“Urea Manufacturing Process”

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Abstract - Urea is an important nitrogenous fertilizer. Its utilization is increasing steadily, it being the preferred nitrogen fertilizer worldwide. It is used in solid fertilizer, liquid fertilizer, formaldehyde resins and adhesives. Rouelle first discovered urea in urine in 1773. His discovery was followed by the synthesis of urea from ammonia and cyanic acid by Woehler in 1828. This is considered to be the first synthesis of an organic compound from an inorganic compound. In 1870, Bassarow produced urea by heating ammonium carbamate in a sealed tube in what was the first synthesis of urea by dehydration [1]. The chemical formula of, NH2CONH2, indicates that urea can be considered to be the amide of carbamic acid NH2COOH, or the diamide of carbonic acid CO(OH)2. Fertilizer is generally defined as “any material, organic or inorganic, natural or synthetic, which supplies one or more of the chemical elements required for the plant growth”. The main aim of the fertilizer industry is to provide the primary and secondary nutrients which are required in macro quantities. Primary nutrients are normally supplied through chemical fertilizers. They are chemical compounds containing one or more of the primary nutrients and are generally produced by chemical reactions. Whatever may be the chemical compounds, its most important ingredient for plant growth is the nutrient content. The primary nutrients are Nitrogen, Phosphorus and Potassium. However, their concentration in a chemical fertilizer is expressed as a percentage of total nitrogen (N), available phosphate (P2O5) and soluble K2O. The grade of a fertilizer is expressed as a set of three numbers in the order of percent N, P2O5 and K2O. If a nutrient is missing in a fertilizer, it is represented by a zero. Thus ammonium sulphate is represented by 20.6-0-0.

INTRODUCTION

Urea is an organic compound with the chemical formula (NH2)2CO. Urea is also known by the International Nonproprietary Name (INN) carbamide, as established by the World Health Organization. Other names include carbamide resin, ISO urea, carbonyl diamide, and carbonyl diamine [1].

1.1 History

Rouelle first discovered urea in urine in 1773. His discovery is followed by the synthesis of urea from ammonia and cyanic acid by Woehler in 1828. This is considered to be the first synthesis of an organic compound from an inorganic compound. In 1870, Bassrow produced urea by heating ammonium carbamate in a sealed tube in what is the first synthesis of urea by dehydration.

1.2 Synthetic urea

It is the first organic compound to be artificially synthesized from inorganic starting materials, in 1828 by Friedrich Wohler, who prepared it by the reaction of potassium cyanate with ammonium sulfate. This artificial urea synthesis is mainly relevant to human health because of urea cycle in human beings. Within the 20th century it is found to be the best nitrogenic fertilizer for the plants and became widely used as a fertilizer. Urea is the leading nitrogen fertilizer worldwide. Apart from that urea is being utilized in many other industries. Urea’ is produced on a scale of some 100,000,000 tons per year worldwide. For use in
industry, urea is produced from ammonia and carbon dioxide. Urea can be produced as prills, granules, flakes, pellets, crystals, and solutions. More than 90% of world production is destined for use as a fertilizer. Urea has the highest nitrogen content of all solid nitrogenous fertilizers in common use (46.7%). Therefore, it has the lowest transportation costs per unit of nitrogen nutrient. Urea is highly soluble in water and is, therefore, also very suitable for use in fertilizer solutions (in combination with ammonium nitrate) [1].

1.3 Commercial production of urea

Urea is commercially produced from two raw materials, ammonia, and carbon dioxide. Large quantities of carbon dioxide are produced during the manufacture of ammonia from coal or from hydrocarbons such as natural gas and petroleum-derived raw materials. This allows direct synthesis of urea from these raw materials. The production of urea from ammonia and carbon dioxide takes place in an equilibrium reaction, with incomplete conversion of the reactants. The various urea processes are characterized by the conditions under which urea formation takes place and the way in which unconverted reactants are further processed. Unconverted reactants can be used for the manufacture of other products, for example ammonium nitrate or sulfate, or they can be recycled for complete conversion to urea in a total recycle process. Two principal reactions take place in the formation of urea from ammonia and carbon dioxide. The first reaction is exothermic:

$$2 \text{NH}_3 + \text{CO}_2 \leftrightarrow \text{H}_2\text{N-COONH}_4 \text{ (ammonium carbamate)} \quad H= -37.4 \Delta \text{Kcal/gm mol}$$

Whereas the second reaction is endothermic:

$$\text{H}_2\text{N-COONH}_4 \leftrightarrow (\text{NH}_2)_2\text{CO} + \text{H}_2\text{O} \quad H= +6.3 \text{Kcal/gm mol} \Delta$$

Both reactions combined are exothermic [1].

1.4 Chemical characteristics of urea

The urea molecule is planar and retains its full molecular point symmetry, due to conjugation of one of each nitrogen's P orbital to the carbonyl double bond. Each carbonyl oxygen atom accepts four N-H-O hydrogen bonds, a very unusual feature for such a bond type. This dense (and energetically favorable) hydrogen bond network is probably established at the cost of efficient molecular packing: The structure is quite open, the ribbons forming tunnels with square cross-section. Urea is stable under normal conditions [2].

### Table 1.1: Chemical characteristics of urea

<table>
<thead>
<tr>
<th>IUPAC name</th>
<th>Diaminomethanal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>(NH$_2$)$_2$CO</td>
</tr>
<tr>
<td>Molecular Mass</td>
<td>60.07 g/mol (approximate) Ph (100g/L-1 in water, 20°C)~9</td>
</tr>
<tr>
<td>Dipole moment</td>
<td>4.56</td>
</tr>
</tbody>
</table>

1.5 Physical characteristics of urea

Urea is a white odourless solid. Due to extensive hydrogen bonding with water (up to six hydrogen bonds may form-two from the oxygen atom and one from each hydrogen) urea is very soluble [2].

### Table 1.2: Physical Characteristics of Urea

<table>
<thead>
<tr>
<th>Density</th>
<th>1330 kg/m$^3$, solid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point,</td>
<td>132.7 °C (406 K) decompose</td>
</tr>
<tr>
<td>Boiling point</td>
<td>NA</td>
</tr>
<tr>
<td>Solubility in water</td>
<td>108 g/100 ml (20 °C) 167 g/100 ml (40 °C) 251 g/ 100 ml (60 °C)</td>
</tr>
</tbody>
</table>
1.6 Raw materials

1.6.1 Ammonia

Ammonia (NH₃) is a comparatively stable, colourless gas at ordinary temperatures, with a boiling point of -33 °C. Ammonia gas is lighter than air, with a density of approximately 0.6 times that of air at the same temperature. The characteristic pungent odors of ammonia can be detected as low as 1-2 Sppm. Ammonia can be highly toxic to a wide range of organisms. When dissolved in water, elevated levels of ammonia are also toxic to a wide range of aquatic organisms. Ammonia is highly soluble in water, although solubility decreases rapidly with increased temperature. Ammonia reacts with water in a reversible reaction to produce ammonium (NH₄⁺) and hydroxide (OH⁻) ions, as shown in reaction. Ammonia is a weak base, and at room temperature only about 1 in 200 molecules are present in the ammonium form (NH₄⁺). The formation of hydroxide ions in this reaction increases the pH of the water, forming an alkaline solution. If the hydroxide or ammonium ions react further with other compounds in the water, more ammonia will react to reestablish the equilibrium.

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)^+ + \text{OH}^- 
\]

While ammonia-air mixtures are flammable when the ammonia content is 16-25% by volume, these mixtures are quite difficult to ignite. About 85% of the ammonia produced worldwide is used for nitrogen fertilizers. The remainder is used in various industrial products including fibers, animal feed, and explosives [3].

1.6.2 Carbon Dioxide

CO₂ is an odorless and colorless gas which contains 0.03% in the atmosphere. It is emitted as a pollutant from number of industries. CO₂ can be obtained from ammonia production process as a byproduct [3].

1.7 Applications of urea

1.7.1 Agricultural use

More than 90% of world production is destined for use as a fertilizer. Urea is used as a nitrogen-release fertilizer, as it hydrolyses back to ammonia and carbon dioxide, but its most common impurity, biuret, must be present at less than 2%, as it impairs plant growth. Urea has the highest nitrogen content of all solid nitrogenous fertilizers in common use (46.4%N.). Urea is highly soluble in water and is therefore also very suitable for use in fertilizer solutions, e.g. in foliar feed fertilizers.

Commercially, fertilizer urea can be purchased as prills or as a granulated material. In the past, it is usually produced by dropping liquid urea from a "prilling tower" while drying the product. The prills formed a smaller and softer substance than other materials commonly used in fertilizer blends. Today, though, considerable urea is manufactured as granules. Granules are larger, harder, and more resistant to moisture. As a result, granulated urea has become a more suitable material for fertilizer blends [3].

1.7.2 Spreading of Urea

Urea can be bulk-spread, either alone or blended with most other fertilizers. Urea often has a lower density than other fertilizers with which it is blended. Urea and fertilizers containing urea can be blended quite
readily with monoammonium phosphate (11-52-0) or Diammonium phosphate (18-46-0). Urea should not be blended with superphosphates unless applied shortly after mixing. Urea will react with superphosphates, releasing water molecules and resulting in a damp material which is difficult to store and apply.

Urea fertilizer can be coated with certain materials, such as sulphur, to reduce the rate at which the nitrogen becomes available to plants. Under certain conditions these slow-release materials result in more efficient use by growing plants. Urea in a slow release form is popular for use on golf courses, parks, and other special lawn situations.

1.7.3 Industrial use

I Urea have the ability to form 'loose compounds', called clathrates, with many organic compounds. The organic compounds are held in channels formed by interpenetrating helices comprising of hydrogen-bonded urea molecules. This behaviour can be used to separate mixtures, and has been used in the production of aviation fuel and lubricating oils. As the helices are interconnected, all helices in a crystal must have the same 'handedness'. This is determined when the crystal is nucleated and can thus be forced by seeding. This property has been used to separate racemic mixtures [3].

1.7.4 Further commercial uses,

- A stabilizer in nitrocellulose explosives.
- A component of fertilizer, providing a relatively cheap source of nitrogen to promote growth. A raw material for the manufacture of plastics, to be specific, urea-formaldehyde resin.
- A raw material for the manufacture of various glues (urea-formaldehyde or urea melamine-formaldehyde); the latter is waterproof and is used for marine plywood.
- An alternative to rock salt in the de-icing of roadways and runways; it does not promote metal corrosion to the extent that salt does.
- An additive ingredient in cigarettes, designed to enhance flavour.
- A browning agent in factory-produced pretzels. An ingredient in some hair conditioners, facial cleansers, bath oils, and lotions.
- A reactant in some ready-to-use cold compresses for first-aid use, due to the endothermic reaction it creates when mixed with water.
- A cloud seeding agent, along with salts, to expedite the condensation of water in clouds, producing precipitation.
- An ingredient used in the past to separate paraffin’s, due to the ability of urea to form clathrates (also called host-guest complexes, inclusion compounds, and adducts).
- A Flame proofing agent (commonly used in dry chemical fire extinguishers as Urea potassium bicarbonate).
- An ingredient in many tooth whitening products.
- A cream to soften the skin, especially cracked skin on the bottom of one’s feet.
- Feed for hydrolyzation into ammonia which in turn is used to reduce emissions from Power plants and combustion engines. Other, miscellaneous products such as de-icing material for airport runways.
- Although on a smaller scale than as a fertilizer or as raw material for synthetic resins, urea is...
also used as a raw material or auxiliary material in the pharmaceutical industry, the fermenting and rewing industries and in the petroleum industry [3].

1.7.5 Laboratory use

Urea is a powerful protein denaturant. This property can be exploited to increase the solubility of some proteins. For this application, it is used in concentrations up to 10M. Urea is used to effectively disrupt the covalent bonds in proteins. Urea is an ingredient in the synthesis of urea nitrate. Urea nitrate is also a high explosive very similar to ammonium nitrate; however it may even be more powerful because of its complexity.

1.7.6 Global uses of urea

Urea can be added directly to feed, such as in urea-treated wheat or rice straw, or mixed with molasses (urea-molasses licks” or urea multi-nutrient blocks”) for sheep, cattle, buffalo and horses. Urea may also be used as a fertilizer of the grasslands on which cattle or sheep may graze.

Another direct application of urea to land is as urea-based herbicides or pesticides (sulfonyl urea pesticides). In this case, urea is chemically synthesized with a poison or inhibitor. Sulfonyl urea is one of the preferred herbicides for broadleaf and grassy weeds. Urea may also be spread on agricultural crops to prevent frost when temperatures drop «to a level that may cause crop damage and commercial formulations of urea are available for this purpose. It is used in the growing world aquaculture industry. In intensive shrimp culture, for example, ponds may be fertilized with urea and superphosphate to initiate an algal bloom that eventually serves as food for the commercial resource. A significant proportion of such nutrients are subsequently discharged to local waters with pond effluent, as only a small fraction of added nutrients ultimately winds up in marketable product.

May also be spread on coastal oil spills, to stimulate the growth of natural bacteria populations which break down the oil. In addition to the direct applications of urea to land and sea, urea is used in many other applications, including manufacture of a wide range of common materials such as urea formaldehyde and plastics. This use represents about 50% of the non-fertilizer urea. There are numerous uses of urea in holistic medicine therapies. One application currently being considered which would greatly expand the global use of urea is as a reductant in catalytic and non catalytic reduction of combustion products in vehicles [3].

2. Body of Paper

The body of the paper consists of numbered sections that present the main findings. These sections should be organized to best present the material.

It is often important to refer back (or forward) to specific sections. Such references are made by indicating the section number, for example, “In Sec. 2 we showed…” or “Section 2.1 contained a description…” If the word Section, Reference, Equation, or Figure starts a sentence, it is spelled out. When occurring in the middle of a sentence, these words are abbreviated Sec., Ref., Eq., and Fig.

At the first occurrence of an acronym, spell it out followed by the acronym in parentheses, e.g., charge-coupled diode (CCD).

LITERATURE REVIEW

Several processes are used for urea manufacturing. Some of them used are conventional technologies and others use modern technologies to achieve high efficiency. These processes have several comparable advantages and disadvantages based on capital cost, maintenance cost, energy cost, efficiency and product quality.

Some of the widely used urea production processes are [4].
i. Conventional processes
ii. Stamicarbon CO2 stripping process
iii. Snarnprogetti Ammonia and self-stripping process
iv. Isobaric double recycle process

2.1 Conventional Processes

2.1.1 Once through Process

In this process as shown in figure 2.1 non converted ammonia is neutralized with acid such as nitric acid to produce ammonium salt such as ammonium nitrate as co-products of urea production. In this way, a relatively simple urea process scheme is realized. The main disadvantages of this process are the large quantity of ammonia salt formed as co-product and the limited amount of overall carbon dioxide conversion that can be achieved [4].

2.1.2 Conventional Recycle Process

Here all of the non-converted ammonia and carbon dioxide are recycled to the urea reactor. In first generation of this process the recirculation of non-converted NH₃ and CO₂ is performed in two stages. The first recirculation is operated at medium pressure (18-25 bars); the second at low pressure (2-5 bars). The first recirculation comprises at least a decomposition heater, in which carbamate decomposes into gaseous NH₃ and CO₂, and while excess NH₃ evaporate simultaneously. The off gas from this first decomposition step is subjected to rectification, from which relatively pure ammonia at the top and a bottom product consisting of an aqueous ammonium carbamate solution are obtained. Both products are recycled separately to the urea reactor. In these processes, all non-converted CO₂ is recycled as associated water recycle. All conventional processes therefore typically operate at high NH₃:CO₂ ratios (4-5 mol/mol) to maximize CO₂ conversion per pass. Although some of these conventional processes partly equipped with ingenious heat exchanging networks have survived until now.

Their importance decreased rapidly as the so-called stripping process is developed [4].

Fig. 2.1: Once through Process Flow Diagram [4]

2.2 Stamicarbon CO₂ -stripping process

In this process to achieve maximum urea yield per pass through the reactor at the stipulated optimum pressure of 140 bars, an NH₃:CO₂ molar ratio of 3:1 is applied. The greater part of the unconverted carbamate is decomposed in the stripper, where ammonia and carbon dioxide are stripped off. This stripping action is effected by counter current contact between the urea solution and fresh carbon dioxide at synthesis pressure. Low ammonia and carbon dioxide concentration in the stripped urea solution are obtained. Such that the recycle from the low pressure recirculation stage is minimized. This low concentration of both ammonia and carbon dioxide in the stripper effluent can be obtained at relatively low temperatures of the urea solution because carbon dioxide is only sparingly soluble under such conditions. Condensation of ammonia and carbon dioxide gases, leaving the stripper, occurs in the high pressure carbamate condenser as synthesis pressure. As a result, the heat liberated from ammonium carbamate formation is at a high temperature. This heat is used for
the production of 4.5bar steam for use in the urea plant itself. The condensation in the high pressure carbamate condenser is not effected completely. Remaining gases are condensed in the reactor and provide the heat required for the dehydration of carbamate, as well as for heating the mixture to its equilibrium temperature. In recent improvement to this process, the condensation of off gas from the stripper is carried out in a pre-reactor, where sufficient residence time for the liquid phase is provided.

As a result of urea and water formation in condensing zone, the condensation temperature is increased, thus enabling the production of steam at higher pressure level. The feed carbon dioxide, invariably originating from an associated ammonia plant, always contains hydrogen. To avoid the formation of explosive hydrogen oxygen mixture in the tail gas of the plant, hydrogen is catalytically removed from the CO2 feed. Apart from the air required for this purpose, additional air is supplied to the fresh CO2 input stream. This extra potion of oxygen is needed to maintain a corrosion-resistance layer on the stainless steel in the synthesis section. Before the inert gases, mainly oxygen and nitrogen, are purged from the synthesis section, they are washed with carbamate solution from the low pressure recirculation stage in the high pressure scrubber to obtain a low ammonia concentration in the subsequently purged gas. Further washing of the off gas is performed in a low pressure absorber to obtain a purge gas that is practically ammonia free. Only one low pressure recirculation stage is required due to the low ammonia and carbon dioxide in the stripped urea solution. Because of the ideal ratio between ammonia and carbon dioxide in the recovered gases in this section, water dilution of the resultant ammonium carbamate is at a minimum despite the low pressure (about 4 bar). As a result of efficiency of the stripper, the quantities of ammonium carbamate for recycle to the synthesis section are also minimized, and no separate ammonia recycle is required. The urea solution coming from the recirculation stage contains about 75 wt. % urea. This solution is concentrated in the evaporation section. If the process is combined with a prilling tower for final product shaping, the final moisture content of urea from the evaporation section is 0.25 wt. %. If the process is combined with a granular unit, the final moisture content may vary from 1 to 5 wt. %, depending on granulation requirements. Higher moisture content can be realized in a single stage vaporator; whereas low moisture content is economically achieved in a two stage evaporation section.

When urea with extremely low biuret content is required (at maximum of 0.3 wt. %) pure urea crystals are produced in a crystallization section. These crystals are separated from the mother liquor by combination of sieve bends and centrifuges and are melted prior to final shaping in a prilling tower or granulation unit.

The process condensate emanating from water evaporation from the evaporation or crystallization sections contains ammonia and urea. Before this process condensate is purged, urea is hydrolysed into ammonia and carbon dioxide, which are stripped off with steam and return to urea synthesis via the recirculation section. This process condensate treatment section can produce water with high purity, thus transforming this “waste water” treatment into the production unit of a valuable process condensate, suitable for, e.g., cooling tower or
boiler feed water makeup. Since the introduction of the Stamicarbon CO₂ stripping process, some 125 units have been built according to this process all over the world [5].

**Fig. 2.2 CO₂ stepping process flow diagram**

### 2.3 Snamprogetti Ammonia and self-stripping process N

In the first generation of NH₃ and self-stripping processes, ammonia is used as stripping agent. Because of the extreme solubility of ammonia in the urea containing synthesis fluid, the stripper effluent contained rather large amounts of dissolved ammonia, causing ammonia overload in downstream section of the plant. Later versions of the process abandoned the idea of using ammonia as stripping agent; stripping is achieved only by supply of heat. Even without using ammonia as a stripping agent, the NH₃:CO₂ ratio in the stripper effluent is relatively high. So the recirculation section of the plant requires an ammonia-carbamate separation section the process uses a vertical layout in the synthesis section. Recycle within the synthesis section, from the stripper via the high pressure carbamate condenser, through the carbamate separator back to the reactor, is maintained by using an ammonia-driven liquid-liquid ejector. In the reactor, this is operated at 150 bars, NH₃:CO₂ molar feed ratio of 2:1 is applied. The stripper is of the falling film type. Since stripping is achieved thermally, relatively high temperatures (200-210 °C) are required to obtain a reasonable stripping efficiency. Because of this high temperature, stainless steel is not suitable as a construction material for the stripper from a corrosion point of view; titanium and bimetallic zirconium stainless steel tubes have been used off gas from the stripper is condensed in a kettle type boiler. At the tube side of this condenser the off gas is absorbed in recycled liquid carbamate from the medium pressure recovery section. The heat of absorption is removed through the tubes, which are cooled by the production of low pressure steam at the shell side. The steam produced is used effectively in the back end of the process. In the medium pressure decomposition and recirculation section, typically operated at 18 bar, the urea solution from the high pressure stripper is subjected to the decomposition of carbamate and evaporation of ammonia. The off gas from this medium pressure decomposer is rectified. Liquid ammonia reflux is applied to the top of this rectifier; in this way a top product consisting of pure gaseous ammonia and a bottom product of liquid ammonium carbamate are obtained. The pure ammonia off gas is condensed and recycled to the synthesis section.

To prevent solidification of ammonium carbamate in the rectifier, some water is added to the bottom section of the column to dilute the ammonium carbamate below its crystallization point. The liquid ammonium carbamate-water mixture obtained in this way is also recycled to the synthesis section. The purge gas of the ammonia condenser is treated in a scrubber prior to being purged to the atmosphere. The urea solution from the medium pressure decomposer is subjected to a second low pressure decomposition step. Here further decomposition of ammonium carbamate is achieved, so that a substantially carbamate-free aqueous urea solution is obtained. Off gas from this low pressure decomposer is condensed and recycled as an aqueous ammonium carbamate solution to the synthesis section via the medium pressure recovery section. Concentrating the urea water mixture obtained from the low pressure decomposer is performed in a single or double evaporator depending on the requirement of the finishing section. Typically, if prilling is chosen as the final shaping procedure, a two stage evaporator is required, whereas in the case of a fluidized bed granulator a single evaporation step is sufficient to achieve the required final moisture content of the urea.
melt. In some versions of the process, heat exchange is applied between the off gas from the medium pressure decomposer and the aqueous urea solution to the evaporation section. In this way, the consumption of low pressure steam by the process is reduced. The process condensate obtained from the evaporation section is subjected to desorption hydrolysis operation to recover the urea and ammonia contained in the process condensate [6].

![Fig 2.3: SW diagram [6]](image)

**2.4 Isobaric double recycle process**

This process is developed by Mont Edison, is characterized by recycle of most of the unreacted ammonia and ammonium carbamate in two decomposer in series, both operating at the synthesis pressure. A high molar NH$_3$:CO$_2$ ratio (4:1 to 5:1) in the reactor is applied. As a result of this choice ratio, the reactor effluent contains a relatively high amount of non-converted ammonia. In the first, steam heated, high pressure decomposer, this large quantity of free ammonia is mainly removed from the urea solution. Most of the residual solution, as well as some ammonium carbamate, is removed in the second high pressure decomposer where steam heating and CO$_2$ stripping are applied. The high pressure synthesis section is followed by two low pressure decomposing stages of traditional design, where heat exchange between the condensing off gas of the medium pressure decomposition stage and the aqueous urea solution to the final concentration section improves the overall energy consumption of the process. Probably because of the complexity of this process, it has not achieved great popularity so far. This process or parts of the process are used in four revamps of older conventional plant [6].

**PROCESS SELECTION**

3.1 Selection of the Process

Snamprogetti ammonia-stripping urea process is selected because it involves a high NH$_3$ to CO$_2$ ratio in the reactor, ensuring the high conversion of carbamate to urea. The highly efficient ammonia stripping operation drastically reduces the recycling of carbamate and the size of equipment in the carbamate decomposition. Some comparison based on various Advantages & disadvantage among the processes are given below [7].

**Table 3.1: Comparison of processes**

<table>
<thead>
<tr>
<th>Process</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
- High energy cost.  
- High environment pollution  
- Large quantity of ammonia salt is formed as a coproduct |
| Conventional Process-Conventional recycle process | High CO$_2$ conversion | High production cost  
High energy cost |
Among above urea manufacturing processes, Snamprogetti process is selected because of it has following advantages compared to other processes

3.1.1 Advantages of Snamprogetti Ammonia and self-stripping process

- Less HP piping and construction materials owing to lower elevation layout, fewer HP vessels and simplified synthesis loop.
- Easier erection using commonly available construction equipment and techniques owing to low elevation layout and fewer and smaller HP vessels.
- Easier operation supported by forced circulation by HP ejector.
- Easier maintenance owing to low elevation layout and fewer HP equipment.
- Less energy consumption owing to optimized synthesis conditions and proprietarily designed reactor and stripper.
- Even though initial capital investment is higher than the other processes, it will overcome by lower production cost per metric ton of urea [7].

3.2 Manufacturing Process

In the reactor, when liquid ammonia reacts with compressed CO₂ (at 162 atm) at high temperature & pressure gives urea according to the following reactions:

\[
2\text{NH}_3 + \text{CO}_2 \rightarrow \text{NH}_2\text{COONH}_4
\]

exothermic

\[
\text{NH}_2\text{COONH}_4 \rightarrow \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O}
\]

endothermic

As the reactions are reversible in nature only partial conversion occurs in the reactor. Urea solution consisting of Urea, Carbamate, Water & unconverted CO₂ & NH₃ are fed into the stripper where stripping action of NH₃ favors decomposition of carbamate, and hence 80% of carbamate is decomposed here. Pressure in the stripper is same as that of the reactor.

Urea solution from the stripper is sent to Medium pressure decomposer where Urea purification takes place by the dehydration of the Carbamate. Urea solution is further purified in Low pressure decomposer. Off gases from the M P decomposer & L P decomposer are sent to the Medium pressure condenser & Medium pressure absorber for the recovery of unconverted Ammonia. In this way 71.12% of Urea solution resulting from L P decomposer is sent to Vacuum concentrators operating in two stages:

1) 1st Vacuum evaporator.
2) 2nd Vacuum evaporator

Finally, 98 % molten urea is sent to the Prilling Towers where Urea prills are formed by passing a current of cold air in the tower from the bottom. Proper size Urea prills are sent to bagging section through belt conveyors. In bagging section, coating of Urea prills may be done if required. Oversized Urea prills or lumps are sent to lump dissolving tank [8].

Urea Synthesis

NH₃ & CO₂ react under specific concentration, temperature & pressure 00nditions to form Urea as per the following reactions:

1) \( \text{CO}_2 (g) + 2\text{NH}_3 (g) \rightarrow \text{NH}_2\text{COONH}_4(S) \)

\[ H = -37.64 \text{ kcal/gm mol} \]
2) $\text{NH}_2\text{COONH}_4\ (s) \rightarrow \text{NH}_2\text{CONH}_2\ (s) + \text{H}_2\text{O}$
$H = 6.32 \text{ kcal/gm mol}$

**Overall Reaction:**

$\text{CO}_2\ (g) + 2\text{NH}_3\ (g) \rightarrow \text{NH}_2\text{CONH}_2\ (s) + \text{H}_2\text{O}$
$H = -31.32 \text{ kcal/gm mol}$

So, overall urea synthesis is exothermic, releasing heat of 31.32 kcal/gm mol at standard conditions of 1 atm pressure & 25°C. But actual heat available in a urea synthesis reaction will be only 5.74 kcal/gm mol because of the heat lost in evaporation of liquid $\text{NH}_3$, evaporation of water & melting of urea. This is based on the actual plant data. Further energy is consumed in feeding $\text{CO}_2$ & $\text{NH}_3$ at high temperature & pressure, in recycling of carbamate, in vacuum concentration of urea, for operating different pumps & compressors etc. which altogether makes the urea production energy consuming.

**3.3 Effect of Various Parameters Temperature**

In above reactions 1st reaction is exothermic & 2nd done is endothermic. So, according to Le chatelier’s Principle 1st reaction is favoured at low temp & 2nd done at high temp. Further, reaction no. 1 is fast & teaches to completion but reaction no. 2 is slow & determines the overall rate of urea production. For sufficient completion of reaction No.2 optimum temp is maintained. It is observed that max equilibrium conversion occurs between 190 to 200°C. If temp is increased beyond 200°C corrosion rate increases.

$\text{NH}_2\text{COONH}_4\ (s) \rightarrow 2\text{NH}_3\ (g) + \text{CO}_2\ (g)$
$H = -\text{ve} \ (K1)$

$\text{NH}_3\text{COONH}_4\ (s) \rightarrow \text{NH}_3\text{CONH}_2\ (s) + \text{H}_2\text{O}$
$H = \text{we} \ (K2)$

Both the reactions are favored at high temp but our objective is to maximize 2nd reaction as 1st reaction is undesirable in the reactor. So, our operating zone should be in the region where $K2>K1$.

**Pressure**

Overall urea synthesis reaction is given below:

$\text{CO}_2\ (g) + 2\text{NH}_3\ (g) \rightarrow \text{NH}_2\text{CONH}_2\ (s) + \text{H}_2\text{O}$

There is reduction in volume in the overall reaction & so high pressure favors the forward reaction. This pressure is selected according to the temp to be maintained & $\text{NH}_3$, $\text{CO}_2$ ratio.

**Concentration**

Higher the concentration of the reactants, higher will be the forward reaction according to the law of mass action. $\text{CO}_2$ being limiting reagent higher $\text{NH}_3$,$\text{CO}_2$ ratio favors conversion. Since, dehydration of carbamate results in urea production, lesser $\text{H}_2\text{O}$:$\text{CO}_2$ ratio favors conversion, water intake to the reactor should be therefore min. Residence Time

Since, urea conversion reaction is slowing, sufficient time is to be provided to get higher conversion. Reactor is designed to accommodate this with respect to the other parameters of temperature, pressure & concentration [9].

**3.4 Snamprogetti Stripping Process**

Formation of urea from ammonia & carbon-dioxide takes place through reversible reactions with formation of ammonium carbamate as intermediate product. Now, success of any urea manufacturing process depends on how economically we can recycle carbamate to the reactor. Snamprogetti process of urea manufacturing accomplishes the above task by stripping process.

$\text{NH}_2\text{COONH}_4\ (s) \rightarrow 2\text{NH}_3\ (g) + \text{CO}_2\ (g)$
$H = +37.4 \text{ Kcal/gm-mole}$

This reaction involves increase in volume & absorption of heat. Thus this reaction will be favoured by decrease in pressure & increase in temp. Moreover decreasing the partial pressure of either of the products will also favour the forward reaction. Process based on first principle of decrease in pressure & decrease in temp is called conventional process, whereas process based on increase/decrease of partial pressures of $\text{NH}_3$ or $\text{CO}_2$ is called stripping process. According to above equation we have:
\[ K = (P_{NH3})^2 \cdot (P_{CO2}) \]  
(where, \( K \) = equilibrium constant)

The stripping is effected at synthesis pressure itself using \( CO_2 \) or \( NH_3 \) as stripping agent. If \( CO_2 \) is selected, it is to be supplied to the decomposers/stripper as in Stamicarbon \( CO_2 \) stripping process. While if \( NH_3 \) is selected, it is to be obtained from the system itself because excess \( NH_3 \) is present in the reactor as in Snamprogetti process. \( CO_2 \) stripping is advantageous because introducing \( CO_2 \) increases \( P_{CO2} \). So \( P_{NH3} \) will be reduced to maintain \( P \) constant as \( P = P_{CO2} + P_{NH3} \). At a particular temp \( K \) is constant so when \( P_{NH3} \) is reduced to keep \( K \) constant, carbamate will be reduced much faster by decomposition as \( P_{NH3} \) appears in the equilibrium equation with a power of two. Selection of 1st stage decomposition should be in such a way that min water evaporates because the recovered gases go along with the carbamate to reactor again & if water enters reactor, production will be affected adversely due to hydrolysis of urea. So, stage wise decomposition of carbamate is done. Second consideration in favour of isobaric stripping is those higher carbamates recycle pressure results in condensation at higher temp & that recovery in the form of low pressure steam. This is why stage wise reduction in pressure is practiced [9].

### 3.4.1 Process Description

The urea production, process takes place through the following main operations:

i. Urea synthesis & high pressure recovery.

ii. Urea purification & low pressure recovery.

iii. Urea concentration.

iv. Urea prilling.

#### 3.4.1.1 Urea Synthesis & High Pressure Recovery

Urea is synthesized from liquid ammonia & gaseous carbon-di-oxide. The carbon dioxide drawn from battery limits at about 1.6 atm pressure & about 40°C temp is compressed in a centrifugal compressor up to 162 atm. A small quantity of air is added to the \( CO_2 \) compressor suction in order to passivate the stainless steel surfaces. Thus protecting them from corrosion due both to the reagent & the reaction product. The liquid ammonia coming directly from battery limits is collected in the ammonia receiver tank from where it is drawn to & compressed at about 23 atm pressures by means of centrifugal pump. Part of this ammonia is sent to medium pressure absorber & remaining part enters the high pressure synthesis loop. The \( NH_3 \) of this synthesis loop is compressed to a pressure of about 240 atm. Before entering the reactor it is' used as a driving fluid in the carbamate ejector, where the Carbamate coming from carbamate separator is compressed up to synthesis pressure. The liquid mixture of ammonia & carbamate enters the reactor where it reacts with compressed \( CO_2 \). In the reactor the \( NH_3 \& gaseous \ CO_2 \) react to form amm. Carbamate, a portion of which dehydrates to form urea & water. The fraction of carbamate that dehydrates is determined by the ratios of various reactants, operating temp, the residence time in the reactor & reaction pressure. The mole ratio of \( NH_3 / CO_2 \) is around 2:1; the mole ratio of water to \( CO_2 \) is around 0.67: 1.

\[
2NH_3 (g) + CO_2 (g) \rightarrow NH_2COONH_4(s) \quad \text{exothermic}
\]

\[
NH_2COONH_4(s) \rightsquigarrow NH_2CONH_2(s) + H_2O \quad \text{endothermic}
\]

In the synthesis conditions (\( T= 190^\circ C, P= 154 \) atm), the 1st reaction occurs rapidly & is completed. The 2nd reaction occurs slowly & determines the reactor volume. Urea reactor is a plug flow type with 10 no’s of sieve trays to avoid back mixing & to avoid escape of gaseous \( CO_2 \) which must react in the lower part of the reactor. Stage wise decomposition is carried out to reduce water carry over to the reactor which could adversely affect conversion. Urea solution containing...
urea, carbamate, H₂O & unconverted CO₂ & NH₃ enters the high pressure stripper where the pressure is same as that of the reactor. The mixture is heated as it flows down the falling film exchangers. The CO₂ content of the solution is reduced by the stripping action of NH₃ as it boils out of the solution. The carbamate decomposition heat is supplied by 24 atm steam. The overhead gases from shipper and the recovered solution from the MP absorber, all flow to the high pressure carbamate condenser through mixer, where total mixture, except for a few inert is condensed & recycled to the reactor by means of carbamate ejector. Condensing the gases at high temp & pressure permits the recovery of condensation heat in the production of steam at 4.5 atm in the high pressure carbamate condenser. From the top of the carbamate separator the incondensable gases come out consisting of inerts & a little quantity of NH₃ & CO₂ unreacted in the condenser. These are sent to the bottom of MP decomposer [9].

3.4.1.2 Urea Purification & Low Pressure Recovery

Urea purification takes place in two stages at decreasing pressure as follows:

1st stage at 18 atm pressure, i.e., MP decomposer
2nd stage at 4.5 atm pressure, i.e., LP decomposer

1st stage purification & recovery stage at 18 atm:

It is falling film type 1va decomposer. It is divided into 2 parts: Top separator, where the released flash gases, the solution enters the tube bundle & decomposition section where the residual carbamate is decomposed & required heat is supplied by means of 24 atm steam condensate flowing out of the stripper.

2nd purification & recovery stage at 4.5 atm:

The solution leaving the bottom of MP decomposer is expanded at 4.5 atm pressure & enters the LP decomposer (falling film type). This is again divided in to two parts, top separator where the released flash gases are removed before the solution enters the tube bundle. Decomposition section where the last residual carbamate is decomposed & the required heat is supplied by means of steam saturated at 4.5 atm.

Fig. 3.1: Snarnprogetti urea process flow diagram [9].

3.4.1.3 Urea Concentration

Next section is urea concentration & objective is to reduce water content of urea to as low as 1 %. For the purpose a vacuum concentrator in two stages is provided. The solution leaving the LP decomposer bottom with about 72% urea is sent to the 1st vacuum concentrator operating at a pressure of 0.23 atm. The mixed phase coming out enters the gas liquid separator, wherefrom the vapors are extracted by the 1st vacuum system, while the solution enters the 2nd vacuum concentrator operating at a pressure of 0.03 atm. The two concentrators are fed by saturated steam at 4.5 atm. The mixed phase coming out enters the gas liquid separator, wherefrom the vapors are extracted by the 2nd vacuum system.

3.4.1.4 Urea Prilling
The molten urea leaving the 2nd vacuum separator is sent to the prilling bucket by means of a centrifugal pump. The urea coming out of the bucket in the form of drops fall along the prilling tower & encounters a cold air flow which causes its solidification. The solid prills falling to the bottom of the prilling tower are sent through the screeners to retain lumps only, & then to belt conveyor which carries the product to the automatic weighing machine & to the urea storage sections. Urea lumps by the means of belt conveyor are recycled to the underground tank, where they are dissolved.

**MATERIAL AND ENERGY BALANCE**

**4.1 Material Balance**

Selected capacity: 100 tons/day

Urea: 4083.33 kg/hr. of 98% purity

Composition of the final product:

Urea: 98 % (61,250 Kg/hr)

Biuret: 1 % (625 Kg/hr)

Water: 1 % (625 Kg/hr)

Assumption: Overall conversion to urea is assumed to be 95%.

**Main Reactions:**

1) \( \text{CO}_2 + 2\text{NH}_3 \rightarrow \text{NH}_2\text{COONH}_4 \)  
   \((44) \quad (17) \quad (78)\)

2) \( \text{NH}_2\text{COONH}_4 \rightarrow \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \)  
   \((60) \quad (18)\)

3) \( \text{CO}_2 + 2\text{NH}_3 \rightarrow \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \)  
   (Overall reaction)

4) \( 2\text{NH}_2\text{CONH}_2 \rightarrow \text{NH}_2\text{CONHCONH}_2 + \text{NH}_3 \)  
   \((103)\)

**4.1.1 Reactor**

**Fig. 4.1: Flow of material across reactor**

From reaction 4

Concentration of biuret in product = 1 %

i.e. biuret = 41.66 kg/hr.

Biuret produce from Urea = \( \frac{120}{103} \times 41.66 \) 

= 48.536 kg/hr. Urea produced by reaction 2

= 4083.33 + 48.536

= 4131.866 kg/hr.

NH3 required from reaction 3

= \( \frac{34}{60} \times 4131.87 \)

= 2341.39 kg/hr.

& CO2 required

= \( \frac{44}{60} \times 4131.87 \)

= 3030.04 kg/hr.

Our conversion is 95%

NH3 actually fed = 2464.62 kg/hr

CO2 actually fed = 3189.52 kg/hr.

If the reaction 3 is 100% complete

Urea produced = \( \frac{60}{44} \times 3189.52 \)

= 4349.35 kg/hr.

But actual conversion is 95% Urea produced

= 0.95 \times 4349.35

= 4131.86 kg/hr.

Urea converted to biuret & NH3

= 4131.86 - 4083.33

= 48.536 kg/hr.
From reaction 4
Biuret produced = \( \frac{103}{120} \times 48.53 \) = 41.66 kg/hr.

H2O produced in reaction 2
= \( \frac{18}{60} \times 4131.86 \) = 1239.56 kg/hr.

At reactor exit (urea = 34%)
Exit flow rate = \( \frac{4083.33}{0.34} \) = 12009.79 kg/hr.

Actual urea produced = 4083.33 - 48.53
= 4083.33 kg/hr.

NH3:

From reaction 3, NH3 reacted is
= \( \frac{34}{60} \times 4131.86 \) = 2341.39 kg/hr.

From reaction 4 NH3 produced
= \( \frac{17}{120} \times 48.53 \) = 6.88 kg/hr.
NH\textsubscript{3} unreacted = 2464.6 2341.49 + 6.88  
= 129.99 kg/hr.

CO\textsubscript{2}:
From reaction 3 CO\textsubscript{2} reacted = 44/60*4131.86  
= 3030.03 kg/hr.
CO\textsubscript{2} unreacted = 31892-303003  
= 159.49 kg/hr.
Carbamate flowrate = exit flow rate-[urea + biuret + water + NH\textsubscript{3} + CO\textsubscript{2}]  
= 6361.76 kg/hr.

4.1.2 Stripper

The amount of ammonia, carbon-dioxide, water & biuret will remain constant as no reaction is taking place.
x = 0.7221,
y = 0.7411
Fx = Py
F = (Py)/x  
= (5509.528 x 0.7411)/0.7221  
= 5659.458 Kg/hr.
NH\textsubscript{3} + CO\textsubscript{2} Removed  
= 5654.458-5509.528  
= 144.98 Kg/hr.
50 % of ammonia & carbon di-oxide are assumed to escape from the top of the separator & rest goes with the bottom product. Amount of water & biuret remains constant as no reaction takes place.

4.1.3 Medium Pressure Separator

4.1.4 Low Pressure Separator

The amount of ammonia, carbon-di-oxide, water & biuret will remain constant as no reaction is taking place.

y = 0.7611
x = 0.7411
P = 5364.55 kg/hr
F = 5364.55*0.7611/0.7411
F = 5509.53 kg/hr
(NH\textsubscript{3}+CO\textsubscript{2}) separated from top = 144.98 kg/hr
4.1.5 Evaporator

Fig. 4.5: Flow of material across evaporator

Let x & y be the mass fractions of Urea in feed (F) & product (P) resp.

\[ x = 0.7611 \]
\[ y = 0.9788 \]

Taking urea balance:

\[ F \cdot x = P \cdot y \]
\[ F \cdot 0.7611 = 4171.39 \cdot 0.9788 \]
\[ F = 5364.55 \text{ Kg/hr.} \]

Overall material balance gives:

\[ F = P + E \]
\[ 5364.55 = 4171.39 + E \]
\[ E = 1193.16 \text{ Kg/hr.} \]

4.1.6 Prilling Tower

Fig. 4.6: Flow of material across prilling tower

Let x & y be the mass fractions of Urea in feed (F) & product (P) resp.

\[ x = 0.9788 \quad y = 0.9796 \]

Making urea balance:

\[ F \cdot x = P \cdot y \]
\[ F \cdot 0.9788 = 4167.98 \cdot 0.9796 \]
\[ F = 4171.39 \text{ Kg/hr.} \]

Water removed = 4171.39 4167.98 = 3.41kg/hr.

4.2 Energy Balance

Assumption: Datum temperature = 0°C

4.2.1 Reactor

Fig. 4.7: Energy 110w across reactor

Inlet Stream

<table>
<thead>
<tr>
<th>Material</th>
<th>specific heat at 40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>0.53 cal/gm°C = 2.219 KJ/Kg °C</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.22 cal/gm °C = 0.9211 KJ/Kg °C</td>
</tr>
</tbody>
</table>

Specific heat at 180°C

Carbamate 0.62 cal/gm°C = 2.596 KJ/Kg °C

Heat input

\[ \Delta H_R = -31.32 \text{ Kcal/gm mol} \]
\[ = -0.013 \times 10^7 \text{ KJ/Kmol of Urea formed.} \]

Amount of urea formed during the reaction = 68.056 Kmol/hr.

\[ \Delta H_R = 68.056 \times 0.013 \times 10^7 \text{ KJ/hr.} \]
\[ = 8.85 \times 10^6 \text{ KJ/hr.} \]
Outlet Stream

Table 4.1: Outlet Stream Composition from reactor

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific heat at 180°C</th>
<th>Molfractions (x)</th>
<th>Flow rate (Kmol/hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>0.55 cal/gm°C = 39.15 KJ/Kmol°C</td>
<td>0.0334</td>
<td>7.646</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.23 cal/gm°C = 42.37 KJ/Kmol°C</td>
<td>0.01586</td>
<td>3.6248</td>
</tr>
<tr>
<td>Carbamate</td>
<td>0.62 cal/gm°C = 202.49 KJ/Kmol°C</td>
<td>0.354</td>
<td>80.279</td>
</tr>
<tr>
<td>Urea</td>
<td>0.4828 cal/gm°C = 121.32 KJ/Kmol°C</td>
<td>0.296</td>
<td>68.056</td>
</tr>
<tr>
<td>Water</td>
<td>1 cal/gm°C = 75.37 KJ/Kmol°C</td>
<td>0.299</td>
<td>68.364</td>
</tr>
<tr>
<td>Biuret</td>
<td>183.8 KJ/Kmol°C</td>
<td>0.002</td>
<td>0.4045</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td></td>
<td><strong>228.874</strong></td>
</tr>
</tbody>
</table>

\[ \text{Cp of mixture} = \sum x_i \text{Cp}_i \]

SO, CD = 0.0334 x 39.15 + 0.01586 x 42.37 + 0.296 x 121.32 + 0.354 x 202.49 + 0.296 x 75.37 = 132.46 KJ/Kmol °C

+ 0.299 x 75.37 = 132.46 KJ/Kmol °C

So, heat carried by outlet stream = \( m \times \text{Cp} \times \Delta t \)

= 228.874 x 132.46 x 180

= 5.4569 \times 10⁶ KJ/hr.

Heat input + AHR Heat output = rate of accumulation

3.309x \( 10^6+8.85 \times 10^6-54569 \times 10^6 \) = rate of accumulation

Rate of accumulation = 6.697x \( 10^6 \) KJ/hr.

Brine at -17°C is used to remove heat from the reactor. The outlet is stream at temperature 35°C.

So, heat gained by brine = 6.697 x \( 10^6 \) KJ/hr.

\( m \times \text{Cp} \times \Delta t \) = 6.697 x \( 10^6 \) KJ/hr.

\( m \times 3.2408 \times (-17-35) = 6.697 \times 10^6 \) KJ/hr.

\( m = 39095.01 \) Kg/hr.

4.2.2 Stripper

Heat input + AHR Heat output = rate of accumulation

3.309x \( 10^6+8.85 \times 10^6-54569 \times 10^6 \) = rate of accumulation

Rate of accumulation = 6.697x \( 10^6 \) KJ/hr.

Brine at -17°C is used to remove heat from the reactor. The outlet is stream at temperature 35°C.

So, heat gained by brine = 6.697 x \( 10^6 \) KJ/hr.

\( m \times \text{Cp} \times \Delta t \) = 6.697 x \( 10^6 \) KJ/hr.

\( m \times 3.2408 \times (-17-35) = 6.697 \times 10^6 \) KJ/hr.

\( m = 39095.01 \) Kg/hr.

**Fig. 4.8:** Energy flow across stripper

Total heat input = 5.4569 x \( 10^6 \) KJ/hr.

Outlet Stream

Table 4.2: Outlet stream composition of liquid from stripper

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific heat at 185°C</th>
<th>Molfractions (x)</th>
<th>Flow rate (Kmol/hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>0.58 cal/gm°C = 41.31 KJ/Kmol°C</td>
<td>0.0514</td>
<td>7.696</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.24 cal/gm°C = 44.22 KJ/Kmol°C</td>
<td>0.24</td>
<td>3.6248</td>
</tr>
<tr>
<td>Urea</td>
<td>0.5385 cal/gm°C = 135.3 KJ/Kmol°C</td>
<td>0.46</td>
<td>68.008</td>
</tr>
<tr>
<td>Water</td>
<td>1 cal/gm°C = 75.37 KJ/Kmol°C</td>
<td>0.463</td>
<td>68.864</td>
</tr>
<tr>
<td>Biuret</td>
<td>183.8 KJ/Kmol°C</td>
<td>0.003</td>
<td>0.4043</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td></td>
<td><strong>148.6</strong></td>
</tr>
</tbody>
</table>

\[ \text{Cp of mixture} = \sum x_i \text{Cp}_i \]

So, \( \text{Cp} = 0.05 \times 41.31 + 0.024 \times 44.22 + 0.46 \times 135.3 + 0.003 \times 183.8 + 0.463 \times 75.37 = 100.81 \) KJ/Kmol °C

So, heat carried by outlet stream = \( m \times \text{Cp} \times \Delta t \)

= 148.6 x 100.81 x 185 = 2771367.7 KJ/hr.

Table 4.3: Outlet stream composition of Vapour (Ammonium carbamate) from stripper

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific heat at 185°C</th>
<th>Flow rate (Kmol/hr.)</th>
</tr>
</thead>
</table>
Carbonate 0.62 cal/g In °C = 202.49 KJ/Kmol°C

For carbamate λ = 210 KJ/Kg
So, heat carried by carbamate = mCp∆t + mλ
= 81.56 x 202.49 x 185 + 6361.76 x 210
= 439126.214 KJ/hr.

Here, steam at 24 atm is used (Ts = 222°C).
1 of steam = 1855.3 KJ/kg
Heat supplied by steam = Heat output Heat input
= (439126.214 + 2771367.7)
= 5.4569 x 10^6 KJ/hr.

m = 170572.914 Kg/hr.

4.2.3 Carbamate Condenser

Fig.4.9: Energy flow across carbamate condenser

Mvλv = mCp∆t

Heat gained by coolant = 6.69*10^6 KJ/hr.
Putting the values we get,
6.69*10^6 = m x 3.2098 x 52
So, m = 39095.01 kg/h

4.2.4 Medium Pressure Separator

Fig. 4.10: Energy flow across medium pressure separator

Heat input = 2771367.7 KJ/hr.

Outlet Stream

Table 4.4: Outlet Stream Composition of Liquid from Medium Pressure Separator

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific heat at 140°C</th>
<th>Molfractions (x)</th>
<th>Flow rate (Kmol/hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>0.54 cal/gm°C = 38.4 KJ/Kmol°C</td>
<td>0.027</td>
<td>3.82</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.23 cal/gm°C = 42.37 KJ/Kmol°C</td>
<td>0.0127</td>
<td>1.813</td>
</tr>
<tr>
<td>Urea</td>
<td>0.493 cal/gm°C = 123.84 KJ/Kmol°C</td>
<td>0.476</td>
<td>68.008</td>
</tr>
<tr>
<td>Water</td>
<td>1 cal/gm°C = 75.37 KJ/Kmol°C</td>
<td>0.4815</td>
<td>68.884</td>
</tr>
<tr>
<td>Biuret</td>
<td>170.92 KJ/Kmol°C</td>
<td>0.0028</td>
<td>0.4046</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td></td>
<td><strong>142.96</strong></td>
</tr>
</tbody>
</table>

Cp of mixture = ∑x_iCp_i

So, Cp = 0.027 x 38.4 + 0.0127 x 42.37 + 0.476 x 123.84 + 0.0028 x 170.92 + 0.4815 x 75.37
= 97.29 KJ/Kmol°C

Heat output = 142.96 x 97.29 x 140 KJ/hr.
= 1.947 x 10^6 KJ/hr.

λ of mixture = ∑x_iλ_i

So, λ = (0.6785 x 22.777 + 0.321 x 20.265) x 10^3
= 21.969 x 10^3 KJ/Kmol°C

Table 4.5: Outlet stream composition of Vapor escaping from top of Medium

<table>
<thead>
<tr>
<th>Material</th>
<th>λ at 140°C</th>
<th>Molfractions (x)</th>
<th>Flow rate (Kmol/hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>0.54 cal/gm°C = 38.4 KJ/Kmol°C</td>
<td>0.027</td>
<td>3.82</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.23 cal/gm°C = 42.37 KJ/Kmol°C</td>
<td>0.0127</td>
<td>1.813</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td></td>
<td><strong>5.65</strong></td>
</tr>
</tbody>
</table>

Cp of mixture = ∑x_iCp_i

So, Cp = 0.678 x 38.4 + 0.3215 x 42.37 KJ/Kmol°C = 39.676 KJ/Kmol°C

Heat escaping from the top = m (Cp∆t + λ)
= 5.633 (39.676x 140 + 21.969 x 10^3)
= 155040.6 KJ/hr.
Assumption: Cooling water enters at 25°C & leaves at 50°C.
So, heat gained by cooling water = Heat input - heat output
= 2771367.7 x 1.947 x 10^6 KJ/hr.

mCpΔt = 669327.1 KJ/hr.
m = 669327.1/(4.187 x 25)
m = 6394.34 Kg/hr.

4.2.5 Low Pressure Separator

Fig. 4.11: Energy flow across low pressure separator

Heat input = 1.947 x 10^6 KJ/hr.

Outlet Stream

Table 4.6: Outlet stream composition of Liquid from Low Pressure Separator

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific heat at 80°C</th>
<th>Mol fraction (x)</th>
<th>Flow rate (Kmol/hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>0.429 cal/gm°C=107.7 6 KJ/Kmol°C</td>
<td>0.496</td>
<td>68.008</td>
</tr>
<tr>
<td>Water</td>
<td>1 cal/gm°C = 75.37 KJ/Kmol°C</td>
<td>0.5</td>
<td>68.884</td>
</tr>
<tr>
<td>Biuret</td>
<td>149 KJ/Kmol°C</td>
<td>0.004</td>
<td>0.4046</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td></td>
<td>137.32</td>
</tr>
</tbody>
</table>

Cp of mixture = Σx_iC_p_i

Table 4.7: Outlet stream composition of Vapor escaping from top of Low Pressure

<table>
<thead>
<tr>
<th>Material</th>
<th>λ at 140°C</th>
<th>Molfractions (x)</th>
<th>Flow rate (Kmol/hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>260 cal/gm°C = 18.51 x 10³ KJ/Kmol°C</td>
<td>0.679</td>
<td>3.82</td>
</tr>
<tr>
<td>CO₂</td>
<td>85 cal/gm°C = 15.66 x 10³ CO₂/ KJ/Kmol°C</td>
<td>0.321</td>
<td>1.813</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td></td>
<td>5.633</td>
</tr>
</tbody>
</table>

λ of mixture = Σx_iλ_i

So, λ = (0.679 x 18.51 + 0.321 x 15.66) x 10³ KJ/Kmol°C

= 17.6 x 10³ KJ/Kmol

Cp of mixture = Σx_iC_p_i

So, Cp = 0.679 x 37.013 + 0.321 x 38.69 KJ/Kmol°C

= 37.55 KJ/Kmol°C

Heat escaping from the top = m(CpΔt + 96) = 5.633(37.55 x 80 + 17.7 x 10³)

= 1.66 x 10⁵ KJ/hr.

Assumption: Cooling water enters at 25°C & leaves at 50°C.

So, heat gained by cooling water = Heat input heat output = 1.947 x 10^6 - 1.009 x 10⁶ KJ/hr.
mCpΔt = 772000 KJ/hr.
m = 772000/(4.187 x 25)
m = 7375.21 Kg/hr.
4.2.6 Evaporator

![Energy flow across evaporator](image)

**Fig. 4.12: Energy flow across evaporator**

**Table 4.8: Product stream coming out of 1St evaporator**

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific heat at 85°C</th>
<th>Molfractions (x)</th>
<th>Flow rate (Kmol/hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>0.435 cal/gm°C=109.28 KJ/Kmol°C</td>
<td>0.75</td>
<td>68.056</td>
</tr>
<tr>
<td>Water</td>
<td>1 cal/gm°C = 75.37 KJ/Kmol°C</td>
<td>0.245</td>
<td>22.226</td>
</tr>
<tr>
<td>Biuret</td>
<td>149 KJ/Kmol°C</td>
<td>0.005</td>
<td>0.4045</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td></td>
<td><strong>90.6565</strong></td>
</tr>
</tbody>
</table>

Cp of mixture = \( \Sigma x_i C_p \)

So, \( C_p = 0.75 \times 109.28 + 0.245 \times 75.37 + 0.005 \times 149 \) KJ/Kmol°C

\( = 101.17 \) KJ/Kmol°C

\( mC_p\Delta t = 90.6565 \times 101.17 \times 85 \)

\( = 779768.028 \) KJ/hr.

**Heat Balance.**

1° evaporator:

Heat input (feed) + Heat input by steam = heat carried by water vapor + energy of the bottom product

Heat input (feed) + \( S_1A_{S1} = E_1H_{E1} \) + energy of the bottom product \( 1.009 \times 10^6 + 81 \times 2123.2 = 839.55 \times 2614.97 + 7.79 \times 10^5 \)

\( S_1 = 926.08 \) Kg/hr.

2° evaporator:

Heat input (feed) + Heat input by steam = heat carried by water vapor + energy of the bottom product

Heat input (feed) + \( S_2A_{S2} = E_2H_{E2} \) + energy of the bottom product

\( 7.79 \times 10^5 + S_2 \times 2123.2 = 353.4 \times 2545.7 + 10.91 \times 10^6 \)

\( S_2 = 144.307 \) Kg/hr.

4.2.7 Prilling Tower

![Energy balance across prilling tower](image)

**Fig. 4.13: Energy balance across prilling tower**

Heat input= 10.91 x 10^7 KJ/hr.

**Outlet stream**

**Table 4.9: Outlet Stream Composition from prilling tower**

<table>
<thead>
<tr>
<th>Material</th>
<th>Specific heat at 30°C</th>
<th>Molfractions (x)</th>
<th>Flow rate (Kmol/hr.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>0.3758 cal/gm°C=94.41 KJ/Kmol°C</td>
<td>0.96</td>
<td>68.056</td>
</tr>
<tr>
<td>Water</td>
<td>1 cal/gm°C = 75.37 KJ/Kmol°C</td>
<td>0.34</td>
<td>2.38</td>
</tr>
<tr>
<td>Biuret</td>
<td>133.02 KJ/Kmol°C</td>
<td>0.005</td>
<td>0.4045</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td></td>
<td><strong>70.85</strong></td>
</tr>
</tbody>
</table>

Cp of mixture = \( \Sigma x_i C_p \)

So, \( C_p = 0.96 \times 94.41 + 0.034 \times 75.37 + 0.006 \times 133.02 \) KJ/Kmol°C

\( = 93.99 \) KJ/Kmol°C

Heat output = 70.85 x 93.99 x 25 = 166479.79 KJ/hr.

Assuming, humidity of air at 25°C = 0.01

Heat carried away by air = heat input heat output

\( (mC_p\Delta t) \) dry air = \( (1091-010) \times 10^6 \)

\( = 10.14 \times 106 \) KJ/hr.

\( m =10.14 \times 10^6/ (1.009 \times 1) \)
m = 10.053 x 10^6 Kg/hr.
So, flow rate of air = 10.053 x 10^6 Kg/hr.

EQUIPMENT DESIGN

5.1 Reactor Design

Type of Reactor Plug Flow Reactor

Values of activation energy and reaction rate constant are taken from the literature.

E = 139500 J/mole
K = 2.5 [14].

We Know,
\[ \frac{V}{V_0} = \left( \frac{1}{K} \right) \times \left[ -\ln (1 - X_A) \right] \]
V = (12.417/2.5) x [-ln 0.95)]
V = 14.88
\[ t = \frac{V}{F} = \frac{14.88}{12.417} \]
t = 1.198 hr.
= 71.88 min.

Taking, L/D = 6
V = (\pi/4) x D^2 L
14.88 = (\pi/4) x D^2 x 6D
D = 1.467
D = 1.5 m.
L = 9 m.

5.1.1 Thickness of Shell Data available:
Pressure inside the reactor = 154 atm.
Material of construction:
Low alloy carbon steel [IS-2002-1975]
Allowable stress = 121 x 108 N/mm^2

Diameter of the reactor = 1.5 m
\[ t = \frac{P-D_t}{(16 - (\pi/2))} \]
Where,
t = thickness of the shell
D_t = Internal diameter
J = joint efficiency
p = design pressure
f = permissible stress
Internal pressure = 154 atm.
Design pressure = p = (10 % extra)
= 1.1 x 154
= 169.4 atm.
= 1.716 x 107 N/m^2
= 17.16 N/mm^2
J = 1 [For class 1 pressure vessels, BIS-2825]
f = 121 N/mm^2
D_t = 1.5 m
So, t = (17.16 x 1.5) / (2 x 121 - 17.16)
t = 0.01145 m
Or, t = 1.2 cm.

5.1.2 Head Design
For 2:1 ellipsoidal dished head
\[ t_h = \frac{pD^2V}{2fJ} \]
Where, p = internal design pressure
D = major axis of ellipse
V = stress intensification factor = (2 + K^2)/4
k = major axis/minor axis So, th = (17.16 x 1.5 x 1) / (2 x 121 x 1)
t_h = 0.0106m.
t_h = 1.2 cm

5.1.3 Skirt Support for Reactor
Wt. of the reactor = wt. of material of construction + weight of the contents of the reactor
Wt. of material of construction = \( \pi \times D \times t \times L \times p 
= \pi \times 1.5 \times 0.12 \times 9 \times 7850 
= 39951.634 Kg

Weight of the reactor = 39951.634 + 12015.88
W = 51967.514 Kg
Wind Pressure = P1= 1226.25 N/m²

Material of construction:
IS: 2002-1962 Grade 2B
Allowable tensile stress = 1.18 x 10⁸ N/m²
Yield stress = 2.55 x 10⁸ N/m²

Stress due to dead weight:
\[ f_d = \Sigma W / (\pi \cdot D_{ok} \cdot t_{sk}) \]
Where,
f_d = Stress due to dead weight
\( \Sigma W \) = Dead wt. of vessel
D_{ok} = Outside diameter of the skirt
t_{sk} = thickness of skirt

\[ f_d = 51967.514 / (3.14 \times 1.5 \times t_{sk}) \]
= 11027.85 /t_{sk} N/m²

Assuming height of skirt = 5 m

**Stress due to seismic load:**
\[ f_{sb} = (2/3) \times CWH / (\pi \cdot R_{ok} \cdot t_{sk}) \]
[Here C = 0.08]
\[ f_{sb} = (2/3) \times (0.08 \times 51967 \times 9) / (3.14 \times 0.81 \times t_{sk}) \]
= 14.73 / t_{sk}

Maximum tensile stress = \( f_{wb} - f_d \)
\[ = 66114.73/t_{sk} 10210.97/t_{sk} \]

(\text{ft}) Max = 55903.76/t_{sk}

Now, permissible tensile stress = 1.18 x 108N/m²=12028542.3 kg/ m²

Now, permissible tensile stress = Maximum tensile stress

Cp of mixture = \( \Sigma x_i C_{pi} \)
So, \(C_p = 0.75 \times 109.28 + 0.245 \times 75.37 + 0.005 \times 149\)
\[= 101.17 \text{ KJ/Kmol}°\text{C}\]
\[mCp\Delta t = 90.6865 \times 101.17 \times 85\]
\[= 7.797 \times 10^5 \text{ KJ/hr.}\]

**Heat balance**

1st evaporator:
Heat input (feed) + Heat input by steam = heat carried by water vapor + energy of the bottom product
Heat input (feed) + S1151 = EIHE + energy of the bottom product
For steam at 150 ºC, 151 = 2123.2 KJ/kg
Putting the values we get
\[1.009 \times 106 + 31 \times 2123.2 = 839.55 \times 2614.97 + 7.79 \times 10^5\]
\[S_1 = 926.08 \text{ Kg/hr.}\]
Economy = 839.55/926.08 = 0.9066
Now,
U₁ value is obtained from fig: 5.3. At 63.1°C (145.58°F) the value of U₁ is 270 Btu/hr.ft².°F. Multiplying this value by 5.6783 gives the value of U₁ in W/m²K
\[A_1 = S_1 \lambda S_1 / U_1 \Delta T_1\]
\[\Delta T_1 = (AT) \text{ app BPR}_1\]
\[= 150 \times 63.1 - 28.11\]
\[= 58.79 \text{ °C}\]
So, \(A_1 = 926.08 \times 2123.2 / 1533 \times 58.79\)
\[A_1 = 21.8149 \text{ m}^2\]

Similarly,
\[A_2 = S_2 \lambda S_2 / U_2 \Delta T_2\]
\[\Delta T_2 = (AT) \text{ app BPR}_2\]
\[= 150 \times 23.7787.097 = 38.903 \text{ °C}\]
So, \(A_2 = 144.307 \times 2123.2 / 738 \times 38.903\)

\[A_2 = 10.6718 \text{ m}^2\]
5.2.1.1 Wall Thickness Calculation

Material of construction: Mild Steel

Specification: IS 2002-1962 Grade-l

\[ f_{\text{all}} = 0.93 \times 10^8 \text{ N/m}^2 \]

\[ c = 0 \text{ m} \]

\[ J = 0.85 \]

\[ t = \frac{P_d D}{(2fj - p) + C} \]

Where,

\[ t = \text{thickness of the shell} \]

\[ D = \text{internal diameter} \]

\[ J = \text{joint efficiency} \]

\[ p_i = \text{design pressure} \]

\[ f = \text{permissible stress} \]

\[ C = \text{Corrosion allowance} \]

\[ P_d = 1.1 \times P_s \]

\[ P_s = 4.5 \text{ atm} = 4.413 \text{ bar} \]

\[ P_d = 4.854 \times 10^5 \text{ N/m}^2 \]

\[ t = \frac{(4.854 \times 10^5 \times 0.4)}{2 \times 0.93 \times 10^8 \times 0.85 \times 4.854 \times 10^5} \]

\[ = 1.23 \text{ mm} \]

Assuming, \( t_{\text{std}} = 3.2 \text{ mm} \)

Checking this thickness for critical buckling pressure:

\[ P_c = \text{critical external buckling pressure} \]

\[ P_c = \left[ \frac{2.42E}{(1 - \mu^2)^{\frac{3}{4}}} \right] \times \left[ \frac{(t/D_0)^{\frac{1}{2}}}{(L/D_0 0.45 \times (t/D_0)^{\frac{1}{2}})} \right] \]

\[ E = 2.2 \times 10^6 \text{ N/cm}^2 \]

\[ u = 0.30 \]

\[ L = 6 \text{ m} \]

\[ D_0 = D_i + 2 \times t \]

\[ = 0.4 + 2 \times 0.032 \]

\[ = 0.4064 \text{ m} \]

Putting values in the above equation of \( P_c \) we get

\[ P_c = 2.13557 \text{ Kg/cm}^2 \]

Taking factor of safety (FOS) = 4

\[ P_{\text{all}} = P_c/4 = 2.13557/4 \]

\[ = 0.533 \text{ Kg/cm}^2 \]

This is less than 1 Kg/cm²

Hence, this thickness is not acceptable.

Again, taking \( t_{\text{std}} = 5 \text{ mm} \)

We get,

\[ P_c = 6.4 \text{ Kg/cm}^2 \]

\[ P_{\text{all}} = 6.4/4 = 1.609 \text{ Kg/cm}^2 \]

This is less than 1 Kg/cm²

This is greater than 1 Kg/cm²

Hence, this thickness is unacceptable.

So, \( t_{\text{min}} = 5 \text{ mm} \)

\( t_{\text{min}} > 6 \text{ mm} \)

5.2.1.2 Separator

Top head (Elliptical head)

For 2:1 ellipsoidal dished head

\[ D_i = 1 \text{ m} \]

\[ L = 4 \text{ m} \]

\[ t_h = pDV/2fJ \]

Where,

\[ p = \text{internal design pressure} \]

\[ D = \text{major axis of ellipse} \]

\[ V = \text{stress intensification factor} = (2 + K^2)/4 \]

\[ k = \text{major axis/minor axis} \]

\[ p = 0.23 \text{ atm} = 0.226 \times 10^5 \text{ N/m}^2 \]

\[ j=0.85, D_i= 1.6m, k=2, v=1.5 \]

For internal pressure:

\[ t_h = \left( \frac{0.226 \times 10^5 \times 1.5 \times 1}{2 \times 0.93 \times 10^8 \times 0.85} \right) \]

\[ = 2.144 \times 10^{-4} \text{ m} \]

\[ = 0.214 \text{ mm} \]

For external pressure:

\[ P_{\text{ext}} = 1 \text{ Kg/cm}^2 \]

Corresponding internal pressure to be used to calculate

\[ t_h = 1.67 \times P_{\text{ext}} \]

So, \( P_{\text{int}} = 1.67 \text{ Kg/cm}^2 \)

So,

\[ t_h = 4.4 \times \text{Re} \left[ 3 \times (1 - \mu^2) \right]^{1/2} \times (p/2E)^{1/2} \]

Where,

\[ p = \text{Design external pressure} \]
Rc = Crown radius for torispherical & hemispherical heads and equivalent crown radius for elliptical head.

\( Rc = Do \)

E = modulus of elasticity

p = Poisson’s ratio

Putting the values we get

\( t_h = 1.84 \) m

So, \( t_{\text{std}} = 2 \) mm

**5.2.1.3 Bottom Head Design**

Assuming an apex angle of 60°

For, conical head

\( D=1 \) m

\[ t_h = \frac{pDV}{2fJ\cos \theta} \]

Here, \( a = \) Half the apex angle

For, internal pressure:

\[ p = 0.226 \times 10^5 \]

\[ t_h = \frac{(0.226 \times 10^5 \times 1.5 \times 1)}{(2 \times 0.93 \times 10^8 \times 0.85 \times 0.5)} = 0.429 \text{ mm} \]

For, external pressure:

\[ p = 1.67 \times P_{\text{ext}} \]

\[ t_h = \frac{1.67 \times 1 \times 1}{0.93 \times 10^8 \times 0.85} \]

\[ t_h = 3.17 \text{ mm} \]

So, \( t_{\text{std}} = 3.2 \) mm

Checking this thickness for critical buckling pressure:

\[ P_c = \left[ \frac{2.42E}{(1 - \mu^2)^{3/4}} \right] \times \left[ \frac{t(D)_{1/2}}{L(D)_{0.45}} \right] \]

For mild steel

\[ \mu = 0.30 \]

\[ L = 6 \text{ In} \]

Putting the values we get,

\[ D_0 = D_i + 2a \times t \]

\[ = 0.325 + 2 \times 0.0032 \]

\[ = 0.3314 \text{ m} \]

No. of tubes,

\[ A = \mu \times OD \times N \times L \]

\[ 10.6718 = \mu \times 0.025 \times N \times 6 \]

N = 22.64

No. of tubes = 24

\[ \frac{n}{4} \times D^2 = N \times (\text{Pitch})^2 \]

\[ D^2 = \frac{[24 \times (0.032)^2 \times 4]}{\mu} \]

D = 0.1718 m.

\[ D_{di} = D + (2 \times C) \]

\[ = 0.1718 + 2 \times 0.075 \]

\[ = 0.3218 \text{ m} \]

\[ D_{di} = 325 \text{ mm} \]

**5.2.2 For 2nd Effect Evaporator**

A = 10.6718 m²

No. of tubes,

\[ A = \mu \times OD \times N \times L \]

\[ 10.6718 = \mu \times 0.025 \times N \times 6 \]

N = 22.64

No. of tubes = 24

\[ \frac{n}{4} \times D^2 = N \times (\text{Pitch})^2 \]

\[ D^2 = \frac{[24 \times (0.032)^2 \times 4]}{\mu} \]

D = 0.1718 m.

\[ D_{di} = D + (2 \times C) \]

\[ = 0.1718 + 2 \times 0.075 \]

\[ = 0.3218 \text{ m} \]

\[ D_{di} = 325 \text{ mm} \]

**5.2.2.1 Wall Thickness Calculation**

Material of construction:

Mild steel Specification: IS 2002-1962 Grade-I

\[ f_{\text{all}} = 0.93 \times 10^8 \text{ N/m}^2 \]

C = 0 mm

\[ J=0.85 \]

\[ t= P_d(D_i/2f_j - P) + c \]

\[ P_d = 1.1 \times p_s \]

\[ p_s = 4.5 \text{ atm} = 4.413 \text{ bar} \]

\[ p_d = 4.854 \times 10^5 \text{ N/m}^2 \]

So, thickness will be

\[ t= (4.854 \times 10^5 \times 0.325)/(2 \times 0.93 \times 10^8 \times 0.85 \times 4.854 \times 10^5) \]

\[ = 1.0008 \times 10^{-3} \text{ m} \]

\[ t= 1 \text{ m} \]

Assuming, \( t_{\text{std}} = 3.2 \) mm

Checking this thickness for critical buckling pressure:

\[ P_c = \text{critical external buckling pressure} \]

\[ P_c = \left[ \frac{2.42E}{(1 - \mu^2)^{3/4}} \right] \times \left[ \frac{t(D)_{1/2}}{L(D)_{0.45}} \right] \]

Here,

\[ \mu = 0.30 \]

\[ L = 6 \text{ In} \]

\[ D_0 = D_i + 2a \times t \]

\[ = 0.325 + 2 \times 0.0032 \]

\[ = 0.3314 \text{ m} \]

Putting values in the above equation of \( P_c \) we get
Pc = 4.3553 Kg/cm^2
Taking factor of safety = 4
Pall = Pc/4 = 4.355/4
= 1.0888 Kg/cm^2
Which is greater than 1 Kg/cm^2
Hence, this thickness is acceptable.
So, t_min = 3.2 mm

**COSTING**

**Capacity of Plant** = 100 ton/day
**Annual production days** = 300 days

6.1 Raw material cost

1) Ammonia:
Cost of Ammonia = Rs. 13171.2 / ton
Annual cost = Flow rate of Ammonia * Cost of Ammonia * Total production days = 2213.9 lacs

2) Carbon dioxide:
Cost of Carbon dioxide = Rs. 1568 / ton
Annual cost = Flow rate of Carbon dioxide * Cost of Carbon dioxide * Total production days = 342 lacs

6.1.1 Equipment cost

**Table 6.1: Equipment cost**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Equipment</th>
<th>Quantity</th>
<th>Cost (in Lac.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Jacketed (PFR)</td>
<td>1</td>
<td>306.69</td>
</tr>
<tr>
<td>2</td>
<td>Evaporator</td>
<td>1</td>
<td>387.02</td>
</tr>
<tr>
<td></td>
<td>1st Effect</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2nd Effect</td>
<td>1</td>
<td>329.73</td>
</tr>
<tr>
<td>3</td>
<td>Prilling Tower</td>
<td>1</td>
<td>125</td>
</tr>
<tr>
<td>4</td>
<td>Stripper</td>
<td>1</td>
<td>105</td>
</tr>
<tr>
<td>5</td>
<td>Separator</td>
<td>MPS</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>LPS</td>
<td>1</td>
<td>129.3</td>
</tr>
<tr>
<td>6</td>
<td>Storage tanks</td>
<td>NH\textsubscript{3}</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>CO\textsubscript{2}</td>
<td>1</td>
<td>226.7</td>
</tr>
<tr>
<td>7</td>
<td>Condensers</td>
<td>10</td>
<td>15.6</td>
</tr>
<tr>
<td>8</td>
<td>Compressor</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TOTAL** = 4916.7 lacs

6.2 Calculation of Direct cost

**Table 6.2: Direct cost (D)**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Equipment</th>
<th>% of PEC</th>
<th>Cost (in Lac.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Purchased equipment installation</td>
<td>39</td>
<td>817.7</td>
</tr>
<tr>
<td>2</td>
<td>Instrumentation and control</td>
<td>30</td>
<td>629</td>
</tr>
<tr>
<td>3</td>
<td>Electrical systems</td>
<td>10</td>
<td>209.67</td>
</tr>
<tr>
<td>4</td>
<td>Yard improvements</td>
<td>10</td>
<td>209.67</td>
</tr>
<tr>
<td>5</td>
<td>Land</td>
<td>4</td>
<td>83.86</td>
</tr>
<tr>
<td>6</td>
<td>Maintenance &amp; Repair</td>
<td>1.5</td>
<td>31.45</td>
</tr>
<tr>
<td>7</td>
<td>Piping (Installed)</td>
<td>100</td>
<td>2096.68</td>
</tr>
<tr>
<td>8</td>
<td>Auxiliary cost</td>
<td>40</td>
<td>838.67</td>
</tr>
</tbody>
</table>

**TOTAL** = 4916.7 lacs

6.2.1 Raw material cost (RMC):
NH\textsubscript{3} Cost + CO\textsubscript{2} Cost = 2213.97 + 342
= 2555.97 lacs.

6.2.2 Labor Cost (LC):
LC = 12% of RMC
= 306.721acs.
Total direct cost = 4916.7 + RMC + LC

Total direct cost = 7779.39 lacs

6.3 Calculation of Indirect cost

**Table 6.3: Indirect cost (1)**

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Equipment</th>
<th>% of PEC</th>
<th>Cost (in Lac.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>Blower</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Pumps</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TOTAL** = 2096.68 lacs

Delivery and transport cost = 10% of total equipment cost = 209.6 lacs
Total equipment purchase cost (PEC) = 2306.35 lacs
Now we will calculate direct and indirect costs
1. Engineering and supervision 32 670.9
2. Construction expenses 34 712.87

Total indirect cost = 1383.77 lacs
Direct cost (D) + Indirect cost (I) = 7779.39 + 1383.77 = 9163.161acs
Contingency = 8 % (D + I) = 733.05 lacs
Contractors fees = 2 % (D + I) = 183.26 lacs.
Fixed capital investment (FCI) = D + I + Contractors fees + Contingency = 10079.47 lacs.
Hence working capital (WCI) = 2519.87 lacs.

6.4 Estimation of Production cost
Capacity = 100 TPD of Urea * 300 days = 30000 TPA
Total product cost (C_{TPC})
C_{TPC} = C_{MC} + C_{GEC} Where,
C_{MC} = Manufacturing Cost
C_{GEC} = General Expenses Cost
C_{MC} = C_{POC} + C_{DPC} + C_{FC}
Where,
C_{POC} = Plant overhead cost = 15 % labor cost
C_{DPC} = Direct Production cost
C_{FC}: Fixed charges = 10 % C_{DPC}
C_{DPC} = Direct Material cost + Direct labor cost + Power & utility cost
C_{DPC} = 2555.97 + 306.72 + 838.67 = 3701.361acs
C_{FC}: 10 % *3701.36 = 370.1 lacs.
C_{POC}= 15 % * 306.72 = 46.008 lacs.
So, C_{MC} = C_{POC} + C_{DPC} + C_{FC} = 46.008 + 3701.36 + 370.1 = 4117.47 lacs
C_{GEC} = C_{U} + C_{DC}
Where, C_{U} = Contingency cost
C_{DC} = Depreciation cost = 5 % of C_{MC}
C_{GEC} = C_{U} + C_{DC} = 733.05 + 5 % * 4117.47 = 938.92 lacs.
C_{TPC} = C_{MC} + C_{GEC} = 4117.47 + 938.92 = 5056.39 lacs/annum
6.5 Estimation of depreciation using double declining balance method [22]
\[ V_a = V * (1-f)^n \]
V_a = asset value for particular year V = Fixed capital investment
n = service life = 20 years
f = 2/n.
1) For 0th year
\[ V = 10079.47 \text{ lacs} \]
\[ V_{a_0} = 10079.47 * (1-0.1)^0 = 1007947 \text{ lacs}. \]
For next year if we use FCI as asset value, formula becomes
\[ V_a = V * (1-f) \]
2) For 1St year
\[ V_{a_1} = V_{a_0} * (1-f) = 10079.47 * 0.9 = 9071.5 \text{ lacs} \]
D_1 = V_{a_0} V_{a_1} = 1007.9 lacs
3) For 2"d year
\[ V_{a_2} = V_{a_1} * (1-f)^2 = 9071.5 * (1.0.1)^2 = 7347.92 \text{ lacs}. \]
\[ d_2 = V_{a1} - V_{a2} \]
\[ = 1723.59 \text{ lacs} \]

Similarly we can calculate depreciation for all next year

### 6.6 Estimation of profit

Market price = 24599.04 Rs/ton

Gross Profit = Selling Price - Production cost
\[ = 7379.71 - 5056.39 \]
\[ = 2323.32 \text{ lacs / annum} \]

As there are no taxes on depreciation, we will calculate profit taxable.

Profit taxable = Gross Profit - Depreciation = 2323.32 lacs 

=1315.421acs

Consider 25% taxes are applicable on profit including all types of tax will calculate net profit Net profit = Profit taxable - 0.25 * Profit taxable

= 986.57 lacs

Similarly we calculate asset values, depreciation, profitable tax, net profit for each year to calculate cash flow.

Cash flow = Net profit + depreciation asset value **Table 6.4 Cash Flow**

<table>
<thead>
<tr>
<th>Year (a)</th>
<th>Asset value</th>
<th>Depreciation</th>
<th>Net profit</th>
<th>Cash Flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10079.47</td>
<td>0</td>
<td>0</td>
<td>-10079.5</td>
</tr>
<tr>
<td>1</td>
<td>9071.523</td>
<td>1007.947</td>
<td>986.5298</td>
<td>-7077.05</td>
</tr>
<tr>
<td>2</td>
<td>7347.934</td>
<td>1723.589</td>
<td>449.798</td>
<td>-5174.55</td>
</tr>
<tr>
<td>3</td>
<td>5356.644</td>
<td>1991.29</td>
<td>249.0225</td>
<td>-3116.33</td>
</tr>
<tr>
<td>4</td>
<td>3514.494</td>
<td>1842.15</td>
<td>360.8777</td>
<td>-1311.47</td>
</tr>
<tr>
<td>5</td>
<td>2075.273</td>
<td>1439.22</td>
<td>663.0747</td>
<td>27.02161</td>
</tr>
<tr>
<td>6</td>
<td>1102.885</td>
<td>972.3881</td>
<td>1013.199</td>
<td>882.7016</td>
</tr>
<tr>
<td>7</td>
<td>527.5067</td>
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<tr>
<td>8</td>
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</tr>
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<td>9</td>
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<tr>
<td>11</td>
<td>9.625944</td>
<td>21.04843</td>
<td>1726.704</td>
<td>1738.126</td>
</tr>
</tbody>
</table>

### NEW ADVANCED TECHNIQUE

#### 7.1 History

NFL was established in 1974, as a public-sector undertaking of the Government of India. NFL initially operated two plants in Bathinda and Panipat. In 1978, the ownership and operations of the Nangal plant of FCI was transferred to NFL. The Govt. of India, in 1984, entrusted the Company to execute the country’s first inland gas based fertilizer project of 7.26 lakh tons Urea capacity in District Guna of Madhya Pradesh and commercial production started from 01-07-1988. The company built and commissioned its Vijaipur plant in Guna district of Madhya Pradesh. The plant's capacity was doubled to 1.45 million tons in 1997.NFL was granted the Mini-Navratna status with additional autonomy due to its profitable operations.

In 2001, the company went public, with listings on the Bombay Stock Exchange and the National Stock Exchange.

#### Industrial and Business operations

NFL has five gas based Urea plants viz Nangal & Bathinda in Punjab, Panipat in Haryana and two at Vijaipur (Madhya Pradesh). The plants at Panipat,
Bathinda & Nangal have recently been converted from fuel oil feedstock to natural gas. Vijaipur plants have also been revamped for energy saving & capacity enhancement. Products NFL is engaged in manufacturing and marketing of Urea, Neem Coated Urea, Bio Fertilizers (solid & liquid) and other allied Industrial products like Ammonia, Nitric Acid, Ammonium Nitrate, Sodium Nitrite, Sodium Nitrate etc.

The value-added Neem Coated Urea developed by NFL & widely recognized for its effectiveness is being produced at its three units at Panipat, Bathinda & Vijaipur. NFL is the first company in India to be permitted by the Government of India to produce and market Neem Coated Urea.

NFL manufactures and markets three types of Bio-Fertilizers namely Rhizobium, Phosphate Solubilizing Bacteria (PSB) and Azetobactor. Starting with a mere 23 MT production in 1995-96, the production has risen to 231 MT (Approx.) in 2010-11.

7.2 Future Projects

An agreement for a Joint Venture Company "Ramagundam Fertilizers And Chemicals Limited" has been signed on 14-Jan-2013 between National Fertilizers Limited, Engineers India Limited (EIL) and FCIL for setting up new Ammonia and Urea plants of 2200 MT per day & 3850 MT per day capacity respectively at the existing site of Ramagundam Fertilizer Plant in Distt. Karim Nagar in Telangana. As per this joint venture agreement, NFL shall provide commissioning, operation, maintenance and marketing services to the Joint Venture Company and EIL shall provide Engineering, Procurement and Construction Management (EPCM) Consultancy Services for the project. The total capital expenditure of 5,000 crore is being funded in Debt: Equity of 70:30 percentage NFL and EIL are contributing equity of 26% each and 11% is from FCIL. The balance equity is in the process of being tied up. The Company also has a Joint Venture (33.33% share) “Urvarak Videsh Limited” with Ms. KRBHCO and RCF as promoters. The main objective of the joint venture company is to explore investment opportunity abroad and within the country in nitrogenous, phosphatic and potassic sectors and to render consultancy services for setting up projects in India and abroad.

7.3 Safety and Environment Management

NFL remains focused towards achieving sustained energy efficient operations of its ageing manufacturing facilities at the same time maintaining pollution free environment and process safety. All manufacturing Units of the Company continue to be ISO 9001-2008, ISO14001-2004 and OHSAS-18001 certified, which indicates Company’s commitment to Quality Management System, Environment Management System and Occupational Health and Safety Systems.

PLANT LAYOUT

After the process flow diagrams are completed and before detailed piping, structural, and electrical design can begin, the layout of process units in a plant and the equipment within these process units must be planned. This layout can play an important part in determining construction and manufacturing costs, and thus must be planned carefully with attention being given to future problems that may arise. Since each plant differs in many ways and no two plant sites are exactly alike, there is no one ideal plant layout. Although conditions for example client specifications, schedule constraints, and availability of information may change significantly among the projects, the designer’s style remains constant. However, proper layout in each case will include arrangement of processing areas, storage areas, and handling areas in efficient coordination. Typical plant layout for Urea manufacturing plant is...
shown in figure 7.1. This includes tank farm for storage of raw material, processing area with extra space allowance for future expansion. Location of plant utilities, fire station, administrative office, canteen, workshop, and laboratory are shown in the layout. Entry and exit for raw materials and finished product are also shown in the layout along with emergency exit for any contingency.

Scale drawings, complete with elevation indications can be used for determining the best location for equipment and facilities. Elementary layouts are developed first. These shows the fundamental relationships between storage Space and operating equipment. The next step requires consideration of the safe operational sequence and gives a primary layout based on the flow of materials, unit operations, storage, and future expansion. By analyzing all the factors that are involved in plant layout, a detailed recommendation can be presented, and drawings and elevations, including isometric drawings of the piping systems, can be prepared [22].

![Plant Layout](image)

**Fig. 7.1 plant layout**

CONCLUSION

Review of all the manufacturing processes has been presented. Snamprogetti process has been selected for the project. The Snamprogetti ammonia-stripping urea process involves a high NH3 to CO2 ratio in the reactor, ensuring the high conversion of carbamate to urea. The highly efficient ammonia stripping operation drastically reduces the recycling of carbamate and the size of equipment in the carbamate decomposition. Snamprogetti technology differs from competitors in being based on the use of excess ammonia to avoid corrosion as well as promote the decomposition of unconverted carbamate into urea.

Material & energy balance for each of the equipment has been done. The design of Plug flow reactor and multiple effect evaporators is done. Costing for whole plant is carried out and payback period is likely to be 6 years.

**REFERENCE**

9. EM Boddu, Wang, L., Wang, N”Production of Urea and Urea Ammonium Nitrate”, European