heat exchangers used to recover this heat are of a conventional shell and tube design, made of standard 316 stainless steel material. Based on the above heat recovery features, this urea process was termed the Heat Recycle Urea Process (HRUP).

The recovery of heat and the redesign of the urea process significantly reduces the consumed energy requirements. The maximum steam pressure required as an input to the process is only 10.2 atm, thus not requiring usage of expensive high pressure steam from the ammonia plant.

For the entire urea plant, the overall steam consumption of 10.2 atm saturated steam is reduced to 0.7 tonnes per tonne of urea produced. This includes the urea synthesis section, the urea evaporation/prilling sections and the removal and recovery of ammonia and urea from the urea plant effluent, which is discharged with less than 2 PPM of residual NH_3 and urea.

Power Consumption

Only 60% of the total make-up CO_2 required to produce urea is delivered to the reactor for reaction with ammonia. The balance of 40% of the total make-up CO_2 is compressed to only 23 atm and injected into the HRUP system for heat recovery and for delivery to the reactor as carbamate for conversion to urea. As 40% of the CO_2 is no longer injected directly into the reactor, it results in considerable savings in compression power and equipment cost.

The overall power consumption is reduced to 75 kWh per metric tonne of urea produced, including the synthesis section, the urea evaporation/prilling sections, and the effluent treatment section.

Ammonium Bicarbonate as Raw Material

Several inquiries were received from China concerning the use of ammonium bicarbonate instead of CO_2 and NH_3 as a raw material for the production of urea. There are numerous ammonium bicarbonate/urea plants presently in operation throughout China.

In the HRUP system, ammonium bicarbonate can be used as an alternate to CO_2 gas, and introduced into the 17 atm First Absorber where the carbamate recycle stream and excess ammonia are collected for recycle to the urea reactor. As determined in tests, ammonium bicarbonate in the presence of excess ammonia very quickly is converted to ammonium carbamate in the First Absorber at the temperature of $\sim 88^\circ\text{C}$.

At bicarbonate feed rates above 70% of the equivalent total make-up CO_2 required to produce urea, the reactor becomes endothermic. As excess heat is now needed to drive the dehydration of carbamate to urea, this requires the internal reactor coil to be steam heated. The coil design remains similar to that of the proven design already used to produce steam in exothermic reactors of total recycle urea processes operated at the relatively low NH_3/CO_2 mole ratio of 2.6-3.2:1 with gaseous CO_2 reactor feed.

In addition, under the above conditions when bicarbonate is used a raw material, less heat is recovered in the Heat Recycle loop and more steam is used to concentrate the urea product.

Even though additional steam is required by the process, the overall economics of a urea plant operating on ammonium bicarbonate received from an existing ammonium bicarbonate plant with additional ammonia from an external source are very attractive. This is because the cost of the bicarbonate-nitrogen required to produce urea is much lower than the equivalent ammonia-nitrogen.

Computerized Urea Process Optimization System

UTI has developed advanced technology in plant computerized process monitoring, process control advisory systems and automatic process optimization control. This capability is installed in a proprietary computer system for optimizing the operations of the entire urea plant. The Optimization Computer system was developed mainly for specific use with a proprietary carbamate recycle solution Concentration Analyzer, also developed by UTI.

The Concentration Analyzer in conjunction with the Optimization Computer continuously gives a complete and very accurate analysis of the carbamate solution recycled to the reactor in terms of CO_2 (fixed in carbamate), NH_3 (free ammonia plus ammonia fixed in carbamate), water, and urea (if present).

Such analysis is essential for the calculation of the actual NH_3/CO_2 and $\text{H}_2\text{O}/\text{CO}_2$ reactor mole ratios, of the reactor conversion and of reactor efficiency, on the basis of the reactor feed streams and of the actual urea production rate. A complete breakdown of the carbamate recycle solution composition is calculated by the computer program every three seconds, thus allowing for a very fine control of the water content in the carbamate recycle solution, for the purpose of either preventing crystallization of carbamate in the carbamate recycle solution, or of preventing a drop in conversion in the reactor due to an excessive amount of water delivered to the reactor.

Powerful minicomputers are used to monitor approximately 200 process variables on a continuous basis, and to display on the computer screen about 25 important actual and target plant operating parameters, refreshed every 10 seconds. These target parameters can be implemented by the urea plant operators for the purpose of achieving optimum plant efficiency at the process conditions under which the urea plant is currently being operated.

In addition to monitoring the process variables, the minicomputer has the provision of optionally resetting the ten most critical automatic process controllers on the basis of a sophisticated software program. This a software program, consisting of about 20,000 program lines, was developed by UTI on the basis of actual plant operating data accumulated throughout years of observation and detection of various complicated relationships existing between process variables in a urea synthesis process. The very minute and continuous hourly automatic adjustments of the set points on the ten most critical process controllers result in a gradual decrease in overall energy consumption per tonne of urea to its lowest possible level. Using this method, a new and reliable set of operating data is developed for each new urea plant in order to achieve optimum operation and to supplement inexact or preconceived concepts about optimum urea plant process parameters.

The flexibility of the software program is such that it is able to continuously establish a new set of target operating process parameters, in case the performance of a specific piece of equipment changes due to deterioration or replacement. As an overall result, the urea plant is always maintained at the point of its lowest energy consumption, while achieving the maximum production rate, regardless of the potential change in efficiency of specific critical equipment. One of the most important benefits of such a constantly balanced and steady plant operation is the considerable reduction in plant shutdowns and in maintenance costs, resulting in an average 98% on-stream factor. As a result of the above mentioned improvements implemented in a MEC designed urea plant, the profitability of the installation is markedly increased.

Prilling Tower (refer to Figures 3 and 4)

Urea prills produced in towers utilizing concepts developed by UTI are hard, non-porous, spherical, cool, uniform in size and free of dust and hollow fragmented shells.

The average prill size is in the range of 1.6-2.2 minimum diameter for ~96% of the solid urea product. The crushing strength of the urea prills is in the range of 900 grams per prill, sufficient to allow for a pile of bagged urea ~25 meters high without product disintegration. This method for producing a 99.7 wt% urea melt containing 0.7 wt% biuret ready for prilling, consists of a very economical atmospheric air swept evaporator in which the air exhausted from the top of the evaporator is completely scrubbed of residual NH_3 in a water washed tray section (refer to Figure 3).

Prill towers using UTI's concepts are less expensive to build and are easier to operate with a high on-stream factor. All the large conventional urea prilling towers based on natural draft, with peripheral air intake at the bottom and peripheral air exhaust at the top have the same problem in common. This problem is that the air introduced into the tower has the tendency of rising through the tower along its walls, thus bypassing the stream of molten urea droplets falling through the central portion of the tower. As a consequence, very poor prill cooling efficiency results with consequent agglomeration of semi-molten urea product at the bottom of the prilling tower. This problem cannot be resolved by simply increasing the height of the prilling tower and the free fall of the molten urea, as was attempted in the past by designers of conventional prilling towers.

Furthermore, as urea plants grew in size, the diameter of the prilling tower increased. As a consequence, the intensity of the natural up-draft due to the chimney effect of the tower, originally very high in smaller prilling towers of relatively smaller diameter, diminished with the increase in tower diameter to the point of becoming negligible, thus requiring a considerable increase in prill free fall height and overall prilling tower height. The above facts led UTI to develop its own design for prilling towers, based on the novel principle of cross flowing the air and prills. Air is introduced into the tower peripherally at its base as in conventional towers, but it is exhausted from the top of the prilling tower centrally (refer to Figure 4), crossing the falling curtain of prills.

As a further improvement, the stream of molten urea is sprayed at the top of the tower through several gravity fed individual spray heads of unique design, and it is installed peripherally between the ductwork for the exhausted air and the tower walls. As a result, the stream of rising air inside the tower crosses the path of the free falling urea droplets, greatly increasing the prill cooling efficiency. Exhaust fans are added to the top of the air exhaust point, in order to compensate for the loss of the "chimney effect" in a large diameter tower.

As an example, a conventional prilling tower operating with difficulties at 700 MTPD prilling rate because of high urea prills temperature at the bottom discharge section, was redesigned to what is now MEC's cross-flow system and operated at 2,400 MTPD prilling rate at a bottom prill temperature below 70°C.

In this design, the importance of the actual prilling tower height and the prill free fall height is secondary, as long as a minimum free fall height of about 30 meters is ensured. For example, an existing conventional prilling tower with a prill free fall height of 31 meters was discharging hot urea prills above 70°C at the bottom during hot days in summer, when operating at its original design production rate of 160 MTPD. After redesign and conversion to central take off of air and cross flow within the tower, the same prilling tower produced 300 MTPD of prilled urea at a product temperature on the bottom discharge conveyor below 60°C.

The urea dust carryover in the air exhausted from the prilling tower is eliminated by spray heads with an improved design. This design consists of sizing the spray plate holes as to eliminate the formation of the fine molten urea mist that normally appears at the exit from conventional sprays. Such a fine mist of molten urea, if formed, quickly solidifies into very fine dust that remains entrained in the air stream and is carried overhead into the atmosphere. The pressure drop through UTI designed spray plate holes is maintained within an optimum range preventing the formation of the molten urea mist. The tower dust emission is well below governmental standards, in the range of about 10 mg of urea dust per cubic meter of exhausted air.

Hydrolyzer Stripper (refer to Figure 5)

Air and water pollution are two of the greatest concerns throughout the industrial world. In urea plants utilizing the UTI process, the liquid combined waste streams from ammonia and urea plants are reduced to less than 2

PPM each of residual ammonia and urea. Such cleaned streams can be recycled back to the plant as makeup to cooling towers or to low pressure boilers.

The main sources of pollution in urea plants are the liquid effluent contaminated with residual dissolved ammonia and urea, and the air from the prilling tower contaminated with entrained urea dust and urea degradation compounds. For each 60 tonnes of urea produced, 18 tonnes of process water are formed in the urea reactor by dehydration of 78 tonnes of ammonium carbamate to urea and water. Such process water formed in the urea reactor, contaminated with ammonia and urea, must be continuously discharged from the urea plant battery limits.

The aqueous urea product solution, discharged from the urea synthesis section, is usually concentrated and evaporated to 99.7 wt. % urea melt suitable for the production of a solid prilled or granulated urea. The urea concentration and evaporation are conventionally done under vacuum, and the resulting water vapor is condensed to a liquid. Such liquid inevitably contains residual ammonia and urea, from carry-over into the vapor phase during concentration and evaporation. Alternate methods are used in the industry to separate urea from the process water. One of them consists of the crystallization of urea in a crystallizer by evaporation of water under vacuum, followed by separation of urea crystals from the mother liquor. In another case, the water is evaporated under vacuum from the urea product and condensed to liquid. In either case, the re-condensed water vapor contains residual ammonia and urea, resulting in a large amount of contaminated liquid effluent requiring treatment.

Initially such contaminated effluents were delivered either to deep injection wells, to atmospheric evaporation ponds or to surrounding rivers. Such practices proved to be quite counterproductive due to the harmful effect of ammonia and urea in the water and in the atmosphere. The problem became so acute with the passing of years, that the fertilizer industry was forced to develop new technology to deal with the disposal of the contaminated liquid effluent from urea and ammonia plants, and in some cases from melamine plants.

Out of the need for new technology to reduce this growing pollution problem, and from years of research and development, UTI finalized a new design for a system capable of economically purifying such contaminated liquid effluent streams in a single step. Due to the fact that two chemically different compounds - ammonia and urea, each with different chemical properties - were present in the contaminated effluent, the general concept in the industry was to hydrolyze urea back to ammonium carbamate in one separate vessel at high pressure and temperature, and to strip ammonia from the contaminated effluent in another vessel at low pressure. Such a dual system, due to its complexity, proved to be quite expensive to build and operate. Furthermore, the effluent discharged from this complex system still contained an excessive amount of 100-200 PPM of both residual NH_3 and urea. Contrary to the above concept, UTI's development consists of a single vessel, operating at an intermediate pressure, in which the hydrolysis of urea back to ammonium carbamate for decomposition to ammonia and carbon dioxide is carried out concurrently with the stripping of ammonia from the liquid phase. The above simultaneous hydrolysis and stripping process operation prompted the name for this proprietary unit to be the Hydrolyzer Stripper.

The Hydrolyzer Stripper single unit consists of a tower with distillation trays. The bottom section of the Hydrolyzer Stripper is steam heated to hydrolyze urea and to expel ammonia from the liquid phase. A small stream of CO_2 gas is added to the bottom section to facilitate the stripping of ammonia. The overhead gas discharged from the Hydrolyzer Stripper is condensed in an overhead condenser and delivered to the urea plant for total recovery of ammonia and CO_2 . The contaminated effluent fed to the Hydrolyzer Stripper is discharged from the bottom as pure condensate for reuse either as cooling tower makeup or as feed water makeup to a low pressure boiler system. With the addition of a deionizer, it can be fed to a high pressure boiler system.

During the past fifteen years, UTI has installed Hydrolyzer Strippers ranging in size from 5 to 75 M³/HR of contaminated feed. The Hydrolyzer Stripper is completely automated and does not require any supervision. It can accept effluent feeds containing up to 15 wt% NH_3 . The average 10.2 atm steam consumption is 0.06 tonnes per tonne of urea produced, at a residual NH_3 and urea content in the treated effluent of less than 2 PPM.

The Hydrolyzer Stripper can be either field erected, or delivered to the plant site in pre-fabricated and pre-tested modules for direct setting on concrete slabs. The latter method results in considerable savings in construction labor, and in a faster completion schedule. The period of time from receipt of such prefabricated modules at the plant site to test run of the unit usually averages five weeks. The value of the ammonia recovered from the contaminated effluent and returned to the urea plant can reduce the pay out period of the Hydrolyzer Stripper to approximately one year. Although this is an economic advantage, the main benefit of the Hydrolyzer Stripper remains to be the complete elimination of wastewater pollution.

Conclusions

Prompted by the rapid rise in energy costs, the Heat Recycle Urea Process was first implemented in the 1970's for complete process redesign and reduction in utility consumption for existing urea plants, which were based on inefficient and uneconomical process designs. Subsequently, numerous urea plants in the U.S. and abroad were successfully modified for a 60% increase in capacity, and redesigned to reduce their specific steam consumption from an average of 1.5 tonne/tonne to 0.6 tonne/tonne, or less. This was achieved at a fraction of the cost of a brand new urea plant designed to handle the incremental tonnage.

The advantages of the MEC urea process are many. The proprietary isothermal reactor design provides maximized conversion for any given feedstock while at the same time practically eliminating corrosion, maximizing reactor lifetime. The application of energy recovery using the HRUP system and the optimized equipment designs significantly reduce the power consumption, minimizing operating cost. The use of the Optimization Computer along with the Concentration Analyzer optimize the plant performance by maximizing efficiency and on-stream time. And from the back end of the plant, the modified prill tower design produces superior prills whose characteristics allow for easy storage and transportation.

The option to use ammonium bicarbonate or melamine as feedstocks, an impossibility in other urea plants, shows the flexibility of the MEC urea plant design, and its economical application to the varying urea markets in China.

The simplicity of the Hydrolyzer Stripper offers recovery of expensive raw materials and their recycle back to the urea plant. This maximizes efficiency of the plant performance while minimizing waste streams. The Hydrolyzer Stripper virtually eliminates the waste of NH_3 and urea from the plant, also minimizing any environmental impact.

UTI's urea technology, now available from MEC, is capable of solving many urea plant problems by maximizing operation efficiency to eliminating environmental waste problems. So, for any client's urea needs, whether they be process studies, plant revamps, or complete grassroots projects, Monsanto Enviro-Chem has the experience and capability to offer premiere urea technology in a high quality design package. This, along with a partnership of local capabilities, provides world class quality and services to the fertilizer industry.

Figure 1

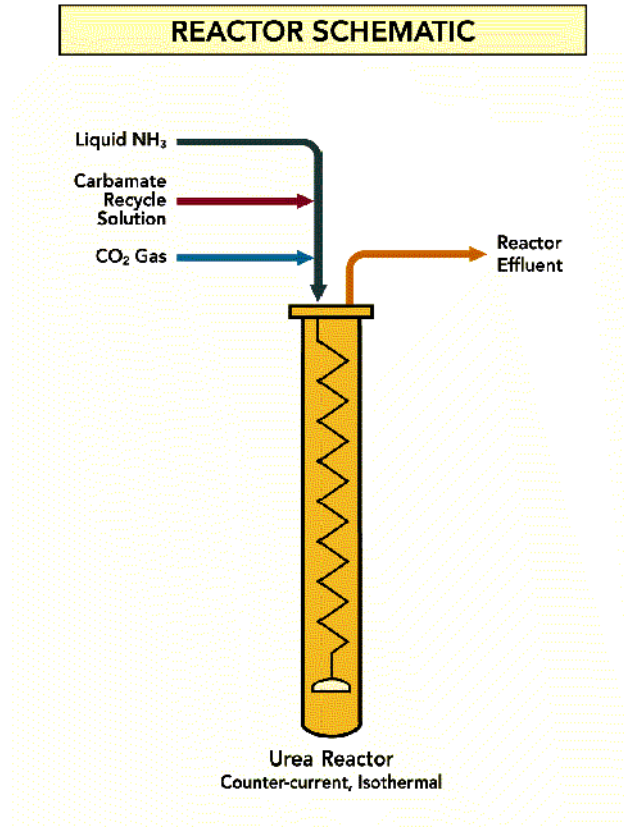


Figure 2

HEAT RECYCLE PROCESS

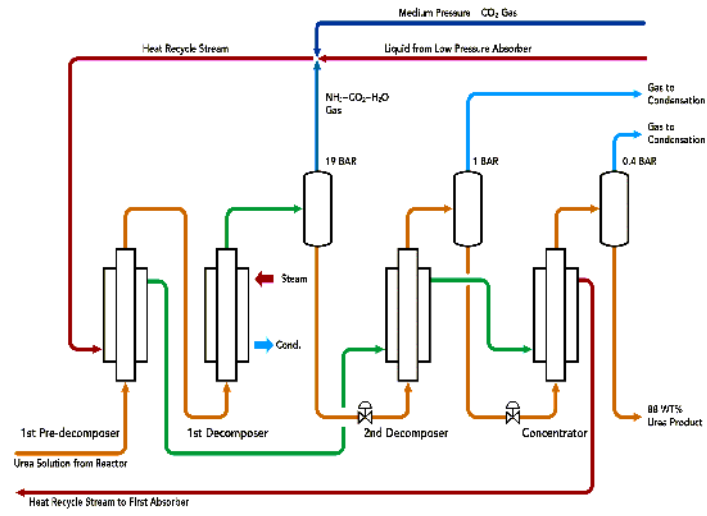


Figure 3

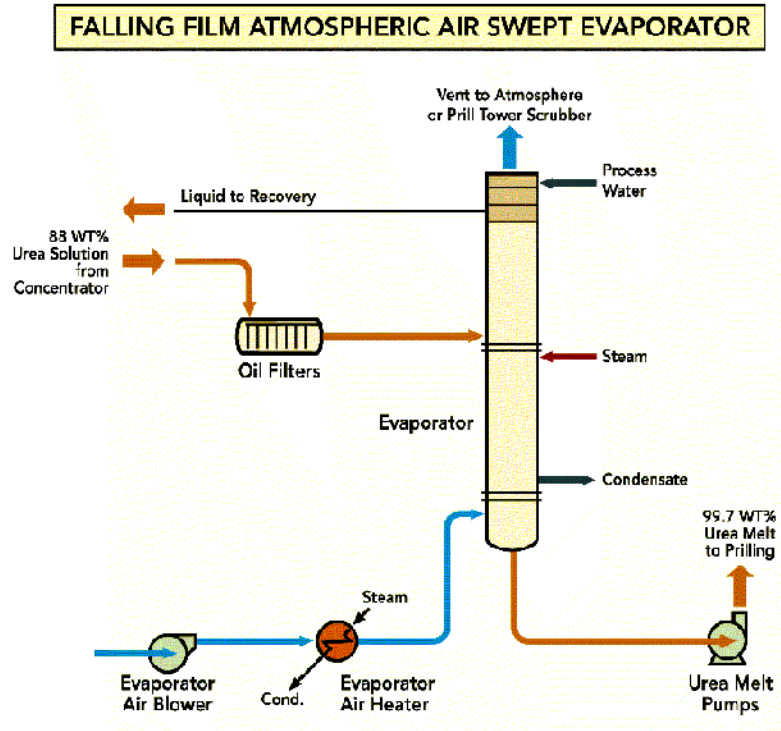


Figure 4

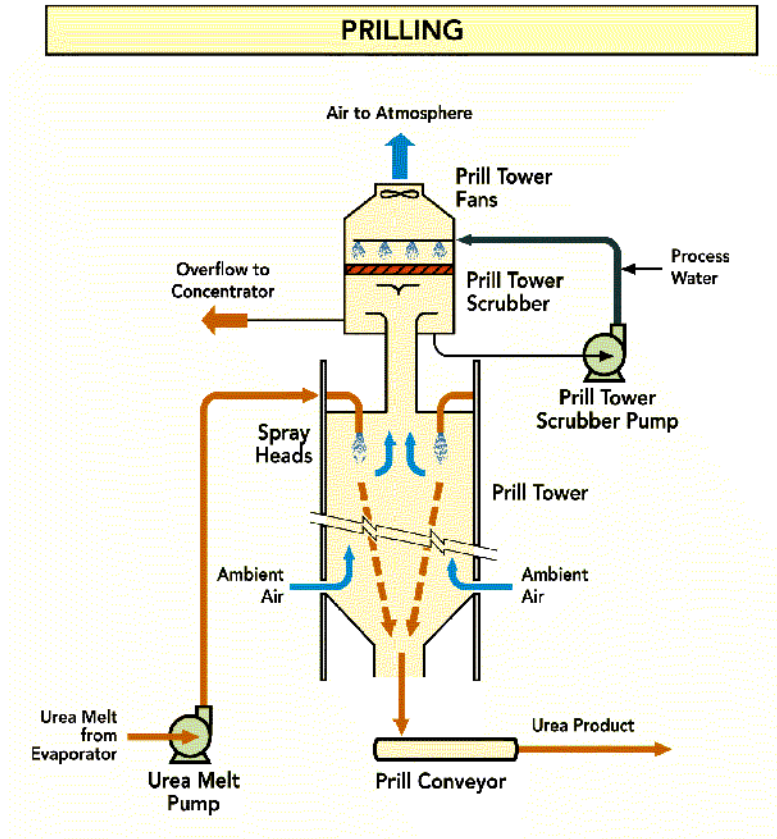


Figure 5

