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A study on production of urea starting from natural gas by steam reforming to produce hydrogen

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Abstract
Urea (CO (NH)2) is one in each of the compositions in making fertilizer. Fertilizer is critical, in particular for plant increase (affecting plant fertility). If a plant had urea fertilizer on the soil, nitrogen inside the fertilizer releases speedy, and it will cause environmental pollutants. Therefore, many research need to expand urea fertilizer to be greater efficient to apply. The aim of this review is to search out the foremost appropriate technique for the efficient use of urea as seen from the material used, the technique used, and also the results received. This overview shows that the most appropriate technique is that the sluggish launch technique with NaOH and ash substances. Because this method can increase the powerful usage of urea, reduce environmental pollutants, and be pretty extra trustworthy, the cloth is extra cost-effective and spread extensively inside the market.
KEYWORDS*: Production of urea, natural gas, steam reforming , produce hydrogen.*

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I. Introduction

Nitrogen is an vital nutrient in vegetation that function in protein formation, chlorophyll synthesis, and metabolic procedures. Nitrogen is likewise one of the macronutrients required by way of vegetation. Urea is widely used as fertilizer due to its excessive nitrogen content (± forty six%). However, as lots as 50-60% nitrogen is lost via leaching, decomposition, and evaporation of ammonia. Although nitrogen losses may be decreased by re-fertilization in a single planting season, this technique is inefficient because farmers' manufacturing expenses can be higher. Urea is a polar, fairly soluble in water, and rate-impartial molecule, with oxygen and two nitrogen atoms serving as hydrogen bond acceptors. Two amino functions offer a complete of 4 hydrogen bonds for donation. The molecular system is CO(NH2)2; the molecular mass is 60.06 g/mol. Based on Dazmiri, MK et al., 2019, formaldehyde to urea has three preliminary molar ratios F/U of one.Nine, 2.1, and a pair of,3 resin synthesis have been examined on this paintings . While in Dorieh A. Et al., 2018 initial molar ratio formaldehyde F/U ~ 5 and 4.Three molar ratio

Nitrogen in agricultural and plantation sports is met via a fertilization method, such as urea. Excess use of urea fertilizer in agricultural and plantation sports outcomes in environmental pollution. Urea fertilizer handiest gives a small part of the nutrients that vegetation soak up, and the rest is wasted inside the environment. Based at the researches, CO(NH2) various methods can produce 2, along with slow-launch fertilizer with a couple of materials (chitosan matrix; fluidized mattress; coal fly ash and NaOH; cooking oil and paraffin; PVA

polymer; aldehyde with three-4 atoms of carbon), gasification with the help of temperature regulation, nuclear cogeneration, the nuclear steam reforming procedure, spectro photometry, and graphene education.

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II. FINANCIAL CONSIDERATIONS

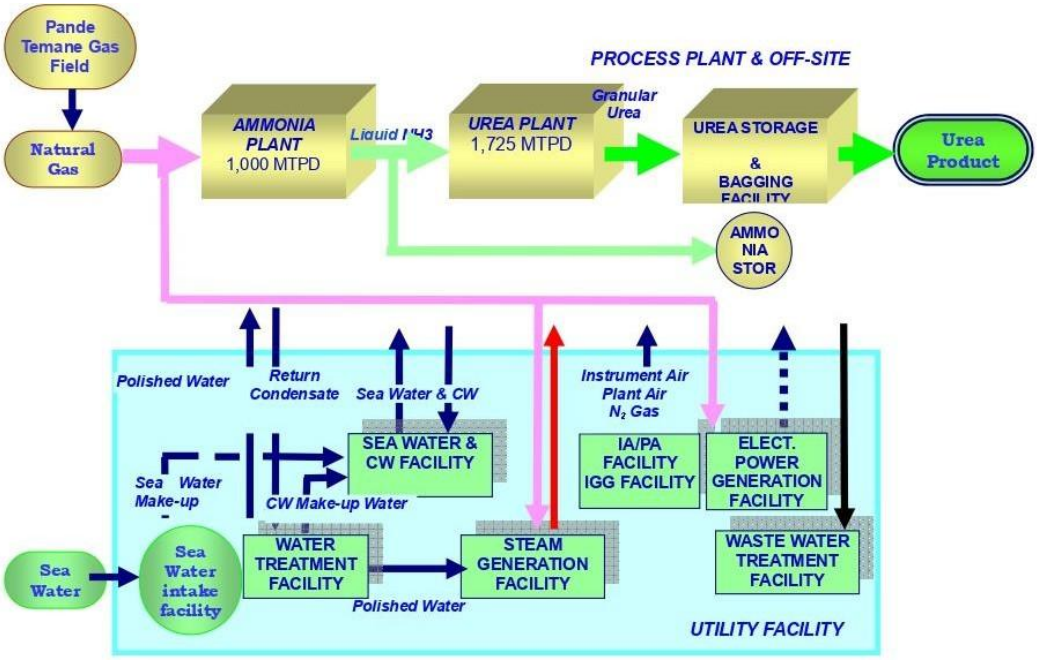
The technique makes use of 3 important raw substances: herbal gas, air and water. Petrochem's plant is situated adjoining to the Kapuni fuel remedy plant so herbal fuel is effortlessly accessible. Natural fuel is used for both gas gasoline and as a source of carbon dioxide and hydrogen for the technique. Air is, of direction, in considerable deliver. Water is pumped from the close by Waingongoro circulation for head water to the boilers, cooling water and procedure water. This water is treated after exiting the technique and back to the move. Thus, all raw materials are reasonably-priced and effectively to be had.

Costs are minimised all through the manner by means of using waste heat boilers and heat exchangers. There is a co-era plant and turbo generator on web page which collectively produce around 80% of the electricity had to run the plant.

Petrochem has gone through an upgrade to growth the production capacity of the plant. When this growth is fully commissioned, manufacturing capacity will boom to 750 tonnes of urea according to day.

The number one purpose of this LCA is to quantify and examine the overall environmental components of producing hydrogen thru herbal gas steam reforming. In recognition of the truth that upstream methods required for the operation of the steam methane reforming

(SMR) plant also produce pollutants and consume power and herbal assets, this LCA changed into accomplished in a cradle-to-grave way.



Hydrogen Plant Description and Assumptions

The device studied on this LCA is hydrogen production via catalytic steam reforming of natural gasoline, that is a mature generation and is the route with the beneficial aid of which most hydrogen is made in recent times. The method is the same as that used and defined in element in in advance LCAs finished with the resource of NREL (Mann and Spath, 1997 and Spath and Mann, 1999). The fabric and power stability statistics for the hydrogen plant had been taken from SRI, 1994. This file offers an correct photograph of cutting-edge everyday SMR plant with one exception; the layout does no longer encompass a low temperature shift (LTS) reactor.

Past evaluation (Mann, 1995) and modern workout within the hydrogen manufacturing industrial agency have demonstrated the addition of an LTS reactor to be inside your approach because of the small amount of extra hydrogen produced. Therefore, for this LCA, the SRI format emerge as modified to embody an LTS conversion step. For evaluation, a sensitivity assessment have turn out to be finished to have a have a examine the distinction within the everyday emissions if an LTS reactor had been now not covered within the hydrogen plant layout (see segment 7.Zero).

Another direction for hydrogen economic machine has been advised thru the integration of fuel cellular gadget with the bio-hydrogen production tool. Such setups may be positioned strategically close to to the ones places wherein deliver of feedstock is effortlessly available in extremely good sufficient quantities. The energy generated with the resource of manner of such device may be used to affect villages in a decentralized manner. It is commonly recommended to take-up such sports activities in Mission Mode as much as 2022.

Figure 1 is a block glide diagram of the herbal fuel steam reforming plant studied on this analysis. Prior to steam reforming, the herbal gas is pretreated in a hydrogenation vessel so that you can convert any sulfur compounds to H2S. A small quantity of hydrogen, that's recycled from the product circulate, is used on this step. The H2S is then eliminated in a ZnO bed. After pretreatment, the natural fuel and a pair of.6 MPa (380 psi) steam are fed to the steam reformer. The resulting synthesis fuel is then fed to excessive temperature shift (HTS) and LTS reactors where the water gas shift reaction converts 92% of the CO into H2. The hydrogen is purified

using a stress swing adsorption (PSA) unit. The reformer is fueled ordinarily with the aid of the PSA off-gasoline, but a small amount of natural gas (four.4 wt% of the entire reformer gas requirement) is used to supply the balance of the reformer responsibility. The PSA off-gasoline is comprised of CO2 (fifty five mol%), H2 (27 mol%), CH4 (14 mol%), CO (three mol%), N2 (zero.Four mol%), and a few water vapor. The steam reforming system produces four.Eight MPa (seven hundred psi) steam, which is assumed to be exported to be used with the aid of some different process or facility. Electricity is bought from the grid to perform the pumps and compressors. Table 1 gives the essential overall performance and layout records for the hydrogen plant.

Figure 1: Hydrogen Plant Block Flow Diagram

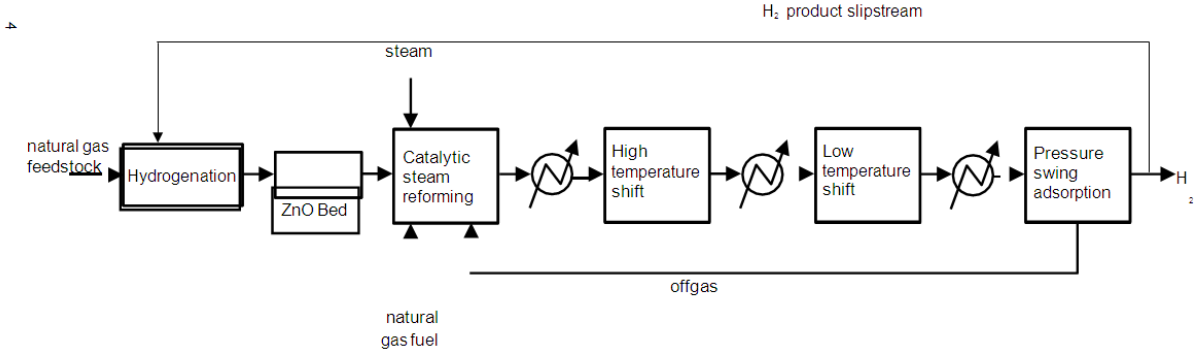


Table : Steam Methane Reforming Hydrogen Plant Data

Design Parameter	Data
Plant size (hydrogen production capacity)	1.5 million Nm^3/day(57 million scfd)
Hydrogen purity	Industrial grade (>99.95 mol% H_2)
Average operating capacity factor	90%
Natural gas consumed @ 100% operating capacity	392 Mg/day (feed) 43 Mg/day (fuel)
Steam requirement (2.6 MPa or 380 psi) @ 100% operating capacity	1,293 Mg/day
Steam production (4.8 MPa or 700 psi) @ 100% operating capacity	1,858 Mg/day
Electricity requirement @ 100% operating capacity	153,311 MJ/day
Hydrogen plant energy efficiency (higher heating value (HHV) basis)	89% (defined in text below)

Note: The hydrogen plant efficiency changes if the excess steam can not be utilized by a nearby source. However, thisdoes not change the amount of hydrogen produced by the plant

The hydrogen plant energy efficiency is defined as the total energy produced by the hydrogen plant dividedby the total energy into the plant, determined by the following formula:

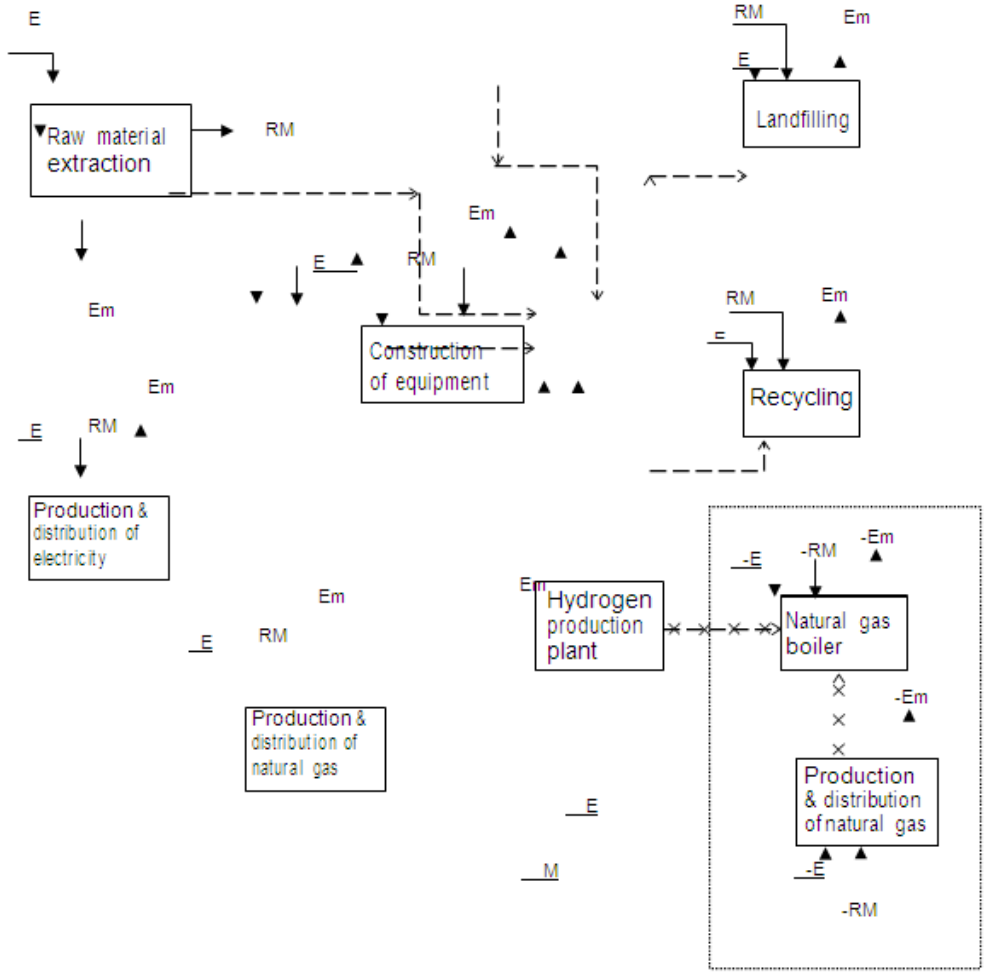
$$\frac{\text{energy in product hydrogen + 4.8 MPa steam energy (exported)}}{\text{natural gas energy + electricity + 2.6 MPa steam energy (required)}}$$

If the steam have been no longer blanketed inside the above equation, the conversion efficiency could decrease to seventy nine.2% (i.E., the 2.6 MPa steam is produced internally and the 4.Eight MPa steam couldn't be utilized by another supply). Additionally, if a user could not be found for the 4.8 MPa steam however the 2.6 MPa steam were nonetheless included as an electricity enter, then the hydrogen plant energy efficiency drops to 69.1%. While this will be the favored operation for a hydrogen plant integrated with petroleum refining, a stand-on my own committed hydrogen manufacturing facility would generate the 2.6 MPa steam internally in preference to purchase it if a purchaser for the four.Eight MPa steam could not be located. Additionally, if a customer couldn't be found for the 4.8 MPa steam, the operator might bear in mind the usage of it to generate energy to be used internally or for sale to the grid. However, it need to be referred to that given equal possibility to find customers, a steam byproduct credit is well worth more than an electricity byproduct credit score because of performance losses in converting steam to power.In addition to including an LTS reactor to the plant layout, the reformer flue gasoline composition became corrected to encompass NOx, CO, and particulate emissions. Since the reformer furnace is ready with a low NOX burner which reduces the emissions to 20 ppm (SRI, 1994),

this quantity turned into assumed to be emitted from the hydrogen plant. CO and particulate emissions had been acquired from the U.S. Environmental Protection Agency's (EPA) statistics on natural gasoline combustion furnaces (U.S. EPA, 1995). The quantity of the pollutant is given per the quantity of natural gasoline fired based on a median natural gasoline HHV of eight,270 kcal/m3 (1,000 Btu/scf). The records have been ratioed to account for the difference in the heating value of the reformer fuel as opposed to that of herbal fuel. The resulting CO and particulate emissions from the reformer are zero.084 g/kg H2 and
0.023 g/kg H2, respectively.

The stressors associated with herbal fuel production and distribution, in addition to those for electricity technology, were taken from the TEAM® database, called Data for Environmental Analysis and Management (DEAM). The steps associated with obtaining the herbal gasoline feedstock are drilling/extraction, processing, and pipeline transport. Processing consists of glycol dehydration and gas sweetening the use of the amine method in which sulfur is recovered as elemental sulfur. The emissions related to each method step within the natural gasoline production block were obtained through a joint examine through Ecobalance, Inc. And the Gas Research Institute (GRI). Electricity manufacturing become assumed to be the generation blend of the mid-continental United States, which according to the National Electric Reliability Council, uses sixty four.7% coal, 5.1% lignite, 18.4% nuclear, 10.3% hydro, 1.4% natural gasoline, and 0.1% oil; power distribution losses are taken at 7.03%. The stressors associated with this mix were also decided in a cradle-to-grave manner in DEAM, and as a result taken into consideration in this LCA. Some information about the DEAM database modules may be observed inside the appendix of Mann and Spath

System Boundaries for Hydrogen Productionvia Natural Gas Steam Reforming



Em = emissionsM = materials
RM = raw materials

Because hydrogen manufacturing by steam reforming of natural fuel is a exceptionally exothermic method extra steam is produced by the hydrogen plant than is fed on. The extra steam generated via the plant is assumed to be utilized by every other supply. Because this different source does now not must generate steam itself, a credit score is taken for the stressors that could have resulted from producing and transporting natural

fuel and combusting it in a boiler assuming a boiler performance of seventy five%. The emissions for natural gas production are the same as the ones mentioned inside the previous paragraph. The natural gas boiler emissions were based on emissions from EPA for natural gas combustion in industrial boilers (U.S. EPA, 1995). A sensitivity evaluation was finished to study the modifications in the LCA results for the case in which no person for the steam might be determined, and consequently credit couldn't be taken for the extra steam.

Construction Material Requirements

Methods for figuring out plant creation and decommissioning are the same as those used in NREL's past LCAs (see Mann and Spath, 1997 and Spath and Mann, 1999). Table lists the fabric requirements used for the plant in this examine. A sensitivity analysis become done to determine how converting those numbers could affect the outcomes

Table : Hydrogen Plant Material Requirements (Base Case)

Material	Amount required(Mg)
Concrete	10,242
Steel	3,272
Aluminum	27
Iron	40

Steam Methane Reforming

Approximately ninety seven% of commercially available hydrogen is produced by using Steam Methane Reforming (SMR).

SMR includes several techniques:

The reaction of methane (CH4) and steam to shape H2 and CO Endothermic reaction happening at approximately 815°C and 3.Five MPa over a nickel based totally catalyst.The 2d response is known as the water-gasoline shift response which converts CO and steam to CO2 and H2 and is cut up into two steps, the low temperature shift (LTS) and excessive temperature shift (HTS). LTS - Exothermic response happening at 200°C the use of a CuO catalyst HTS - Exothermic reaction going on at 350°C in the presence of an Fe2O3 catalyst In a very last manner known as ‘strain-swing adsorption’, CO2 and different impurities are removed from the gas circulation, leaving basically natural hydrogen.

*Steam reforming can also be used to produce hydrogen from other fuels, such as ethanol, propane or even gasoline.

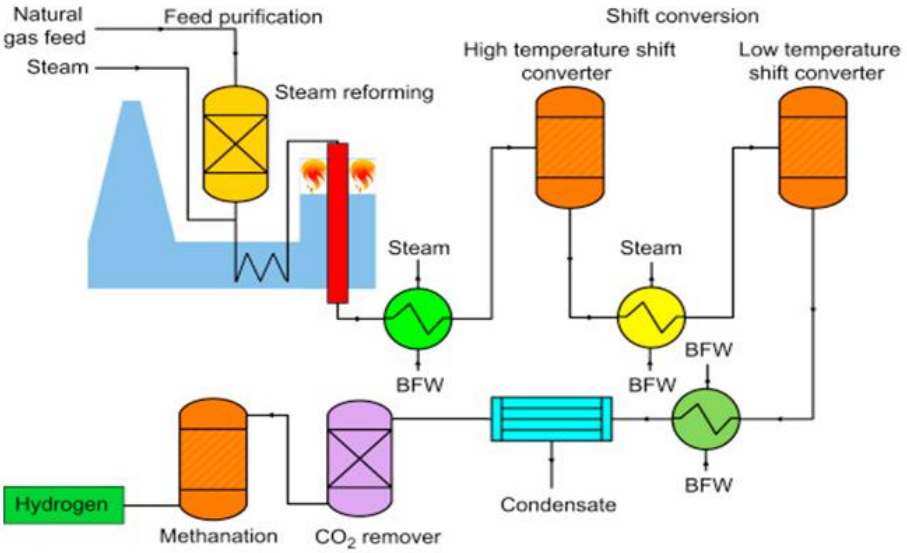
Natural fuel reforming is a sophisticated and mature manufacturing method that builds upon the present herbal gasoline pipeline transport infrastructure. Today, 95% of the hydrogen produced in the United States is made by way of natural gasoline reforming in big relevant flowers. This is an crucial technology pathway for near-term hydrogen manufacturing.

How Does It Work?

Natural gasoline consists of methane (CH4) that can be used to produce hydrogen with thermal tactics, which includes steam-methane reformation and partial oxidation.Steam-Methane Reforming Most hydrogen produced nowadays inside the United States is made through steam-methane reforming, a mature production procedure in which excessive-temperature steam (seven hundred°C–1,000°C) is used to provide hydrogen from a methane supply, together with herbal gasoline. In steam-methane reforming, methane reacts with steam underneath 3–25 bar strain (1 bar = 14.Five psi) within the presence of a catalyst to provide hydrogen, carbon monoxide, and a enormously small quantity of carbon dioxide. Steam reforming is endothermic—this is, warmness have to be furnished to the process for the reaction to proceed. Subsequently, in what's called the "water-gas shift response," the carbon monoxide and steam are reacted the use of a catalyst to supply carbon dioxide and greater hydrogen. In a final manner step known as "pressure-swing adsorption," carbon dioxide and other impurities are eliminated from the fuel move, leaving basically pure hydrogen. Steam reforming can also be used to provide hydrogen from other fuels, such as ethanol, propane, or maybe gas.

Steam-methane reforming reaction: $CH_4 + H_2O$ (+ heat) $\rightarrow CO + 3H_2$

Water-gas shift reaction : $CO + H_2O \rightarrow CO_2 + H_2$ (+ small amount of heat)



urea production:

The Profertil plant in Bahia Blanca, Argentina is designed to supply 1.1 million tonnes of urea and 775 thousand tonnes of ammonia each yr (Profertil 2000). The start-up of the ammonia plant changed into completed within the first week of October 2000. In contemporary months, some of releases of ammonia have passed off at the Profertil plant.

On August twenty 8th, an ammonia leak took place inside the route of begin up strategies. The leak is believed to had been because of extra strain in a tank maintaining hundred cubic metres of aqueous ammonia. Measurements taken after the release showed levels of ammonia inside the air of amongst forty and one hundred ppm. The maximum allowable interest is 35ppm. Levels of ammonia in the air at the time of the release also can were extensively excessive than the ones degrees.

People within the place said burning eyes and respiration tract, and referred to that it end up "now not possible to breathe". More than 80 people had been hospitalised, many requiring respiratory assist. Students at colleges near to the economic complicated were evacuated. As a give up stop stop result of the discharge, the Argentinean regulatory company Sectretaria de Polytica Ambiental (SPA) ordered the plant to prevent manufacturing at the facility after August 31.On November eighth, a leak of ammonia fuel took place within the course of the begin-up of the urea plant. The cognizance of ammonia have end up measured at 4-12 ppm for lots much less than one hour at the plant fence line. As a end result of the discharge, the Argentinean regulatory organisation Sectretaria de Polytica Ambiental (SPA) ordered the plant to prevent manufacturing. The ammonia plant remained in operation.This file covers the manufacturing and uses of ammonia and urea, collectively with a speak of accidental commercial releases of ammonia. The toxicology and regulation of those compounds are also mentioned.

Fertilizers

Fertilizers fall into 3 fashionable categories; nitrogen (N) based totally, phosphorus (P) primarily based, and mixed nitrogen-phosphorus (N-P) based.

The majority of nitrogen based totally fertilizers are derived from ammonia. In the 1990s, over 95% of all industrial nitrogen fertilizer was derived from synthetic ammonia. Worldwide, the once a year production of synthetic ammonia is ready 120 million tonnes, of which approximately 85% is used in fertilizers, along with urea (Kroschwitz & Howe-Grant 1995b).

Ammonia

Ammonia, NH3, is a relatively stable, colourless gasoline at ordinary temperatures, with a boiling point of –33°C. Ammonia gas is lighter than air, with a density of about zero.6 instances that of air at the equal temperature (Marshall 1987). The feature stinky odors of ammonia may be detected as low as 1-5ppm (USDHHS 1978).

Ammonia can be incredibly toxic to a extensive range of organisms. In humans, the best risk is from inhalation of ammonia vapour, with effects such as infection and corrosive damage to pores and skin, eyes and

breathing tracts. At very high degrees, inhalation of ammonia vapour may be deadly. When dissolved in water, elevated degrees of ammonia also are poisonous to a huge range of aquatic organisms. The toxicology of ammonia is discussed in greater element in Section four. Ammonia is incredibly soluble in water, although solubility decreases unexpectedly with multiplied temperature. Ammonia reacts with water in a reversible response to produce ammonium (NH4+) and hydroxide (OH-) ions, as proven in equation [1]. Ammonia is a susceptible base, and at room temperature simplest approximately 1 in 200 molecules are present within the ammonium form (NH4+). The formation of hydroxide ions in this reaction increases the pH of the water, forming an alkaline answer. If the hydroxide or ammonium ions react similarly with other compounds within the water, more ammonia with react to reestablish the equilibrium.

NH3 + H2O D NH4+ + OH- [1]

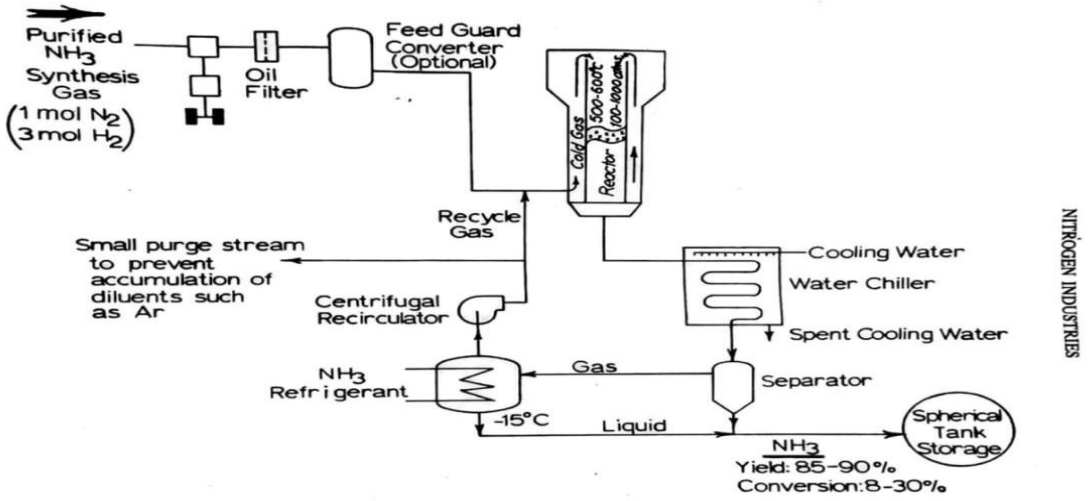
While ammonia-air mixtures are flammable when the ammonia content is 16-25% by way of extent, these combinations are quite tough to ignite (Kroschwitz & Howe-Grant 1995a).

Ammonia

Essentially all of the strategies employed for ammonia synthesis are versions of the HaberBosch approach, advanced in Germany from 1904-1913. This approach entails the response of hydrogen and nitrogen below immoderate temperatures and pressures with an iron primarily based definitely catalyst. This procedure moreover requires big strength intake (Kroschwitz & Howe-Grant 1995b). Ammonia is normally produced at some big flora with flow capacities of 1 thousand tonnes/day or greater (Marshall 1987).

The formation of ammonia from hydrogen and nitrogen is a reversible response, as tested in equation [2]. The fraction of ammonia in the final gasoline combination is relying on the conditions hired. Unreacted hydrogen and nitrogen gases separated from the ammonia and are commonly recycled. In almost all modern flora, the ammonia produced is recovered via condensation to offer liquid ammonia (Kroschwitz & Howe-Grant 1995a).

H2 + 3N2 D 2NH3 2



Synthetic ammonia process.

Urea

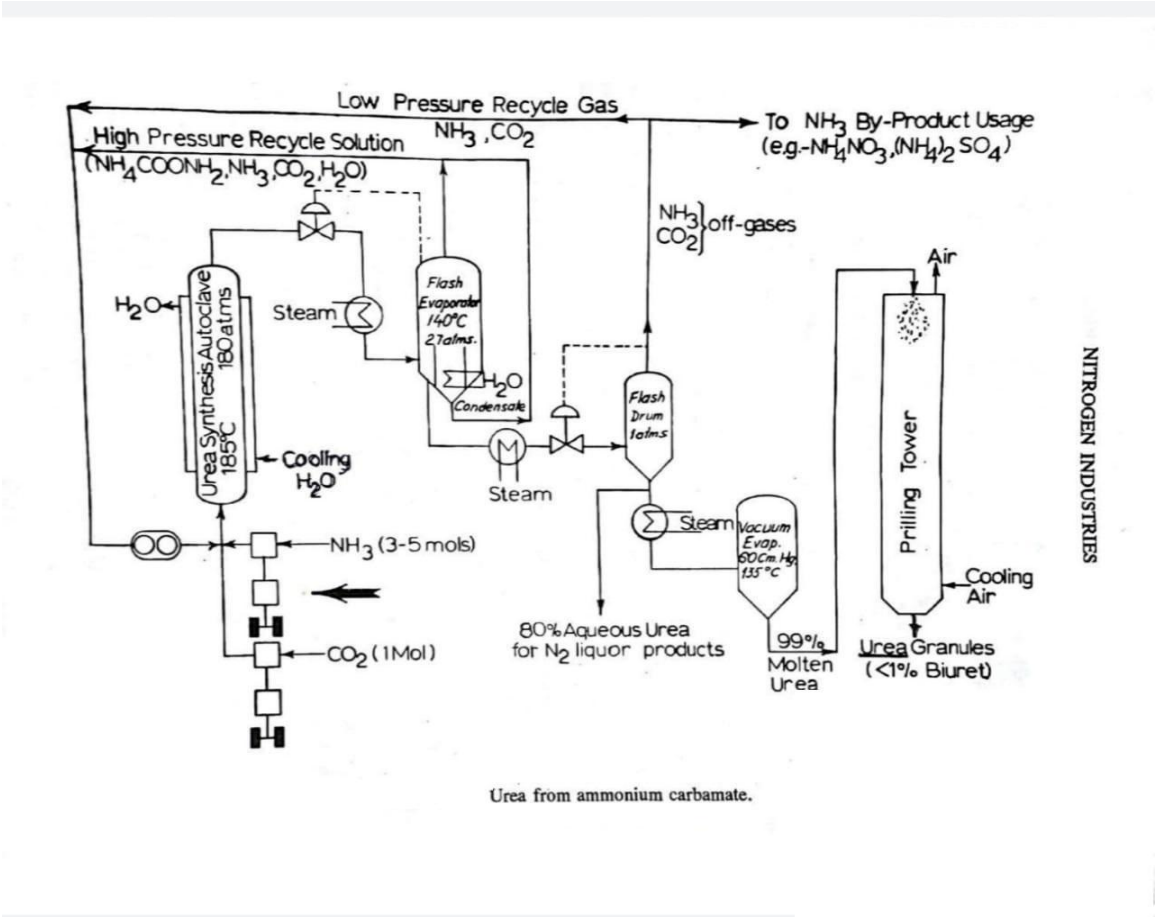
Urea (NH2CONH2) is comprised of ammonia (NH3) and gaseous carbon dioxide (CO2) at excessive stress and comparatively high temperature. Both reactants are obtained from ammonia synthesis, as discussed in Section 2.1. The manufacturing of urea includes the formation of ammonium carbamate (NH2COONH4), that is dehydrated to form urea. For all realistic functions, those reactions take area concurrently (see equations).

2 NH3 + CO2 D NH2COONH4 + warm temperature

NH2COONH4 + warm temperature D NH2CONH2 + H2O

Both of these reactions are reversible, and consequently ammonia and carbon dioxide exit the reactor in conjunction with ammonium carbamate and urea. The components of this combination are then separated, normally with the aid of stripping off gaseous ammonia observed via carbon dioxide, to yield urea.

There are some of technique for dealing with ammonia in this system, including the as soon as through, the partial recycle and the whole recycle procedures (Kroschwitz & Howe-Grant 1995b)



Urea from ammonium carbamate.

III. Conclusion

Hydrogen manufacturing has improved 4-fold within the remaining 40 years. Steam reformer of herbal gas remains the most common and most inexpensive way to supply hydrogen; indeed, hydrogen from renewable resources is luxurious as compared to fossil fuels and besides for biomass gasification, the modern-day technology are at laboratory scale. Moreover, the steam reforming is a key era for promoting decarbonization of fossil fuels pathways.

Pre-combustion carbon-capture strategies primarily based at the reforming of hydrocarbons look like the most geared up and lower priced way to reduce CO2 emissions whilst anticipating a future energy transition. In this paper, the commercial steam reformer (SR) has been compared with two emerging technologies: the membrane reactor, with catalyst packed within the tube section (MR1) or in the annuls section (MR2), and the reformer and membrane module (RMM).

These architectures permit to boom the production yields, to couple the steam reforming to solar strength harvesting and to recognize pre-combustion capture schemes such as the separation of CO2-rich currents from the ones wealthy in hydrogen. A one-dimensional mathematical model has worked out for mass, warmness and momentum balances for the 3 configurations considering the same running conditions, void fraction of the mattress and geometrical length. The benchmarking between the price of manufacturing and fee of permeation of hydrogen highlighted that only at the cease of the reactor the two velocities are identical with an average fee of production ten times more than the opposite one. The RMM configuration allows to in shape this phenomenology; indeed, by using decoupling the response section and permeation one is viable to optimize the 2 equipment independently.

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