

S T U · ·
· · · · ·
F C H P T
· · · · ·

SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA

FACULTY OF CHEMICAL AND FOOD TECHNOLOGY

INSTITUTE OF CHEMICAL AND ENVIRONMENTAL ENGINEERING

Nitrogen Chemical Fixation Technologies

REPORT ON TRAINING VISIT

In the frame work of the project

No. 2007/147-063

“A Euro-Asia Partnership for Development Human Resource Capacity of
Engineering Education in Afghanistan”

Funded by

EUROPEAN COMMISSION



SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA
FACULTY OF CHEMICAL AND FOOD TECHNOLOGY
DEPARTMENT OF CHEMICAL AND BIOCHEMICAL ENGINEERING

REPORT

ON MY ACADEMIC AND SCIENTIFIC ACTIVITIES IN TRAINING COURSE
AT THE SLOVAK UNIVERSITY OF TECHNOLOGY IN BRATISLAVA

PREPARED BY: AHMAD ALI FARHAT, M.S

Assoc. Professor of Chemical Technology Faculty of Kabul Polytechnic University
in Afghanistan

GUIDENCE BY: DIPL. ING. JUMA HAYDARY, PhD

Professor of Chemical and Biochemical Engineering Department, Faculty of
Chemical and Food Technology of Slovak University of Technology in Bratislava

2011

Preface

I, Ahmad Ali "Farhat", am a professor in Nonorganic Substances Technology Department of Chemical Technology Faculty of Kabul Polytechnic University. I attended a two month training stay from 25.03.2011 to 01.06.2011 in Slovak University of Technology in Bratislava, Slovakia.

Main purpose of this training stay was familiarity with new pedagogic methods, and collecting new scientific articles and books on chemical technology topics.

Activities I've done during this training stay are listed below:

- Visiting and being familiar with chemical engineering laboratories.
- Visiting and being familiar with inorganic chemistry & inorganic substances technology laboratories.
- Visiting microbiology laboratories.
- Participating in some lectures, seminars, and laboratorial works of bachelor, master & PHD classes of chemical engineering department.
- Visiting faculty bookstore and library.
- Participating in chemical engineering annual conference, the 38th International conference of Slovak Society of Chemical Engineering.
- Collecting scientific articles and books (published 2000) in related nitrogen topics.

I want to appreciate and thank, doc. Ing. Juma Haydary, PhD. Prof. Jozef Markoš, DrSc. , and other teachers of the faculty of Chemical and Food Technology of the Slovak University of Technology in Bratislava for their excellent cooperation and collaboration.

Some parts of collected materials are inserted in continuation of this report.

With Respect

Ahmad Ali Farhat, ms

Contents

| Title | Page |
|---|-------------|
| Introduction | 4 |
| Section 1: Synthesis Gas Production | |
| 1.1- Syngas | 5 |
| 1.2- Syngas Uses | 6 |
| 1.3- Syngas Production | 7 |
| 1.4- Syngas Production Catalysts | 8 |
| 1.5- Syngas Production from natural gas using ZrO ₂ supported metals | 8 |
| 1.6- Syngas Production Scheme | 10 |
| References | 11 |
| Section 2: Nitrogen Production | |
| 2.1- Nitrogen | 12 |
| 2.2- Electromagnetic spectrum | 17 |
| 2.3- Reactions | 18 |
| 2.4- Compounds | 20 |
| 2.5- Production and applications | 22 |
| 2.6- Applications of nitrogen compounds | 23 |
| 2.7- Safety | 25 |
| 2.8- Nitrogen Uses | 26 |
| 2.9- Air Separation into oxygen, nitrogen, and argon background | 28 |
| References | 32 |
| Section 3: Ammonia Production | |
| 3.1- Ammonia | 33 |
| 3.2- Structure and basic chemical properties | 34 |
| 3.3- Natural Occurrence | 35 |
| 3.4- History | 35 |
| 3.5- Synthesis and production | 36 |
| 3.6- Haber Process | 38 |
| 3.7- Biosynthesis | 42 |
| 3.8- Ammonia Uses | 42 |
| 3.9- Safety precautions | 45 |
| 3.10- Ammonia Synthesis Promoted by Iron Catalysts | 48 |
| 3.11- A Better Catalyst for Ammonia Production | 49 |
| 3.12- World Ammonia Production | 51 |
| 3.13- Ammonia Production Scheme and Reactor | 53 |
| 3.14- Modeling and Simulation of Ammonia Synthesis Reactor | 54 |

| | |
|---|----|
| 3.15- Latest Developments in Ammonia Production | 55 |
| References | 57 |
| Section 4: Urea Production | |
| 4.1- Urea | 58 |
| 4.2- History | 58 |
| 4.3- Physiology | 59 |
| 4.4- In Humans | 59 |
| 4.5- In other species | 60 |
| 4.6- Urea Uses | 60 |
| 4.7- Urea Production | 65 |
| 4.8- Chemical Properties | 67 |
| 4.9- Safety | 68 |
| 4.10- Urea Production Scheme | 69 |
| References | 70 |

Introduction

Afghanistan has many resources of natural gas. Alone in its northern parts the resources of natural gas is estimated 60 billion cubic meters.

As Afghanistan is a agricultural country, and most of its people's income is from agriculture; the production of chemical fertilizers is one of the first needs of the people.

One of the excellent and universal fertilizers is urea, which's raw materials are natural gas, water, and air.

Afghanistan's national economy growth and development is not possible without developing the agricultural section. One of important factors for reaching that goal is production of nitrogen fertilizers and especially urea, which's raw materials are available inside Afghanistan.

In this report different steps of urea production is written & mentioned. The materials are taken from different valid and new scientific sources.

Section 1: Synthesis Gas Production

1.1- Syngas

Syngas (from synthetic gas or synthesis gas) is the name given to a gas mixture that contains varying amounts of carbon monoxide and hydrogen. Examples of production methods include steam reforming of natural gas or liquid hydrocarbons to produce hydrogen, the gasification of coal, biomass, and in some types of waste-to-energy gasification facilities. The name comes from their use as intermediates in creating synthetic natural gas (SNG) and for producing ammonia or methanol. Syngas is also used as an intermediate in producing synthetic petroleum for use as a fuel or lubricant via the Fischer–Tropsch process and previously the Mobil methanol to gasoline process.

Syngas consists primarily of hydrogen, carbon monoxide, and very often some carbon dioxide, and has less than half the energy density of natural gas. Syngas is combustible and often used as a fuel source or as an intermediate for the production of other chemicals.

Syngas can be used in the Fischer-Tropsch process to produce diesel, or converted into e.g. methane, methanol and dimethyl ether in catalytic processes.

If the syngas is post treated by cryogenic processing, it should be taken into account that this technology has great difficulty in recovering pure carbon monoxide if relatively large volumes of nitrogen are present due to carbon monoxide and nitrogen having very similar boiling points which are $-191.5\text{ }^{\circ}\text{C}$ and $-195.79\text{ }^{\circ}\text{C}$ respectively. Certain process technology selectively removes carbon monoxide by complexation/decomplexation of carbon monoxide with cuprous aluminum chloride (CuAlCl_4), dissolved in an organic liquid such as toluene. The purified carbon monoxide can have a purity greater than 99%, which makes it a good feedstock for the chemical industry. The reject gas from the system can contain carbon dioxide, nitrogen, methane, ethane and hydrogen. The reject gas can be further processed on a pressure swing adsorption system to remove hydrogen and the hydrogen and carbon monoxide can be recombined in the proper ratio for catalytic methanol production, Fischer-Tropsch diesel etc. Cryogenic purification, being very energy intensive, is not well suited to simply making fuel, because of the greatly reduced net energy gain.

Syngas that is not methanized typically has a specific heat capacity of 120 BTU/scf. Untreated syngas can be run in hybrid turbines that allow for greater

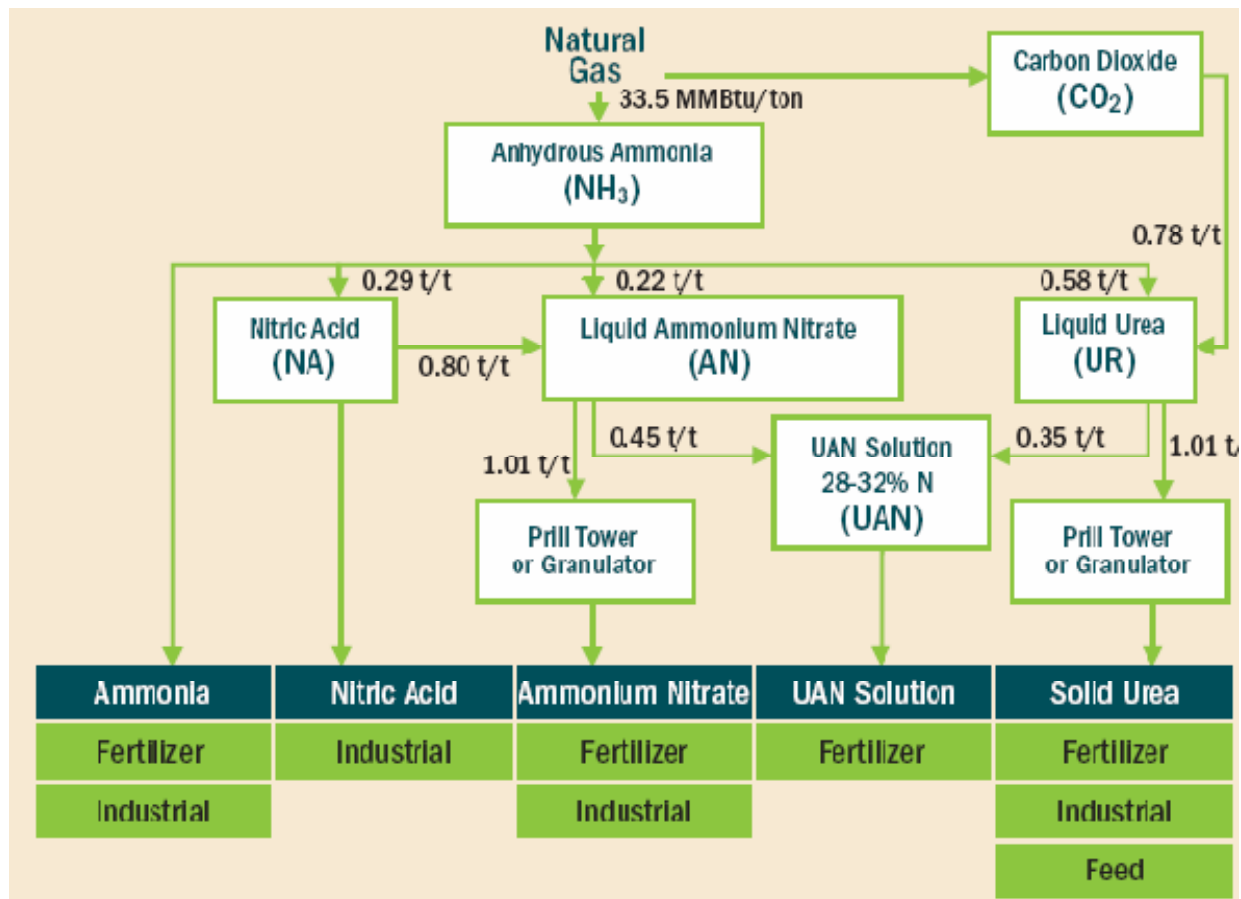
efficiency because of their lower operating temperatures, and extended part lifetime.

1.2- Syngas Uses

Syngas is a mixture of mostly hydrogen, carbon monoxide and carbon dioxide. Depending on the amount of hydrogen, syngas has roughly 25% the energy density of natural gas.

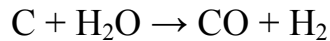
Syngas is one of the basic building blocks of the chemical industry, and can be used as a feedstock to produce products such as hydrogen, ammonia, ethanol and methanol.

Syngas can also be used to produce fuels such as in a Fischer-Tropsch process to produce synthetic diesel or ethanol, or by conversion into methane and dimethyl ether in catalytic reactions.

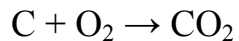


1.3- Syngas Production

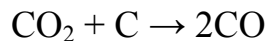
Syngas for use as a fuel is most often produced from coal, first by pyrolysis to coke (impure carbon), aka destructive distillation, followed by alternating blasts of steam and air, or from biomass or municipal waste mainly by the following simple paths:



$$\Delta H^\circ_{298} = 323,1 \text{ kJ/mol}$$



$$\Delta H^\circ_{298} = -394 \text{ kJ/mol}$$



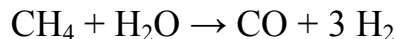
$$\Delta H^\circ_{298} = 282,1 \text{ kJ/mol}$$

The first reaction, between incandescent coke and steam, is strongly endothermic, producing carbon monoxide (CO) and hydrogen H₂ (water gas in older terminology).

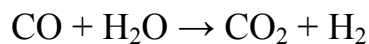
When the coke bed has cooled to a temperature at which the endothermic reaction can no longer proceed, the steam is then replaced by a blast of air.

The second and third reactions then take place, producing an exothermic reaction - forming initially carbon dioxide - raising the temperature of the coke bed - followed by the second endothermic reaction, in which the latter is converted to carbon monoxide, CO. The overall reaction is exothermic, forming "producer gas" (older terminology). Steam can then be re-injected, then air etc., to give an endless series of cycles until the coke is finally consumed. Producer gas has a much lower energy value, relative to water gas, due primarily to dilution with atmospheric nitrogen. Pure oxygen can be substituted for air to avoid the dilution effect, producing gas of much higher calorific value.

When used as an intermediate in the large-scale, industrial synthesis of hydrogen (principally used in the production of ammonia), it is also produced from natural gas (via the steam reforming reaction) as follows:



In order to produce more hydrogen from this mixture, more steam is added and the water gas shift reaction is carried out:



The hydrogen must be separated from the CO_2 to be able to use it. This is primarily done by pressure swing adsorption (PSA), amine scrubbing and membrane reactors.

The syngas produced in large waste-to-energy gasification facilities can be used to generate electricity.

Coal gasification processes were used for many years to manufacture illuminating gas (coal gas) for gas lighting, cooking and to some extent, heating, before electric lighting and the natural gas infrastructure became widely available.

1.4- Syngas Production Catalysts

Short contact time catalytic partial oxidation (SCT-CPO) of natural gas is a promising technology for syngas production, representing an appealing alternative to existing processes. This process is likely to become more important in the future due to its advantages in thermodynamics, mildly exothermic overall reaction, and H_2/CO ratio of 2, ideal for downstream processes. Rh catalysts are preferred among those based on noble metals because they avoid coke deposition. However, Rh is very expensive. Thus, the design of nanocomposite catalysts with the minimum Rh load for a feasible industrial process is the aim of the present work: 0.25, 0.5, and 1% Rh load were considered. The catalytic reactor is made of a fixed bed of Rh deposited on both Al_2O_3 spheres in an egg-shell configuration and Al_2O_3 irregular particles in an egg-yolk configuration. The weight hourly space velocity (WHSV) was varied from 130 to 460 $\text{N L h}^{-1} \text{g}_{\text{cat}}^{-1}$. The 0.5% Rh in the egg-yolk configuration allowed the highest CH_4 conversion (>90%) and H_2 selectivity (>98%) values at any tested WHSV.

1.5- Syngas production from natural gas using ZrO_2 -supported metals

Samples containing 1 wt% of Co, Cu, Fe, Ni, Pd and Pt supported on zirconia have been tested for the steam reforming of methane at temperatures from 400°C to 800°C. The Pt, Pd and Ni materials were found to be the most active. Stability

tests at 800°C showed that the Pt sample was the only stable catalyst, significant carbon deposition occurring on the other samples.

Partial oxidation and CO₂ reforming of methane were also carried out over the t/ZrO₂ catalyst and this material was found to be quite stable under the conditions for these reactions. Additional CO₂ reforming and partial oxidation experiments were carried out using feeds to which steam was added. The H₂/CO ratio could be manipulated, depending on the feed composition used. The addition of steam during partial oxidation gave a much more stable temperature profile through the catalyst bed than was obtained under pure partial oxidation conditions.

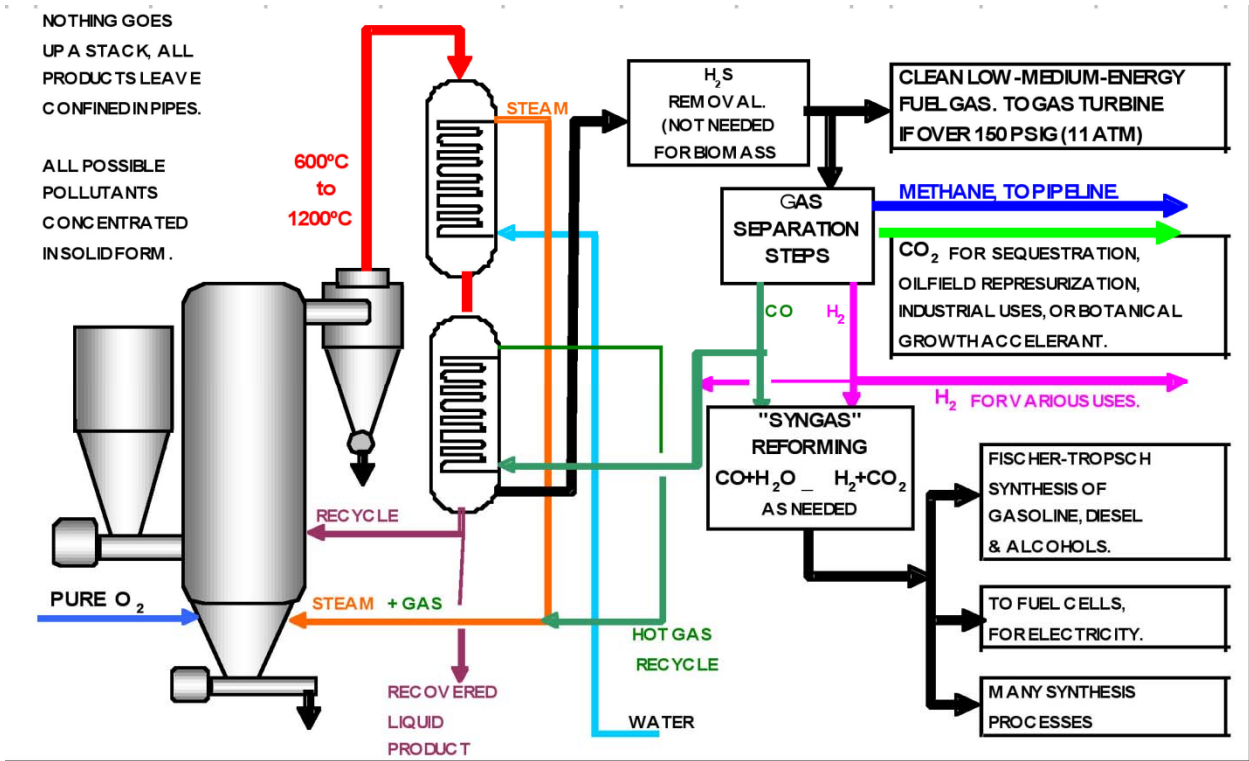
1.6- Partial Oxidation of Methane to Syngas over Monolithic Ni/γ-Al₂O₃ Catalyst-Effects of Rare Earths and Other Basic Promoters A series of monolithic Ni/γ-Al₂O₃ catalysts with and without basic promoters (Na, Sr, La, Ce) were prepared.

Partial oxidation of methane (POM) to syngas was carried out in a continuous-flow, fixed-bed reactor. The influences of reaction conditions, including temperature, CH₄/O₂ ratio and space velocity, on the performance of the catalyst were investigated.

The results show that at a high space velocity of 1 x 10⁴ h⁻¹, optimal CH₄ conversion can be obtained. Effects of promoters such as Na, Sr, Ce, La were also investigated, and the catalyst samples were characterized by means of temperature-programmed reduction and XRD techniques. XRD suggests that the addition of promoters has no influence on the crystal structure of Ni/γ-Al₂O₃ catalyst. The results show that the addition of a small amount of promoters improves the reducibility and activity of the catalyst. The side reaction CH₄ + 2 CO₂ + H₂O, is fully restrained and 100% H₂ selectivity is achieved when Ce and La are used as promoters, respectively.

For further information you can refer to reference [5].

1.6- Syngas Production Scheme



References

- 1-** Kirk, Otheimer (Eds.), Encyclopaedia of Chemical Technology, vol. 12, 3rd ed., Wiley, New York, 1994, p. 951.
- 2-** A.N.J. van Keulen, M.E.S. Hegarty, J.R.H. Ross, P.F. van den Oosterkamp, Stud. Surf. Sci. Catal. 107 (1997) 537.
- 3-** Emmanuel O. Oluyede. "FUNDAMENTAL IMPACT OF FIRING SYNGAS IN GAS TURBINES". Clemson/EPRI.
<http://www.clemson.edu/scies/UTSR/fellowoluyedesum.pdf>. Retrieved 2010-08-07.
- 4-** Xenophon E. Verykios, Catalytic dry reforming of natural gas for the production of chemicals and hydrogen , International Journal of Hydrogen Energy 28 (2003) 1045 – 1063
- 5-** Partial Oxidation of Methane to Syngas over Monolithic Ni/y-A12O3 Catalyst-EffecEffects of REare Earths and Other Basic Promoters , JOURNAL OF RARE EARTHS 24 (2006) 45 1 - 455

Section 2: Nitrogen Production

2.1- Nitrogen

Nitrogen is a chemical element that has the symbol N, atomic number of 7 and atomic mass 14.00674 u. Elemental nitrogen is a colorless, odorless, tasteless, and mostly inert diatomic gas at standard conditions, constituting 78.08% by volume of Earth's atmosphere. The element nitrogen was discovered as a separable component of air, by Scottish physician Daniel Rutherford, in 1772.

Many industrially important compounds, such as ammonia, nitric acid, organic nitrates (propellants and explosives), and cyanides, contain nitrogen. The extremely strong bond in elemental nitrogen dominates nitrogen chemistry, causing difficulty for both organisms and industry in breaking the bond to convert the N₂ into useful compounds, but at the same time causing release of large amounts of often useful energy when the compounds burn, explode, or decay back into nitrogen gas.

| General properties | |
|-------------------------------|---|
| Name, symbol, number | nitrogen, N, 7 |
| Element category | nonmetal |
| Group, period, block | 15, 2, p |
| Standard atomic weight | 14.0067 |
| Electron configuration | 1s ² 2s ² 2p ³ |
| Physical properties | |
| Phase | gas |
| Density | (0 °C, 101.325 kPa) 1.251 g/L |
| Liquid density at b.p. | 0.808 g·cm ⁻³ |
| Melting point | 63.15 K -346.00 °F -210.00 °C, , |
| Boiling point | 77.36 K -320.33 °F -195.79 °C, , |
| Triple point | 63.1526 K (-210°C), 12.53 kPa |
| Critical point | 126.19 K, 3.3978 MPa |
| Heat of fusion | (N ₂) 0.72 kJ·mol ⁻¹ |
| Heat of vaporization | (N ₂) 5.56 kJ·mol ⁻¹ |

Nitrogen occurs in all living organisms, and the nitrogen cycle describes movement of the element from air into the biosphere and organic compounds, then back into the atmosphere. Synthetically-produced nitrates are key ingredients of industrial fertilizers, and also key pollutants in causing the eutrophication of water systems. Nitrogen is a constituent element of amino acids and thus of proteins and nucleic acids (DNA and RNA). It resides in the chemical structure of almost all neurotransmitters, and is a defining component of alkaloids, biological molecules produced by many organisms. The human body contains about 3% by weight of nitrogen, a larger fraction than all elements save oxygen, carbon, and hydrogen.

Nitrogen is formally considered to have been discovered by Daniel Rutherford in 1772, who called it noxious air or fixed air.^[1] The fact that there was an element of air that does not support combustion was clear to Rutherford. Nitrogen was also studied at about the same time by Carl Wilhelm

| | |
|---|--|
| <u>Specific heat capacity</u> | (25 °C) (N ₂) 29.124 J·mol ⁻¹ ·K ⁻¹ |
| <u>Vapor pressure</u> | |
| P (Pa) | 1 10 100 1 k 10 k 100 k |
| at T (K) | 37 41 46 53 62 77 |
| Atomic properties | |
| <u>Oxidation states</u> | 5, 4, 3 , 2, 1, -1, -2, -3 (strongly <u>acidic</u> oxide) |
| <u>Electronegativity</u> | 3.04 (Pauling scale) |
| <u>Ionization energies</u> (<u>more</u>) | 1st: 1402.3 <u>kJ·mol⁻¹</u> 2nd: 2856 <u>kJ·mol⁻¹</u> 3rd: 4578.1 <u>kJ·mol⁻¹</u> |
| <u>Covalent radius</u> | <u>71±1</u> pm |
| <u>Van der Waals radius</u> | <u>155</u> pm |
| Miscellanea | |
| <u>Crystal structure</u> | hexagonal |
| <u>Magnetic ordering</u> | diamagnetic |
| <u>Thermal conductivity</u> | (300 K) 25.83 × 10 ⁻³ W·m ⁻¹ ·K ⁻¹ |

Scheele, Henry Cavendish, and Joseph Priestley, who referred to it as burnt air or phlogisticated air. Nitrogen gas was inert enough that Antoine Lavoisier referred to it as "mephitic air" or azote, from the Greek word ἄζωτος (azotos) meaning "lifeless".^[2] In it, animals died and flames were extinguished. Lavoisier's name for nitrogen is used in many languages (French, Polish, Russian, etc.) and still remains in English in the common names of many compounds, such as hydrazine and compounds of the azide ion.

The English word nitrogen (1794) entered the language from the French nitrogène, coined in 1790 by French chemist Jean Antoine Chaptal (1756–1832), from "nitre" + Fr. gène "producing" (from Gk. γενής means "forming" or "giving birth to."). The gas had been found in nitric acid. Chaptal's meaning was that nitrogen gas is the essential part of nitric acid, in turn formed from saltpetre (potassium nitrate), then known as nitre. However, this word in the more ancient world originally described sodium salts that did not contain nitrate, and is a cognate of natron and nitron.

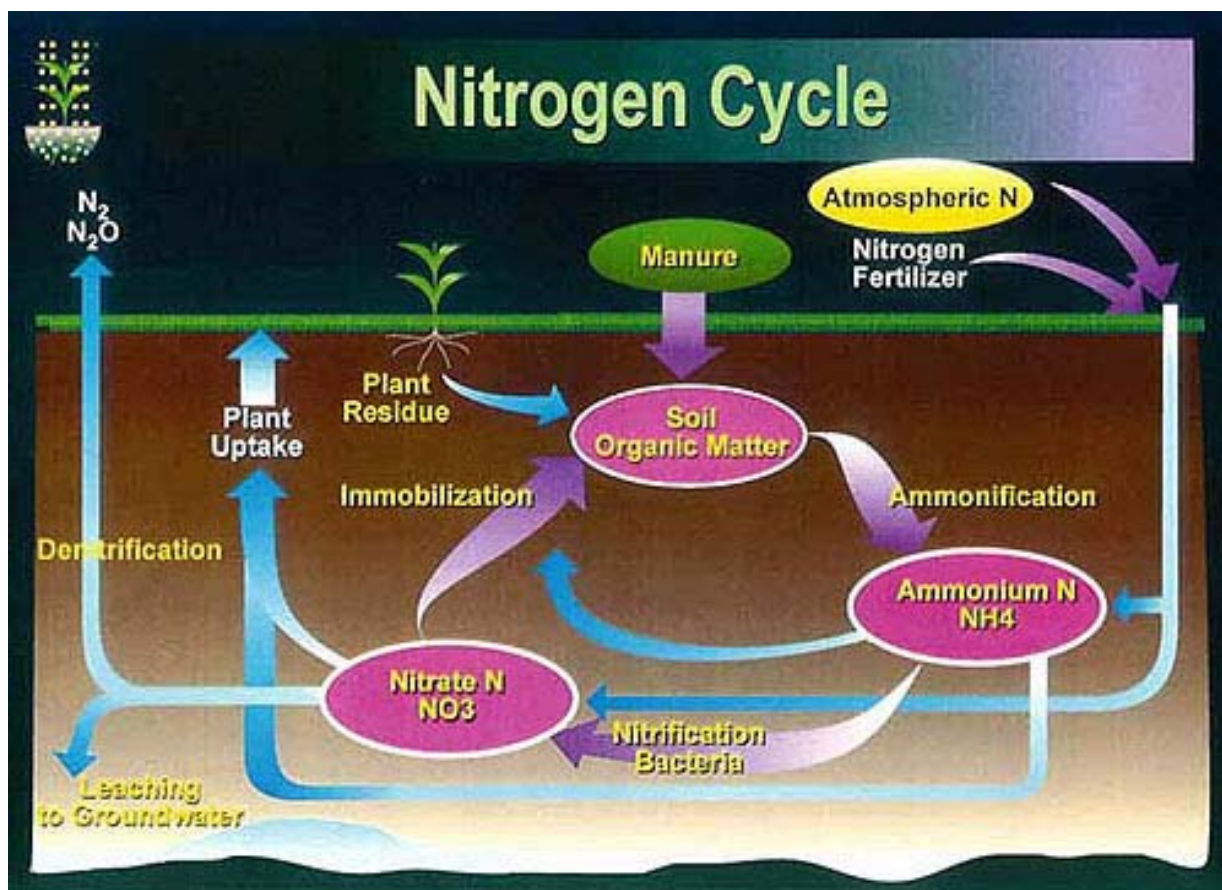
| | | | | | |
|--|----------------------|---|--------------------|--------------------------|--------------------|
| Speed of sound | (gas, 27 °C) 353 m/s | | | | |
| CAS registry number | 7727-37-9 | | | | |
| Most stable isotopes | | | | | |
| Main article: Isotopes of nitrogen | | | | | |
| iso | NA | half-life | DM | DE (MeV) | DP |
| ¹³ N | syn | 9.965 min | ε | 2.220 | ¹³ C |
| ¹⁴ N | 99.634% | ¹⁴ N is stable with 7 neutrons | | | |
| ¹⁵ N | 0.366% | ¹⁵ N is stable with 8 neutrons | | | |

Nitrogen compounds were well known during the Middle Ages. Alchemists knew nitric acid as aqua fortis (strong water). The mixture of nitric and hydrochloric acids was known as aqua regia (royal water), celebrated for its ability to dissolve gold (the king of metals). The earliest military, industrial, and agricultural applications of nitrogen compounds involved uses of saltpeter (sodium nitrate or potassium nitrate), the most notable in gunpowder, and later as fertilizer. In 1910, Lord Rayleigh discovered that an electrical discharge in nitrogen gas produced "active nitrogen", an allotrope considered to be monatomic. The "whirling cloud of brilliant yellow light" produced by his apparatus reacted with quicksilver to produce explosive mercury nitride.

Nitrogen is formally considered to have been discovered by Daniel Rutherford in 1772, who called it noxious air or fixed air. The fact that there was an element of air that does not support combustion was clear to Rutherford. Nitrogen was also studied at about the same time by Carl Wilhelm Scheele, Henry Cavendish, and Joseph Priestley, who referred to it as burnt air or phlogisticated air. Nitrogen gas was inert enough that Antoine Lavoisier referred to it as "mephitic air" or azote, from the Greek word *ἄζωτος* (azotos) meaning "lifeless". In it, animals died and flames were extinguished. Lavoisier's name for nitrogen is used in many languages (French, Polish, Russian, etc.) and still remains in English in the common names of many compounds, such as hydrazine and compounds of the azide ion.

The English word nitrogen (1794) entered the language from the French nitrogène, coined in 1790 by French chemist Jean Antoine Chaptal (1756–1832), from "nitre" + Fr. *gène* "producing" (from Gk. *γενής* means "forming" or "giving birth to."). The gas had been found in nitric acid. Chaptal's meaning was that nitrogen gas is the essential part of nitric acid, in turn formed from saltpetre (potassium nitrate), then known as nitre. However, this word in the more ancient world originally described sodium salts that did not contain nitrate, and is a cognate of natron and nitron.

Nitrogen compounds were well known during the Middle Ages. Alchemists knew nitric acid as aqua fortis (strong water). The mixture of nitric and hydrochloric acids was known as aqua regia (royal water), celebrated for its ability to dissolve gold (the king of metals). The earliest military, industrial, and agricultural applications of nitrogen compounds involved uses of saltpeter (sodium nitrate or potassium nitrate), the most notable in gunpowder, and later as fertilizer. In 1910, Lord Rayleigh discovered that an electrical discharge in nitrogen gas produced "active nitrogen", an allotrope considered to be monatomic. The "whirling cloud of brilliant yellow light" produced by his apparatus reacted with quicksilver to produce explosive mercury nitride.



Nitrogen is a nonmetal, with an electronegativity of 3.04. It has five electrons in its outer shell and is, therefore, trivalent in most compounds. The triple bond in molecular nitrogen (N_2) is the strongest. The resulting difficulty of converting N_2 into other compounds, and the ease (and associated high energy release) of converting nitrogen compounds into elemental N_2 , have dominated the role of nitrogen in both nature and human economic activities.

At atmospheric pressure molecular nitrogen condenses (liquefies) at 77 K ($-195.8\text{ }^\circ\text{C}$) and freezes at 63 K ($-210.0\text{ }^\circ\text{C}$) into the beta hexagonal close-packed crystal allotropic form. Below 35.4 K ($-237.6\text{ }^\circ\text{C}$) nitrogen assumes the cubic crystal allotropic form (called the alpha-phase). Liquid nitrogen, a fluid resembling water in appearance, but with 80.8% of the density (the density of liquid nitrogen at its boiling point is 0.808 g/mL), is a common cryogen.

Unstable allotropes of nitrogen consisting of more than two nitrogen atoms have been produced in the laboratory, like N_3 and N_4 . Under extremely high pressures (1.1 million atm) and high temperatures (2000 K), as produced using a diamond anvil cell, nitrogen polymerizes into the single-bonded cubic gauche crystal

structure. This structure is similar to that of diamond, and both have extremely strong covalent bonds. N_4 is nicknamed "nitrogen diamond."

Other (as yet unsynthesized) allotropes include hexazine (N_6 , a benzene analog) and octaazacubane (N_8 , a cubane analog). The former is predicted to be highly unstable, while the latter is predicted to be stable, for reasons of orbital symmetry.

There are two stable isotopes of nitrogen: ^{14}N and ^{15}N . By far the most common is ^{14}N (99.634%), which is produced in the CNO cycle in stars. Of the ten isotopes produced synthetically, ^{13}N has a half-life of ten minutes and the remaining isotopes have half-lives on the order of seconds or less. Biologically mediated reactions (e.g., assimilation, nitrification, and denitrification) strongly control nitrogen dynamics in the soil. These reactions typically result in ^{15}N enrichment of the substrate and depletion of the product.

A small part (0.73%) of the molecular nitrogen in Earth's atmosphere is the isotopologue $^{14}N^{15}N$, and almost all the rest is $^{14}N_2$.

Radioisotope ^{16}N is the dominant radionuclide in the coolant of pressurized water reactors or boiling water reactors during normal operation. It is produced from ^{16}O (in water) via (n,p) reaction. It has a short half-life of about 7.1 s, but during its decay back to ^{16}O produces high-energy gamma radiation (5 to 7 MeV).

Because of this, the access to the primary coolant piping in a pressurized water reactor must be restricted during reactor power operation. ^{16}N is one of the main means used to immediately detect even small leaks from the primary coolant to the secondary steam cycle.

In similar fashion, access to any of the steam cycle components in a boiling water reactor nuclear power plant must be restricted during operation. Condensate from the condenser is typically retained for 10 minutes to allow for decay of the ^{16}N . This eliminates the need to shield and restrict access to any of the feed water piping or pumps.

2.2- Electromagnetic spectrum

Molecular nitrogen ($^{14}N_2$) is largely transparent to infrared and visible radiation because it is a homonuclear molecule and, thus, has no dipole moment to couple to electromagnetic radiation at these wavelengths. Significant absorption occurs at extreme ultraviolet wavelengths, beginning around 100 nanometers. This is associated with electronic transitions in the molecule to states in which charge is



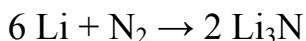
not distributed evenly between nitrogen atoms. Nitrogen absorption leads to significant absorption of ultraviolet radiation in the Earth's upper atmosphere and the atmospheres of other planetary bodies. For similar reasons, pure molecular nitrogen lasers typically emit light in the ultraviolet range.

Nitrogen also makes a contribution to visible air glow from the Earth's upper atmosphere, through electron impact excitation followed by emission. This visible blue air glow (seen in the polar aurora and in the re-entry glow of returning spacecraft) typically results not from molecular nitrogen but rather from free nitrogen atoms combining with oxygen to form nitric oxide (NO).

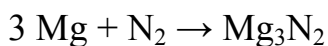
2.3- Reactions

In general, nitrogen is unreactive at standard temperature and pressure. N_2 reacts spontaneously with few reagents, being resilient to acids and bases as well as oxidants and most reductants. When nitrogen reacts spontaneously with a reagent, the net transformation is often called nitrogen fixation.

Nitrogen reacts with elemental lithium.^[11] Lithium burns in an atmosphere of N_2 to give lithium nitride:



Magnesium also burns in nitrogen, forming magnesium nitride.



N_2 forms a variety of adducts with transition metals. The first example of a dinitrogen complex is $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ (see figure at right). Such compounds are now numerous, other examples include $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$, $\text{W}(\text{N}_2)_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$, and $[(\eta^5\text{-C}_5\text{Me}_4\text{H})_2\text{Zr}]_2(\mu_2, \eta^2, \eta^2\text{-N}_2)$. These complexes illustrate how N_2 might bind to the metal(s) in nitrogenase and the catalyst for the Haber process. A catalytic process to reduce N_2 to ammonia with the use of a molybdenum complex in the presence of a proton source was published in 2005.

The starting point for industrial production of nitrogen compounds is the Haber process, in which nitrogen is fixed by reacting N_2 and H_2 over an iron(III) oxide (Fe_3O_4) catalyst at about $500\text{ }^\circ\text{C}$ and 200 atmospheres pressure. Biological nitrogen fixation in free-living cyanobacteria and in the root nodules of plants also produces ammonia from molecular nitrogen. The reaction, which is the source of the bulk of nitrogen in the biosphere, is catalyzed by the nitrogenase enzyme complex that contains Fe and Mo atoms, using energy derived from hydrolysis of adenosine triphosphate (ATP) into adenosine diphosphate and inorganic phosphate (-20.5 kJ/mol).

The main neutral hydride of nitrogen is ammonia (NH_3), although hydrazine (N_2H_4) is also commonly used. Ammonia is more basic than water by 6 orders of magnitude. In solution ammonia forms the ammonium ion (NH_4^+). Liquid ammonia (boiling point 240 K) is amphiprotic (displaying either Brønsted-Lowry acidic or basic character) and forms ammonium and the less common amide ions (NH_2^-); both amides and nitride (N^{3-}) salts are known, but decompose in water. Singly, doubly, triply and quadruply substituted alkyl compounds of ammonia are called amines (four substitutions, to form commercially and biologically important quaternary amines, results in a positively charged nitrogen, and thus a water-soluble, or at least amphiphilic, compound). Larger chains, rings and structures of nitrogen hydrides are also known, but are generally unstable.

Other classes of nitrogen anions (negatively charged ions) are the poisonous azides (N_3^-), which are linear and isoelectronic to carbon dioxide, but which bind to important iron-containing enzymes in the body in a manner more resembling cyanide. Another molecule of the same structure is the colorless and relatively inert anesthetic gas Nitrous oxide (dinitrogen monoxide, N_2O), also known as laughing gas. This is one of a variety of nitrogen oxides that form a family often abbreviated as NO_x . Nitric oxide (nitrogen monoxide, NO), is a natural free radical used in signal transduction in both plants and animals, for example, in vasodilation by causing the smooth muscle of blood vessels to relax. The reddish and poisonous nitrogen dioxide NO_2 contains an unpaired electron and is an important component of smog. Nitrogen molecules containing unpaired electrons show a tendency to dimerize (thus pairing the electrons), and are, in general, highly reactive. The corresponding acids are nitrous HNO_2 and nitric acid HNO_3 , with the corresponding salts called nitrites and nitrates.

The higher oxides dinitrogen trioxide N_2O_3 , dinitrogen tetroxide N_2O_4 and dinitrogen pentoxide N_2O_5 , are unstable and explosive, a consequence of the

chemical stability of N_2 . Nearly every hypergolic rocket engine uses N_2O_4 as the oxidizer; their fuels, various forms of hydrazine, are also nitrogen compounds. These engines are extensively used on spacecraft such as the space shuttle and those of the Apollo Program because their propellants are liquids at room temperature and ignition occurs on contact without an ignition system, allowing many precisely controlled burns. Some launch vehicles such as the Titan II and Ariane 1 through 4 also use hypergolic fuels, although the trend is away from such engines for cost and safety reasons. N_2O_4 is an intermediate in the manufacture of nitric acid HNO_3 , one of the few acids stronger than hydronium and a fairly strong oxidizing agent.

Nitrogen is notable for the range of explosively unstable compounds that it can produce. Nitrogen triiodide NI_3 is an extremely sensitive contact explosive. Nitrocellulose, produced by nitration of cellulose with nitric acid, is also known as guncotton. Nitroglycerin, made by nitration of glycerin, is the dangerously unstable explosive ingredient of dynamite. The comparatively stable, but more powerful explosive trinitrotoluene (TNT) is the standard explosive against which the power of nuclear explosions are measured.

Nitrogen can also be found in organic compounds. Common nitrogen functional groups include: amines, amides, nitro groups, imines, and enamines. The amount of nitrogen in a chemical substance can be determined by the Kjeldahl method.

2.4- Compounds

The main neutral hydride of nitrogen is ammonia (NH_3), although hydrazine (N_2H_4) is also commonly used. Ammonia is more basic than water by 6 orders of magnitude. In solution ammonia forms the ammonium ion (NH_4^+). Liquid ammonia (boiling point 240 K) is amphiprotic (displaying either Brønsted-Lowry acidic or basic character) and forms ammonium and the less common amide ions (NH_2^-); both amides and nitride (N^{3-}) salts are known, but decompose in water. Singly, doubly, triply and quadruply substituted alkyl compounds of ammonia are called amines (four substitutions, to form commercially and biologically important quaternary amines, results in a positively charged nitrogen, and thus a water-soluble, or at least amphiphilic, compound). Larger chains, rings and structures of nitrogen hydrides are also known, but are generally unstable.

Other classes of nitrogen anions (negatively charged ions) are the poisonous azides (N_3^-), which are linear and isoelectronic to carbon dioxide, but which bind to

important iron-containing enzymes in the body in a manner more resembling cyanide. Another molecule of the same structure is the colorless and relatively inert anesthetic gas Nitrous oxide (dinitrogen monoxide, N_2O), also known as laughing gas. This is one of a variety of nitrogen oxides that form a family often abbreviated as NO_x . Nitric oxide (nitrogen monoxide, NO), is a natural free radical used in signal transduction in both plants and animals, for example, in vasodilation by causing the smooth muscle of blood vessels to relax. The reddish and poisonous nitrogen dioxide NO_2 contains an unpaired electron and is an important component of smog. Nitrogen molecules containing unpaired electrons show a tendency to dimerize (thus pairing the electrons), and are, in general, highly reactive. The corresponding acids are nitrous HNO_2 and nitric acid HNO_3 , with the corresponding salts called nitrites and nitrates.

The higher oxides dinitrogen trioxide N_2O_3 , dinitrogen tetroxide N_2O_4 and dinitrogen pentoxide N_2O_5 , are unstable and explosive, a consequence of the chemical stability of N_2 . Nearly every hypergolic rocket engine uses N_2O_4 as the oxidizer; their fuels, various forms of hydrazine, are also nitrogen compounds. These engines are extensively used on spacecraft such as the space shuttle and those of the Apollo Program because their propellants are liquids at room temperature and ignition occurs on contact without an ignition system, allowing many precisely controlled burns. Some launch vehicles such as the Titan II and Ariane 1 through 4 also use hypergolic fuels, although the trend is away from such engines for cost and safety reasons. N_2O_4 is an intermediate in the manufacture of nitric acid HNO_3 , one of the few acids stronger than hydronium and a fairly strong oxidizing agent.

Nitrogen is notable for the range of explosively unstable compounds that it can produce. Nitrogen triiodide NI_3 is an extremely sensitive contact explosive. Nitrocellulose, produced by nitration of cellulose with nitric acid, is also known as guncotton. Nitroglycerin, made by nitration of glycerin, is the dangerously unstable explosive ingredient of dynamite. The comparatively stable, but more powerful explosive trinitrotoluene (TNT) is the standard explosive against which the power of nuclear explosions are measured.

Nitrogen can also be found in organic compounds. Common nitrogen functional groups include: amines, amides, nitro groups, imines, and enamines. The amount of nitrogen in a chemical substance can be determined by the Kjeldahl method.

2.5- Production and applications

Nitrogen gas is an industrial gas produced by the fractional distillation of liquid air, or by mechanical means using gaseous air (i.e., pressurized reverse osmosis membrane or Pressure swing adsorption). Commercial nitrogen is often a byproduct of air-processing for industrial concentration of oxygen for steelmaking and other purposes. When supplied compressed in cylinders it is often called OFN (oxygen-free nitrogen).^[16]

Nitrogen gas has a variety of applications, including serving as an inert replacement for air where oxidation is undesirable;

- As a modified atmosphere, pure or mixed with carbon dioxide, to preserve the freshness of packaged or bulk foods (by delaying rancidity and other forms of oxidative damage)
- In ordinary incandescent light bulbs as an inexpensive alternative to argon.
- The production of electronic parts such as transistors, diodes, and integrated circuits
- Dried and pressurized, as a dielectric gas for high-voltage equipment
- The manufacturing of stainless steel
- Used in military aircraft fuel systems to reduce fire hazard, (see inerting system)
- On top of liquid explosives as a safety measure
- Filling automotive and aircraft tires due to its inertness and lack of moisture or oxidative qualities, as opposed to air, though this is not necessary for consumer automobiles.
- Used as a propellant for draught wine, and as an alternative to or together with carbon dioxide for other beverages.

Nitrogen is commonly used during sample preparation procedures for chemical analysis. To be specific, it is used to concentrate and reduce the volume of liquid samples. Directing a pressurized stream of nitrogen gas perpendicular to the surface of the liquid allows the solvent to evaporate while leaving the solute(s) and un-evaporated solvent behind.

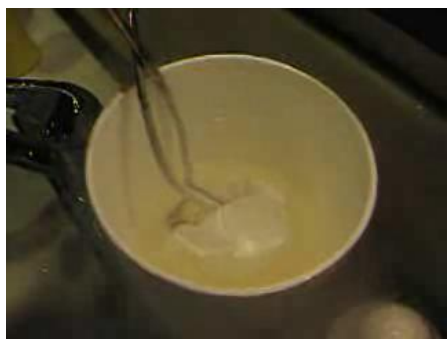
Nitrogen tanks are also replacing carbon dioxide as the main power source for paintball guns. The downside is that nitrogen must be kept at higher pressure than CO₂, making N₂ tanks heavier and more expensive.

Nitrogenated beer

A further example of its versatility is its use as a preferred alternative to carbon dioxide to pressurize kegs of some beers, in particular, stouts and British ales, due to the smaller bubbles it produces, which make the dispensed beer smoother and headier. A modern application of a pressure sensitive nitrogen capsule known commonly as a "widget" now allows nitrogen charged beers to be packaged in cans and bottles.

A mixture of nitrogen and carbon dioxide can be used for this purpose as well, to maintain the saturation of beer with carbon dioxide.

Liquid nitrogen



Air balloon submerged into liquid nitrogen

Liquid nitrogen is a cryogenic liquid. At atmospheric pressure, it boils at -195.8 °C. When insulated in proper containers such as Dewar flasks, it can be transported without much evaporative loss.

Like dry ice, the main use of liquid nitrogen is as a refrigerant. Among other things, it is used in the cryopreservation of blood, reproductive cells (sperm and egg), and other biological samples and materials. It is used in the clinical setting in cryotherapy to remove cysts and warts on the skin. It is used in cold traps for certain laboratory equipment and to cool X-ray detectors. It has also been used to cool central processing units and other devices in computers that are overclocked, and that produce more heat than during normal operation.

2.6- Applications of nitrogen compounds

Molecular nitrogen (N_2) in the atmosphere is relatively non-reactive due to its strong bond, and N_2 plays an inert role in the human body, being neither produced

nor destroyed. In nature, nitrogen is converted into biologically (and industrially) useful compounds by lightning, and by some living organisms, notably certain bacteria (i.e. nitrogen fixing bacteria – see Biological role below). Molecular nitrogen is released into the atmosphere in the process of decay, in dead plant and animal tissues.

The ability to combine or fix molecular nitrogen is a key feature of modern industrial chemistry, where nitrogen and natural gas are converted into ammonia via the Haber process. Ammonia, in turn, can be used directly (primarily as a fertilizer, and in the synthesis of nitrated fertilizers), or as a precursor of many other important materials including explosives, largely via the production of nitric acid by the Ostwald process.

The organic and inorganic salts of nitric acid have been important historically as convenient stores of chemical energy. They include important compounds such as potassium nitrate (or saltpeter used in gunpowder) and ammonium nitrate, an important fertilizer and explosive (see ANFO). Various other nitrated organic compounds, such as nitroglycerin, trinitrotoluene, and nitrocellulose, are used as explosives and propellants for modern firearms. Nitric acid is used as an oxidizing agent in liquid fueled rockets. Hydrazine and hydrazine derivatives find use as rocket fuels and monopropellants. In most of these compounds, the basic instability and tendency to burn or explode is derived from the fact that nitrogen is present as an oxide, and not as the far more stable nitrogen molecule (N_2), which is a product of the compounds' thermal decomposition. When nitrates burn or explode, the formation of the powerful triple bond in the N_2 produces most of the energy of the reaction.

Nitrogen is a constituent of molecules in every major drug class in pharmacology and medicine. Nitrous oxide (N_2O) was discovered early in the 19th century to be a partial anesthetic, though it was not used as a surgical anesthetic until later. Called "laughing gas", it was found capable of inducing a state of social disinhibition resembling drunkenness. Other notable nitrogen-containing drugs are drugs derived from plant alkaloids, such as morphine (there exist many alkaloids known to have pharmacological effects; in some cases, they appear natural chemical defenses of plants against predation). Drugs that contain nitrogen include all major classes of antibiotics and organic nitrate drugs like nitroglycerin and nitroprusside that regulate blood pressure and heart action by mimicking the action of nitric oxide.

2.7- Safety

Rapid release of nitrogen gas into an enclosed space can displace oxygen, and therefore represents an asphyxiation hazard. This may happen with few warning symptoms, since the human carotid body is a relatively slow and a poor low-oxygen (hypoxia) sensing system. An example occurred shortly before the launch of the first Space Shuttle mission in 1981, when two technicians lost consciousness (and one of them died) after they walked into a space located in the Shuttle's Mobile Launcher Platform that was pressurized with pure nitrogen as a precaution against fire. The technicians would have been able to exit the room if they had experienced early symptoms from nitrogen-breathing.

When inhaled at high partial pressures (more than about 4 bar, encountered at depths below about 30 m in scuba diving), nitrogen begins to act as an anesthetic agent. It can cause nitrogen narcosis, a temporary semi-anesthetized state of mental impairment similar to that caused by nitrous oxide.

Nitrogen also dissolves in the bloodstream and body fats. Rapid decompression (in particular, in the case of divers ascending too quickly, or astronauts decompressing too quickly from cabin pressure to spacesuit pressure) can lead to a potentially fatal condition called decompression sickness (formerly known as caisson sickness or the bends), when nitrogen bubbles form in the bloodstream, nerves, joints, and other sensitive or vital areas. Other "inert" gases (those gases other than carbon dioxide and oxygen) cause the same effects from bubbles composed of them, so replacement of nitrogen in breathing gases may prevent nitrogen narcosis, but does not prevent decompression sickness.

Direct skin contact with liquid nitrogen will eventually cause severe frostbite (cryogenic "burns"). This may happen almost instantly on contact, or after a second or more, depending on the form of liquid nitrogen. Bulk liquid nitrogen causes less rapid freezing than a spray of nitrogen mist (such as is used to freeze certain skin growths in the practice of dermatology). The extra surface area provided by nitrogen-soaked materials is also important, with soaked clothing or cotton causing far more rapid damage than a spill of direct liquid to skin. Full "contact" between naked skin and large collected-droplets or pools of liquid nitrogen may be prevented for second or two, by a layer of insulating gas from the Leidenfrost effect. This may give the skin a second of protection from nitrogen bulk liquid. However, liquid nitrogen applied to skin in mists, and on fabrics, bypasses this effect, and causes local frostbite immediately.

2.8- Nitrogen Uses

This article stresses on various nitrogen uses which make it one of the most important elements for mankind and plants alike. Read on to know more about various nitrogen uses and properties...

Nitrogen is a colorless, odorless, and tasteless chemical element with an atomic mass of 14.00674 u. Constituting approximately 78 percent of Earth's atmosphere, nitrogen is found in abundance on this planet, most of which, however, is of no use. Since its discovery by a Scottish physician by the name Daniel Rutherford, in 1772, nitrogen has come a long way to become one of the most important elements for humans, plants, and animals alike. The credit of this goes to the various nitrogen uses and properties. Before we move on to nitrogen usage, let's take a look at the various aspects of this element, in brief.

Nitrogen Uses and Properties

Nitrogen, with 5 electrons in the outer shell, is trivalent in most of the compounds. The vapor density of nitrogen is 14.4, which is slightly lesser than the vapor density of air at 14. In simpler words, nitrogen is slightly lighter than air. It is highly soluble in water. A liter of water has the capacity to dissolve approximately 22 ml of nitrogen at a temperature of 0 degree Celsius. In its cooled and compressed form, nitrogen tends to liquefy into a colorless liquid boiling at -196 degree Celsius. If cooled further, it tends to freeze and take a white snow-like appearance which melts at -210 degree Celsius.

Nitrogen Uses in Everyday Life

Nitrogen is present in all living organisms to some extent. Although we are not aware of it, we do use nitrogen in our day-to-day life, directly as well as indirectly. Nitrogen usage is not just restricted to biological processes in living organisms, it's also used vastly in the industrial sector. The process by which nitrogen goes through several transformations in the atmosphere is referred to as the nitrogen cycle. Read more on facts about the nitrogen cycle.

Nitrogen Uses in the Body

Nitrogen plays an important role in food digestion. Although, plenty of nitrogen is available in the atmosphere, it's literally of no use for us, and hence we are left with no option but to derive nitrogen from our food sources. Nitrogen compounds are basically building blocks which help in growth of the body. In living organisms, nitrogen constitutes approximately 3 percent of the total body mass. When we eat food, nitrogen from that food is absorbed by the body in order to facilitate body growth. This element is especially important during pregnancy, when the fetus grows within the woman's body.

Nitrogen Uses in Plants

Nitrogen plays an important role in various functions necessary for plant life. It is found in several parts of plants, ranging from roots, to the leaves and grains. Nitrogen constitutes around 4 percent of total body mass of plants. It's an important constituent of chlorophyll which helps in converting sunlight into required energy. Like humans, nitrogen compounds act as building blocks in plants as well. The nitrogen found in proteins and enzymes in the roots of the plant, helps the plant to absorb water and various nutrients

Nitrogen Uses in Industry

Owing to the various nitrogen uses and properties, nitrogen gas is regarded as one of the most important industrial gas in several industries. It is either produced by fractional distillation of liquid air, or mechanical treatment of gaseous air. Commercial nitrogen is provided in its compressed form, which is stored in cylinders. Nitrogen gas has plenty of uses in the industrial sector. It is used as an inexpensive alternative to argon gas in incandescent light bulbs. It is also used in manufacturing of stainless steel. In the electronic sector, it is used to make diodes and integrated circuits. Nitrogen usage in fuel systems of military aircrafts reduces the possibility of a fire threat. Owing to its inertness and lack of moisture, it is also used in automobile and aircraft tires.

Although it's one of the most abundant element in the atmosphere, nitrogen in its crude form, is of no use for humans or plants. The various nitrogen uses credited to

this element come only after it is treated, when it becomes one of the most useful elements for many biological as well as industrial processes.

2.9- Air Separation into Oxygen, Nitrogen, and Argon Background

The purification of various components of air, in particular oxygen, nitrogen, and argon, is an important industrial process. A feasibility study is to be performed to investigate the possibility of producing 1500 metric tons per day of 99.5% oxygen, 5000 metric tons per day of 99.5% nitrogen, and 58 metric tons of 99.9% argon from air.

The major cost associated with the separation of air is the cost of electricity to compress the inlet air, which normally comprises 95% of the utility costs of a cryogenic plant. Thus, the goal of the design Process Description

Unit 100

Figure 2 shows a PFD for the cryogenic distillation of air, Unit 100. This process was modeled after the Linde Double Column [1]. In the proposed design, a two-stage centrifugal compressor, with interstage cooling, is used to compress air to 9 atm. The air is then further cooled to 107 K in E-102 and E-103. Stream 7 is then sent to T-101 to begin the separation process. The top product, Stream 10, is throttled to 1.0 atm, and then fed to the top of the vapor column, T-102. The bottoms, Stream 8, is also throttled to 1.0 atm and fed to T-102. The overhead product of T-102, Stream 13, which is 99% nitrogen, is sent to E-101 where it is used as a coolant for the interstage cooling of the compressor. The bottom product, which is 99.5% oxygen, is cooled and sent to storage.

A vapor draw stream, Stream 16, is taken from tray 10 and sent to the argon purification system, Unit 200.

The condenser of T-101 and the reboiler of T-102 are interconnected in E-106 so that the condenser provides the heat needed by the reboiler, and the reboiler provides the cooling needed by the condenser. Stream 20 from the argon purification unit, which is 99% nitrogen, is recycled back to combine with Stream 9. Oxygen rich Stream 15 is recycled back to the bottom of T-102.

Unit 200

A PFD of the argon separation unit is shown in Figure 3. Stream 16, from Unit 100 is sent through E-205 to provide the heat sink for Stream 30. Since Stream 30 has a much smaller flow rate than Stream 16, Stream 16 does not change

appreciably in temperature. Stream 17 is then sent to T-201 where nitrogen is separated from oxygen and argon. The nitrogen-rich distillate, Stream 20, is recycled back to Unit 100. The bottoms, Stream 23, is then sent to T-202 where the argon and oxygen are separated. The oxygen-rich bottom stream, Stream 15, from T-202 is recycled back to Unit 100. Stream 22 is now combined with hydrogen and allowed to heat up to near ambient temperature, Stream 23, compressed and sent to a combustion chamber where hydrogen is catalytically-combusted with oxygen to form water. The effluent, Stream 26, is cooled and then flashed in V-201 to remove any water that is present. The water is removed in Stream 27 and the argon-rich stream is sent to T-203 to separate out the remaining nitrogen that is present. The nitrogen exits as the distillate, Stream 30, and vented to the atmosphere. 99.9% pure argon exits as the bottoms stream, Stream 31, to minimize the cost of compression.

Necessary Information and Simulation Hints

Argon is present in the amount of 0.93% by volume of air. This presence of argon makes it impossible to obtain pure oxygen and nitrogen streams from the air separation plants. Therefore, argon is drawn out of T-102 of the cryogenic system and purified for sale. Tower profiles identify the draw location at the stage where the argon concentration is at a maximum.

Since the boiling point of argon is between that of oxygen and nitrogen, it acts as an impurity in the product streams. If argon were collected and separated from the oxygen product, an oxygen purity of less than 95% by volume would result. On the other hand, if argon were collected with the nitrogen product, the purity of nitrogen would not exceed 98.7% by volume. Both oxygen and nitrogen must be greater than 99.9% pure to sell, so the elimination of argon is necessary.

This process requires very complicated heat integration techniques because the only heat sink for cooling or condensation is another cryogenic stream in the process. E-201 uses liquid nitrogen produced in the plant. E-203 and E-206 can use liquid nitrogen from the plant or cold nitrogen from Stream 13. These are not shown in the PFD.

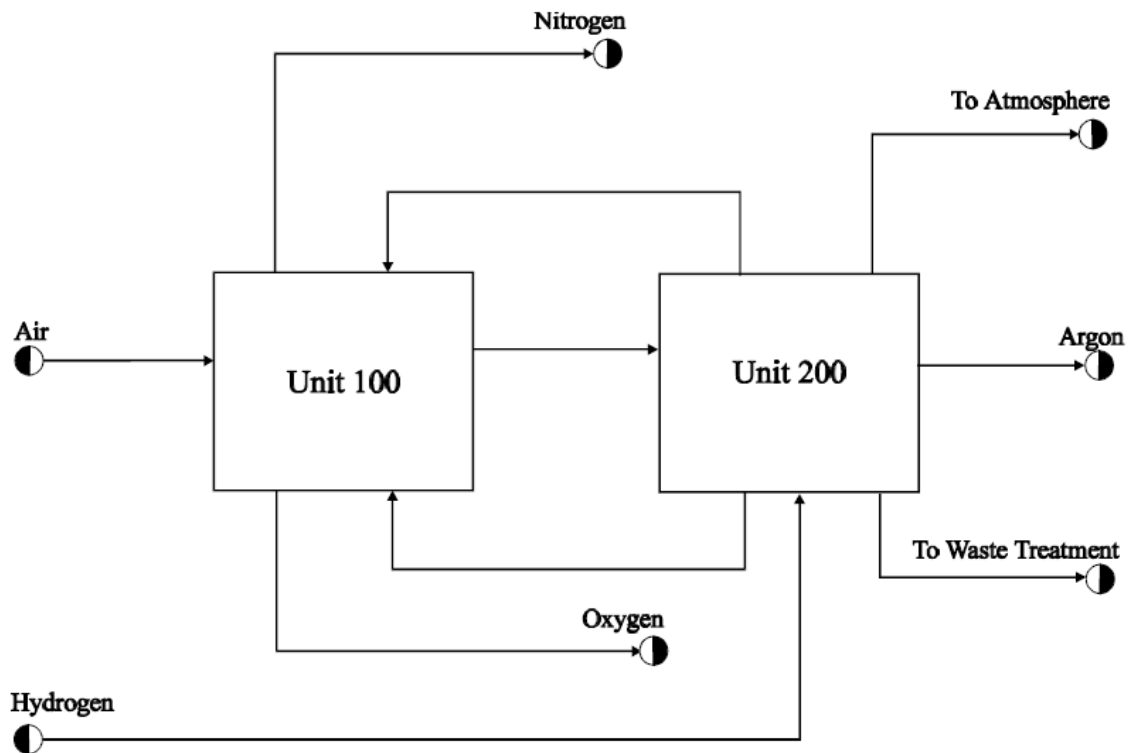


Figure 1: BFD for Overall Process

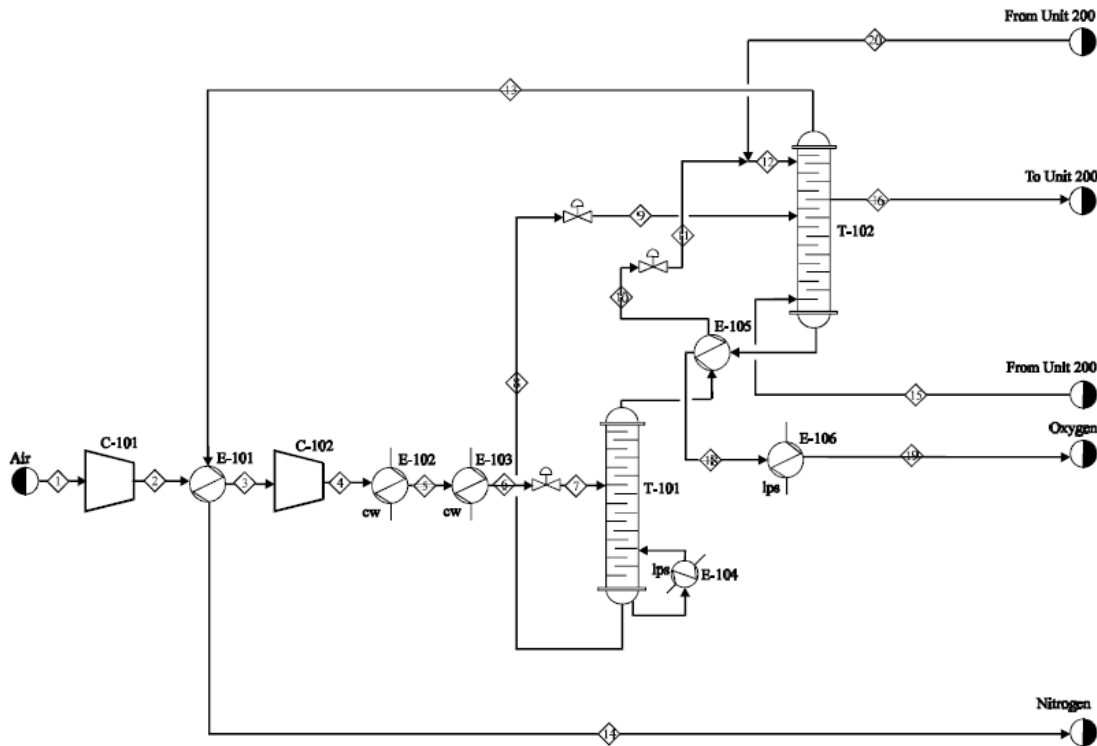


Figure 2: PFD for Unit 100

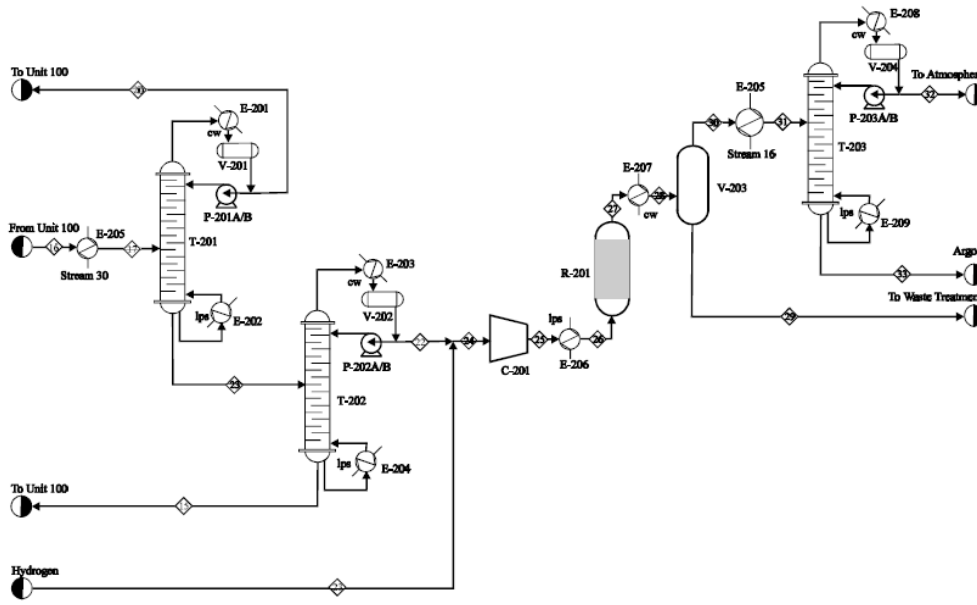


Figure 3: PFD for Unit 200

Equipments Summary

| Number | Equipment | Number | Equipment |
|--------|---------------------------|----------|------------------------------|
| C-101 | Feed Compressor (Stage 1) | E-208 | Argon Purification Condenser |
| C-102 | Feed Compressor (Stage 2) | E-209 | Argon Purification Reboiler |
| C-201 | Compressor | P-201A/B | Reflux Pump |
| E-101 | Interstage Cooler | P-202A/B | Reflux Pump |
| E-102 | Heat Exchanger | P-203A/B | Reflux Pump |
| E-103 | Heat Exchanger | R-201 | Combustion Reactor |
| E-104 | Reboiler | T-201 | Linde Lower Column |
| E-105 | Condenser-Reboiler | T-202 | Linde Upper Column |
| E-106 | Heat Exchanger | T-201 | Nitrogen Separation Tower |
| E-201 | Nitrogen Tower Condenser | T-202 | Argon Separation Tower |
| E-202 | Nitrogen Tower Reboiler | T-203 | Argon Purification Tower |
| E-203 | Argon Tower Condenser | V-201 | Reflux Vessel |
| E-204 | Argon Tower Reboiler | V-202 | Reflux Vessel |
| E-205 | Heat Exchanger | V-203 | Flash Vessel |
| E-206 | Heat Exchanger | V-204 | Reflux Vessel |
| E-207 | Heat Exchanger | | |

Reference

1. Barron, Randall F., Cryogenic Systems, 2nd ed., Oxford University Press, New York, 1985, pp.199-211.
- 2- "A new molecule and a new signature – Chemistry – tetranitrogen". Science News. February 16, 2002.
http://www.findarticles.com/p/articles/mi_m1200/is_7_161/ai_83477565.
Retrieved 2007-08-18.
- 3- "Polymeric nitrogen synthesized". physorg.com. 2004-08-05.
<http://www.physorg.com/news693.html>. Retrieved 2009-06-22.
- 4- <http://www.etymonline.com/index.php?term=nitrogen> Accessed Feb. 28, 2011
- 5- Aleksander Abram and D. Lynn Forster, A PRIMER ON AMMONIA, NITROGEN, FERTILIZERS, AND NATURAL GAS MARKETS, September 30, 2005

Section 3: Ammonia Production

3.1- Ammonia

Ammonia is a compound of nitrogen and hydrogen (and so is covalently bonded) with the formula NH_3 . It is a colourless gas with a characteristic pungent odour. Ammonia contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to food and fertilizers. Ammonia, either directly or indirectly, is also a building block for the synthesis of many pharmaceuticals. Although in wide use, ammonia is both caustic and hazardous. In 2006, worldwide production was estimated at 146.5 million tonnes. It is used in commercial cleaning products.

Ammonia, as used commercially, is often called anhydrous ammonia. This term emphasizes the absence of water in the material. Because NH_3 boils at $-33.34\text{ }^\circ\text{C}$ ($-28.012\text{ }^\circ\text{F}$), the liquid must be stored under high pressure or at low temperature. Its heat of vaporization is, however, sufficiently high so that NH_3 can be readily handled in ordinary beakers, in a fume hood (i.e., if it is already a liquid it will not boil readily).

| Properties | |
|--|---|
| Molecular formula | NH_3 |
| Molar mass | 17.031 g/mol |
| Appearance | Colourless gas with strong pungent odour |
| Density | 0.86 kg/m ³ (1.013 bar at boiling point) 0.73 kg/m ³ (1.013 bar at 15 °C) 681.9 kg/m ³ at $-33.3\text{ }^\circ\text{C}$ (liquid) ^[1] 817 kg/m ³ at $-80\text{ }^\circ\text{C}$ (transparent solid) ^[2] |
| Melting point | $-77.73\text{ }^\circ\text{C}$, 195 K, $-108\text{ }^\circ\text{F}$ |
| Boiling point | $-33.34\text{ }^\circ\text{C}$, 240 K, $-28\text{ }^\circ\text{F}$ |
| Solubility in water | 47% (0 °C) 31% (25 °C) 28% (50 °C) ^[3] |
| Acidity ($\text{p}K_a$) | 36 (water), ^[4] 10.5 (DMSO) |
| Basicity ($\text{p}K_b$) | 4.75 |
| Structure | |
| Molecular shape | Trigonal pyramid |
| Dipole moment | 1.42 |

"Household ammonia" or "ammonium hydroxide" is a solution of NH_3 in water. The strength of such solutions is measured in units of baume (density), with 26 degrees baume (about 30% w/w ammonia at 15.5 °C) being the typical high concentration commercial product. Household ammonia ranges in concentration from 5 to 10 weight percent ammonia.

3.2- Structure and basic chemical properties

The ammonia molecule has a trigonal pyramidal shape with a bond angle of 107.8° , as predicted by the valence shell electron pair repulsion theory (VSEPR). The central nitrogen atom has five outer electrons with an additional electron from each hydrogen atom. This gives a total of eight electrons, or four electron pairs which are arranged tetrahedrally. Three of these electron pairs are used as bond pairs, which leaves one lone pair of electrons. The lone pair of electrons repel more strongly than bond pairs, therefore the bond angle is not 109.5° as expected for a regular tetrahedral arrangement, but is measured at 107.8° . The nitrogen atom in the molecule has a lone electron pair, which makes ammonia a base, a proton acceptor. This shape gives the molecule a dipole moment and makes it polar. The molecule's polarity and, especially, its ability to form hydrogen bonds, makes ammonia highly miscible with water. Ammonia is moderately basic, a 1.0 M aqueous solution has a pH of 11.6 and if a strong acid is added to such a solution until the solution is neutral (pH = 7), 99.4% of the ammonia molecules are protonated. Temperature and salinity also affect the proportion of NH_4^+ . The latter has the shape of a regular tetrahedron and is isoelectronic with methane. It is known to have the highest specific heat capacity of any substance.

| Hazards | |
|---|---|
| EU classification | Toxic (T) Corrosive (C) Dangerous for the environment (N) |
| Flash point | flammable gas (see text) |
| Autoignition temperature | 651 °C |
| Explosive limits | 15–28% |
| U.S. Permissible exposure limit (PEL) | 50 ppm (25 ppm ACGIH - TLV; 35 ppm STEL) |

3.3- Natural Occurrence

Ammonia is found in trace quantities in the atmosphere, being produced from the putrefaction (decay process) of nitrogenous animal and vegetable matter. Ammonia and ammonium salts are also found in small quantities in rainwater, whereas ammonium chloride (sal-ammoniac), and ammonium sulfate are found in volcanic districts; crystals of ammonium bicarbonate have been found in Patagonian guano. The kidneys secrete NH_3 to neutralize excess acid. Ammonium salts also are found distributed through all fertile soil and in seawater. Substances containing ammonia, or those that are similar to it, are called ammoniacal. Ammonia is found on Pluto, Jupiter and, in small amounts, on Uranus.

3.4- History

The Romans called the ammonium chloride deposits they collected from near the Temple of Jupiter Amun (Greek Ἄμμων Ammon) in ancient Libya 'sal ammoniacus' (salt of Amun) because of proximity to the nearby temple. Salts of ammonia have been known from very early times; thus the term Hammoniacus sal appears in the writings of Pliny, although it is not known whether the term is identical with the more modern sal-ammoniac.

In the form of sal-ammoniac (nushadir), ammonia was important to the Muslim alchemists as early as the 8th century, first mentioned by the Islamic chemist Jābir ibn Hayyān, and to the European alchemists since the 13th century, being mentioned by Albertus Magnus. It was also used by dyers in the Middle Ages in the form of fermented urine to alter the colour of vegetable dyes. In the 15th century, Basilius Valentinus showed that ammonia could be obtained by the action of alkalis on sal-ammoniac. At a later period, when sal-ammoniac was obtained by distilling the hooves and horns of oxen and neutralizing the resulting carbonate with hydrochloric acid, the name "spirit of hartshorn" was applied to ammonia.

Gaseous ammonia was first isolated by Joseph Priestley in 1774 and was termed by him alkaline



This high-pressure reactor was built in 1921 by [BASF](#) in [Ludwigshafen](#) and was re-erected on the premises of the [University of Karlsruhe](#) in Germany.

air. 11 years later in 1785, Claude Louis Berthollet ascertained its composition.

The Haber-Bosch process to produce ammonia from the nitrogen in the air was developed by Fritz Haber and Carl Bosch in 1909 and patented in 1910. It was first used on an industrial scale by the Germans during World War I, following the allied blockade that cut off the supply of nitrates from Chile. The ammonia was used to produce explosives to sustain their war effort.

Prior to the advent of cheap natural gas, hydrogen as a precursor to ammonia production was produced via the electrolysis of water or using the chloralkali process. The Vemork 60 MW hydroelectric plant in Norway, constructed in 1911, was used purely for plants using the Birkeland-Eyde process.

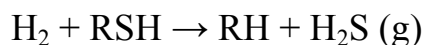
3.5- Synthesis and production

Because of its many uses, ammonia is one of the most highly produced inorganic chemicals. Dozens of chemical plants worldwide produce ammonia. The worldwide ammonia production in 2004 was 109 million metric tonnes. The People's Republic of China produced 28.4% of the worldwide production (increasingly from coal as part of urea synthesis) followed by India with 8.6%, Russia with 8.4%, and the United States with 8.2%. About 80% or more of the ammonia produced is used for fertilizing agricultural crops.

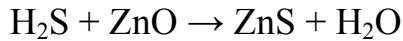
Before the start of World War I, most ammonia was obtained by the dry distillation of nitrogenous vegetable and animal waste products, including camel dung, where it was distilled by the reduction of nitrous acid and nitrites with hydrogen; in addition, it was produced by the distillation of coal, and also by the decomposition of ammonium salts by alkaline hydroxides such as quicklime, the salt most generally used being the chloride (sal-ammoniac) thus:



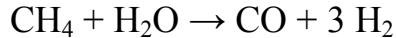
Today, the typical modern ammonia-producing plant first converts natural gas (i.e., methane) or liquefied petroleum gas (such gases are propane and butane) or petroleum naphtha into gaseous hydrogen. The process used in producing the hydrogen begins with removal of sulfur compounds from the natural gas (because sulfur deactivates the catalysts used in subsequent steps). Catalytic hydrogenation converts organosulfur compounds into gaseous hydrogen sulfide:



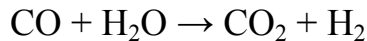
The hydrogen sulfide is then removed by passing the gas through beds of zinc oxide where it is adsorbed and converted to solid zinc sulfide:



Catalytic steam reforming of the sulfur-free feedstock is then used to form hydrogen plus carbon monoxide:

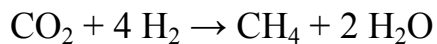
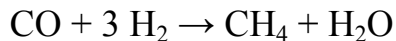


In the next step, the water gas shift reaction is used to convert the carbon monoxide into carbon dioxide and more hydrogen:

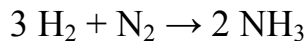


The carbon dioxide is then removed either by absorption in aqueous ethanamine solutions or by adsorption in pressure swing adsorbers (PSA) using proprietary solid adsorption media.

The final step in producing the hydrogen is to use catalytic methanation to remove any small residual amounts of carbon monoxide or carbon dioxide from the hydrogen:



To produce the desired end-product ammonia, the hydrogen is then reacted with nitrogen (derived from process air) using a magnetite catalyst under high pressure to form anhydrous liquid ammonia. This step is known as the ammonia synthesis loop (also referred to as the Haber-Bosch process):



Hydrogen required for ammonia synthesis could also be produced economically using other sources like coal or coke gasification, less economically from the electrolysis of water into oxygen + hydrogen and other alternatives which are presently impractical for large scale. At one time, most of Europe's ammonia was produced from the Hydro plant at Vemork, via the electrolysis route. Various renewable energy electricity sources are also potentially applicable.

3.6- Haber Process

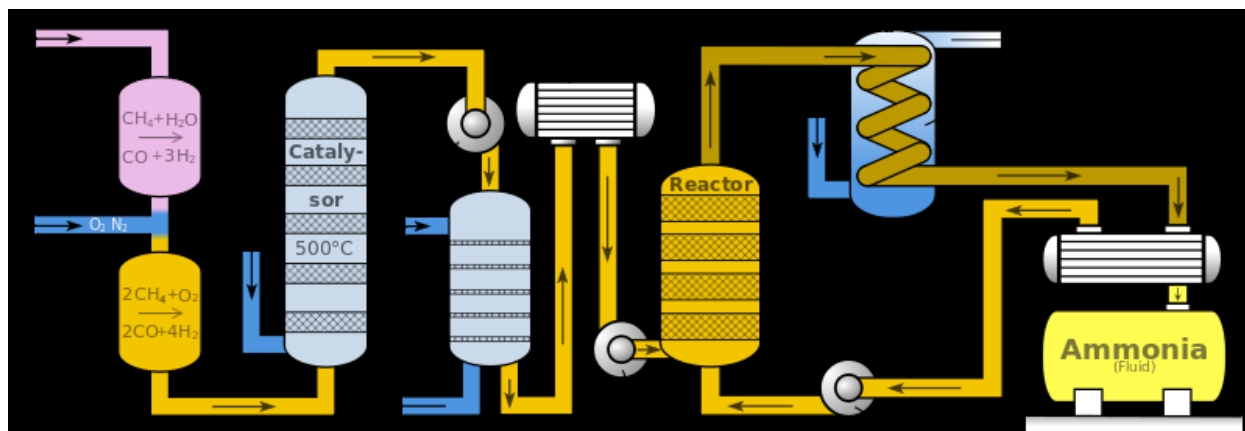
The Haber process, also called the Haber–Bosch process, is the nitrogen fixation reaction of nitrogen gas and hydrogen gas, over an enriched iron or ruthenium catalyst, which is used to industrially produce ammonia.



Fritz Haber, 1918

Despite the fact that 78.1% of the air we breathe is nitrogen, the gas is relatively nonreactive because nitrogen molecules are held together by strong triple bonds. It was not until the early 20th century that the Haber process was developed to harness the atmospheric abundance of nitrogen to create ammonia, which can then be oxidized to make the nitrates and nitrites essential for the production of nitrate fertilizer and explosives.

The Haber process is important because previous to its discovery, ammonia had been difficult to produce on an industrial scale, and fertilizer generated from ammonia today is responsible for sustaining one-third of the Earth's population. It is estimated that half of the protein within human beings globally is made of nitrogen that was originally fixed by this process, the remainder was produced by nitrogen fixing bacteria.

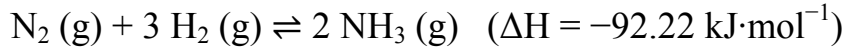


Flow diagram for the Haber Bosch process

By far the major source of the hydrogen required for the Haber-Bosch process is methane from natural gas, obtained through a heterogeneous catalytic process, which requires far less external energy than the process used initially by Bosch at BASF, the electrolysis of water. Far less commonly, in some countries, coal is used as source of hydrogen through a process called coal gasification. However, the

source of the hydrogen makes no difference to the Haber-Bosch process, which is only concerned with synthesizing ammonia from nitrogen and hydrogen.

The final stage, which is the actual Haber process, is the synthesis of ammonia using an iron catalyst promoted with K_2O , CaO and Al_2O_3 :



This is done at 15–25 MPa (150–250 bar) and between 300 and 550 °C, passing the gases over four beds of catalyst, with cooling between each pass to maintain a reasonable equilibrium constant. On each pass only about 15% conversion occurs, but any unreacted gases are recycled, so that eventually an overall conversion of 97% can be achieved.

The steam reforming, shift conversion, carbon dioxide removal, and methanation steps each operate at absolute pressures of about 2.5–3.5 MPa (25–35 bar), and the ammonia synthesis loop operates at absolute pressures ranging from 6–18 MPa (60–180 bar), depending upon which proprietary design is used.

There are many engineering and construction companies that offer proprietary designs for ammonia synthesis plants. Haldor Topsoe of Denmark, Lurgi AG of Germany, Uhde of Germany, Saipem/Snamprogetti of Italy and Kellogg, Brown and Root of the United States are among the most experienced companies in that field.

Reaction rate and equilibrium

There are two opposing considerations in this synthesis: the position of the equilibrium and the rate of reaction. At room temperature, the reaction is slow and the obvious solution is to raise the temperature. This may increase the rate of the reaction but, since the reaction is exothermic, it also has the effect, according to Le Chatelier's principle, of favouring the reverse reaction and thus reducing the amount of product, given by:

$$K_{eq} = \frac{P_{NH_3}^2}{P_{N_2} \cdot P_{H_2}^3}$$

As the temperature increases, the equilibrium is shifted and hence, the amount of product drops dramatically according to the Van't Hoff equation. Thus one might suppose that a low temperature is to be used and some other means to increase rate. However, the catalyst itself requires a temperature of at least 400 °C to be efficient.

Pressure is the obvious choice to favour the forward reaction because there are 4 moles of reactant for every 2 moles of product (see entropy), and the pressure used (around 200 atm) alters the equilibrium concentrations to give a profitable yield.

Economically, though, pressure is an expensive commodity. Pipes and reaction vessels need to be strengthened, valves more rigorous, and there are safety considerations of working at 200 atm. In addition, running pumps and compressors takes considerable energy. Thus the compromise used gives a single pass yield of around 15%.

Another way to increase the yield of the reaction would be to remove the product (i.e. ammonia gas) from the system. In practice, gaseous ammonia is not removed from the reactor itself, since the temperature is too high; but it is removed from the equilibrium mixture of gases leaving the reaction vessel. The hot gases are cooled enough, whilst maintaining a high pressure, for the ammonia to condense and be removed as liquid. Unreacted hydrogen and nitrogen gases are then returned to the reaction vessel to undergo further reaction.

Catalysts

The catalyst has no effect on the position of chemical equilibrium; rather, it provides an alternative pathway with lower activation energy and hence increases the reaction rate, while remaining chemically unchanged at the end of the reaction. The first Haber–Bosch reaction chambers used osmium and ruthenium as catalysts. However, under Bosch's direction in 1909, the BASF researcher Alwin Mittasch discovered a much less expensive iron-based catalyst that is still used today. Part

Variation in K_{eq} for the Equilibrium
 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
 as a Function of Temperature^[9]

| Temperature (°C) | K_{eq} |
|------------------|-----------------------|
| 300 | 4.34×10^{-3} |
| 400 | 1.64×10^{-4} |
| 450 | 4.51×10^{-5} |
| 500 | 1.45×10^{-5} |
| 550 | 5.38×10^{-6} |
| 600 | 2.25×10^{-6} |

of the industrial production now takes place with a ruthenium rather than an iron catalyst (the KAAP process), because this more active catalyst allows reduced operating pressures.

In industrial practice, the iron catalyst is prepared by exposing a mass of magnetite, an iron oxide, to the hot hydrogen feedstock. This reduces some of the magnetite to metallic iron, removing oxygen in the process. However, the catalyst maintains most of its bulk volume during the reduction, and so the result is a highly porous material whose large surface area aids its effectiveness as a catalyst. Other minor components of the catalyst include calcium and aluminium oxides, which support the porous iron catalyst and help it maintain its surface area over time, and potassium, which increases the electron density of the catalyst and so improves its activity.

The reaction mechanism, involving the heterogeneous catalyst, is believed to be as follows:

1. $\text{N}_2 (\text{g}) \rightarrow \text{N}_2 (\text{adsorbed})$
2. $\text{N}_2 (\text{adsorbed}) \rightarrow 2 \text{N} (\text{adsorbed})$
3. $\text{H}_2 (\text{g}) \rightarrow \text{H}_2 (\text{adsorbed})$
4. $\text{H}_2 (\text{adsorbed}) \rightarrow 2 \text{H} (\text{adsorbed})$
5. $\text{N} (\text{adsorbed}) + 3 \text{H} (\text{adsorbed}) \rightarrow \text{NH}_3 (\text{adsorbed})$
6. $\text{NH}_3 (\text{adsorbed}) \rightarrow \text{NH}_3 (\text{g})$

Reaction 5 occurs in three steps, forming NH , NH_2 , and then NH_3 . Experimental evidence points to reaction 2 as being the slow, rate-determining step.

A major contributor to the elucidation of this mechanism is Gerhard Ertl

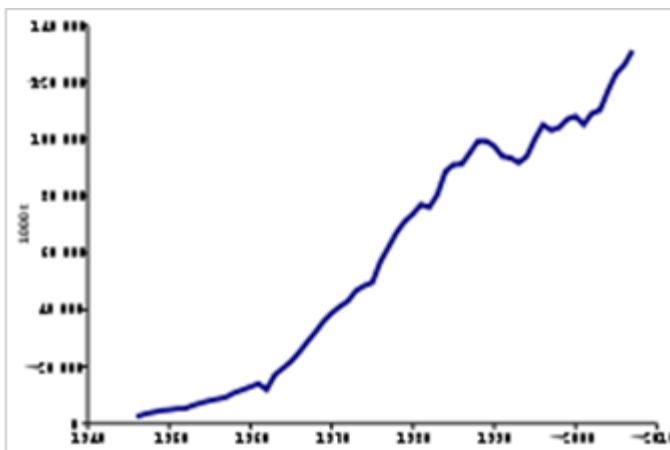
Economic and environmental aspects

The Haber process now produces 100 million tons of nitrogen fertilizer per year, mostly in the form of anhydrous ammonia, ammonium nitrate, and urea. 3–5% of world natural gas production is consumed in the Haber process (~1–2% of the world's annual energy supply). That fertilizer is responsible for sustaining one-third of the Earth's population, as well as various deleterious environmental consequences. Hydrogen production using electrolysis of water powered by renewable energy is not yet competitive cost-wise with hydrogen from fossil fuels, such as natural gas, and so has been responsible for only 4% of current hydrogen production (almost all as a byproduct of the chloralkali process). Notably, the rise of the Haber industrial process led to the "Nitrate Crisis" in Chile when the natural

nitrate mines were no longer profitable and were closed, leaving a large unemployed Chilean population behind.

3.7- Biosynthesis

In certain organisms, ammonia is produced from atmospheric nitrogen by enzymes called nitrogenases. The overall process is called nitrogen fixation. Although it is unlikely that biomimetic methods will be developed that are competitive with the Haber process, intense effort has been directed toward



understanding the mechanism of biological nitrogen fixation. The scientific interest in this problem is motivated by the unusual structure of the active site of the enzyme, which consists of an Fe_7MoS_9 ensemble.

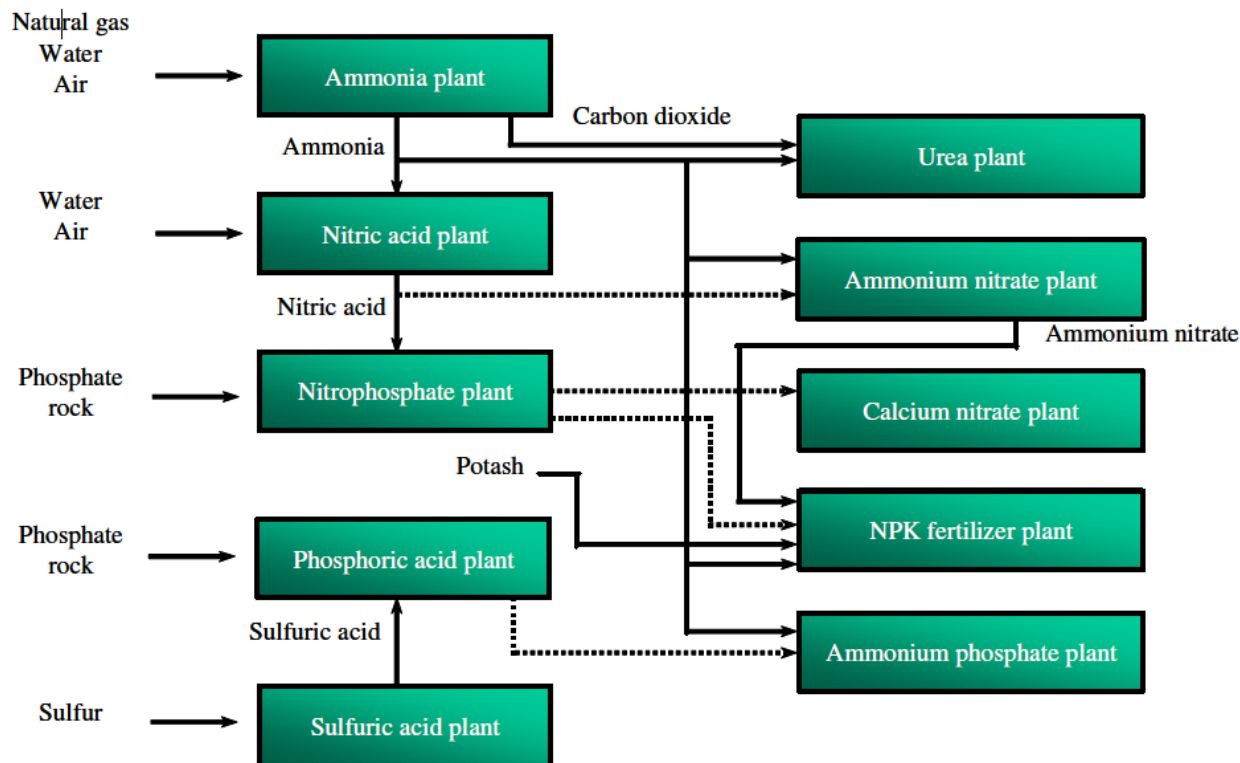
Ammonia is also a metabolic product of amino acid deamination. Ammonia excretion is common in aquatic animals. In humans, it is quickly converted to urea, which is much less toxic. This urea is a major component of the dry weight of urine. Most reptiles, birds, as well as insects and snails solely excrete uric acid as nitrogenous waste.

3.8- Ammonia Uses

Fertilizer

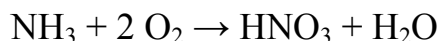
Approximately 83% (as of 2004) of ammonia is used as fertilizers either as its salts or as solutions. Consuming more than 1% of all man-made power, the production of ammonia is a significant component of the world energy budget.

GENERAL NITROGEN-FERTILIZER CONVERSION ROUTES



Precursor to nitrogenous compounds

Ammonia is directly or indirectly the precursor to most nitrogen-containing compounds. Virtually all synthetic nitrogen compounds are derived from ammonia. An important derivative is nitric acid. This key material is generated via the Ostwald process by oxidation of ammonia with air over a platinum catalyst at 700–850 °C, ~9 atm. Nitric oxide is an intermediate in this conversion:



Nitric acid is used for the production of fertilizers, explosives, and many organonitrogen compounds.

Cleaner

Household ammonia is a solution of NH_3 in water (i.e., ammonium hydroxide) used as a general purpose cleaner for many surfaces. Because ammonia results in a relatively streak-free shine, one of its most common uses is to clean glass, porcelain and stainless steel. It is also frequently used for cleaning ovens and

soaking items to loosen baked-on grime. Household ammonia ranges in concentration from 5 to 10 weight percent ammonia.

Antimicrobial agent for food products

As early as in 1895 it was known that ammonia was "strongly antiseptic .. it requires 1.4 grams per litre to preserve beef tea." Anhydrous ammonia has been shown effective as an antimicrobial agent for animal feed and is currently used commercially to reduce or eliminate microbial contamination of beef. The New York Times reported in October, 2009 on an American company, Beef Products Inc., which turns fatty beef trimmings, averaging between 50 and 70 percent fat, into seven million pounds per week of lean finely textured beef by removing the fat using heat and centrifugation, then disinfecting the lean product with ammonia; the process was rated by the US Department of Agriculture as effective and safe on the basis of a study (financed by Beef Products) which found that the treatment reduces E. coli to undetectable levels. Further investigation by The New York Times published in December, 2009 revealed safety concerns about the process as well as consumer complaints about the taste and smell of beef treated at optimal levels of ammonia.

Textile

Liquid ammonia is used for treatment of cotton materials, give a properties like mercerisation using alkalis. In particular, it is used for pre-washing of wool.

Woodworking

Ammonia was historically used to darken quartersawn white oak in Arts & Crafts and Mission style furniture. Ammonia fumes react with the natural tannins in the wood and cause it to change colours.

Ammonia's role in biological systems and human disease

Ammonia is an important source of nitrogen for living systems. Although atmospheric nitrogen abounds (more than 75%), few living creatures are capable of using this nitrogen. Nitrogen is required for the synthesis of amino acids, which are the building blocks of protein. Some plants rely on ammonia and other nitrogenous wastes incorporated into the soil by decaying matter. Others, such as nitrogen-fixing legumes, benefit from symbiotic relationships with rhizobia which create ammonia from atmospheric nitrogen.

Ammonia also plays a role in both normal and abnormal animal physiology. Ammonia is biosynthesised through normal amino acid metabolism and is toxic in high concentrations. The liver converts ammonia to urea through a series of reactions known as the urea cycle. Liver dysfunction, such as that seen in cirrhosis, may lead to elevated amounts of ammonia in the blood (hyperammonemia). Likewise, defects in the enzymes responsible for the urea cycle, such as ornithine transcarbamylase, lead to hyperammonemia. Hyperammonemia contributes to the confusion and coma of hepatic encephalopathy as well as the neurologic disease common in people with urea cycle defects and organic acidurias.

Ammonia is important for normal animal acid/base balance. After formation of ammonium from glutamine, α -ketoglutarate may be degraded to produce two molecules of bicarbonate, which are then available as buffers for dietary acids. Ammonium is excreted in the urine, resulting in net acid loss. Ammonia may itself diffuse across the renal tubules, combine with a hydrogen ion, and thus allow for further acid excretion.

Liquid ammonia as a solvent

Liquid ammonia is the best-known and most widely studied non-aqueous ionising solvent. Its most conspicuous property is its ability to dissolve alkali metals to form highly coloured, electrically conducting solutions containing solvated electrons. Apart from these remarkable solutions, much of the chemistry in liquid ammonia can be classified by analogy with related reactions in aqueous solutions. Comparison of the physical properties of NH_3 with those of water shows that NH_3 has the lower melting point, boiling point, density, viscosity, dielectric constant and electrical conductivity; this is due at least in part to the weaker H bonding in NH_3 and the fact that such bonding cannot form cross-linked networks since each NH_3 molecule has only 1 lone-pair of electrons compared with 2 for each H_2O molecule. The ionic self-dissociation constant of liquid NH_3 at $-50\text{ }^\circ\text{C}$ is about $10^{-33}\text{ mol}^2\cdot\text{L}^{-2}$.

3.9- Safety precautions

The U. S. Occupational Safety and Health Administration (OSHA) has set a 15-minute exposure limit for gaseous ammonia of 35 ppm by volume in the environmental air and an 8-hour exposure limit of 25 ppm by volume. NIOSH recently reduced the IDLH from 500 to 300 based on recent more conservative interpretations of original research in 1943. IDLH (Immediately Dangerous to Life and Health) is the level to which a healthy worker can be exposed for 30 minutes

without suffering irreversible health effects. Other organizations have varying exposure levels. U.S. Navy Standards [U.S. Bureau of Ships 1962] maximum allowable concentrations (MACs): continuous exposure (60 days): 25 ppm / 1 hour: 400 ppm Ammonia vapour has a sharp, irritating, pungent odour that acts as a warning of potentially dangerous exposure. The average odour threshold is 5 ppm, well below any danger or damage. Exposure to very high concentrations of gaseous ammonia can result in lung damage and death. Although ammonia is regulated in the United States as a non-flammable gas, it still meets the definition of a material that is toxic by inhalation and requires a hazardous safety permit when transported in quantities greater than 13,248 L (3,500 gallons).

Toxicity and storage information

The toxicity of ammonia solutions does not usually cause problems for humans and other mammals, as a specific mechanism exists to prevent its build-up in the bloodstream. Ammonia is converted to carbamoyl phosphate by the enzyme carbamoyl phosphate synthetase, and then enters the urea cycle to be either incorporated into amino acids or excreted in the urine. However, fish and amphibians lack this mechanism, as they can usually eliminate ammonia from their bodies by direct excretion. Ammonia even at dilute concentrations is highly toxic to aquatic animals, and for this reason it is classified as dangerous for the environment. Ammonium compounds should never be allowed to come in contact with bases (unless in an intended and contained reaction), as dangerous quantities of ammonia gas could be released.

Household use

Solutions of ammonia (5–10% by weight) are used as household cleaners, particularly for glass. These solutions are irritating to the eyes and mucous membranes (respiratory and digestive tracts), and to a lesser extent the skin. Caution should be used that the chemical is never mixed into any liquid containing bleach, or a poisonous gas may result. Mixing with chlorine-containing products or strong oxidants, for example household bleach can lead to hazardous compounds such as chloramines.

Laboratory use of ammonia solutions

The hazards of ammonia solutions depend on the concentration: "dilute" ammonia solutions are usually 5–10% by weight (<5.62 mol/L); "concentrated" solutions are usually prepared at >25% by weight. A 25% (by weight) solution has a density of

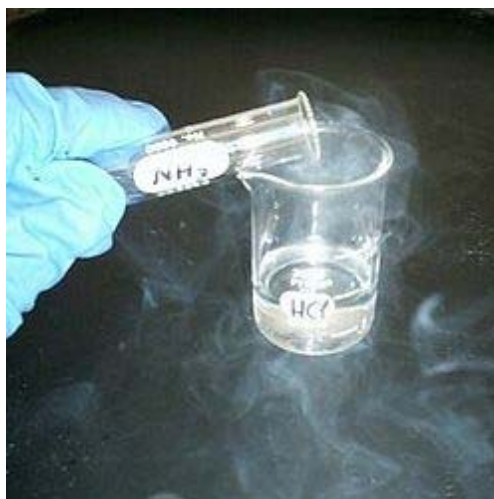
0.907 g/cm³, and a solution which has a lower density will be more concentrated. The European Union classification of ammonia solutions is given in the table.

| Concentration by weight (w/w) | Molarity | Concentration mass/volume (w/v) | Classification | R- Phrases |
|-------------------------------------|----------------------|---------------------------------------|--|---------------|
| 5–10% | 2.87— 5.62 mol/L | 48.9–95.7 g/L | Irritant (Xi) | R36/37/38 |
| 10–25% | 5.62– 13.29 mol/L | 95.7–226.3 g/L | Corrosive (C) | R34 |
| >25% | >13.29 mol/L | >226.3 g/L | Corrosive (C) Dangerous for the environment (N) | R34, R50 |

S-Phrases: (S1/2), S16, S36/37/39, S45, S61.

The ammonia vapour from concentrated ammonia solutions is severely irritating to the eyes and the respiratory tract, and these solutions should only be handled in a fume hood. Saturated ("0.880") solutions can develop a significant pressure inside a closed bottle in warm weather, and the bottle should be opened with care; this is not usually a problem for 25% ("0.900") solutions.

Ammonia solutions should not be mixed with halogens, as toxic and/or explosive products are formed. Prolonged contact of ammonia solutions with silver, mercury or iodide salts can also lead to explosive products: such mixtures are often formed in qualitative chemical analysis, and should be lightly acidified but not concentrated (<6% w/v) before disposal once the test is completed.



Hydrochloric acid sample releasing HCl fumes, which are reacting with ammonia fumes to produce a white smoke of ammonium chloride.

Laboratory use of anhydrous ammonia (gas or liquid)

Anhydrous ammonia is classified as toxic (T) and dangerous for the environment (N). The gas is flammable (autoignition temperature: 651 °C) and can form explosive mixtures with air (16–25%). The permissible exposure limit (PEL) in the United States is 50 ppm (35 mg/m³), while the IDLH concentration is estimated at 300 ppm. Repeated exposure to ammonia lowers the sensitivity to the smell of the gas: normally the odour is detectable at concentrations of less than 50 ppm, but desensitised individuals may not detect it even at concentrations of 100 ppm. Anhydrous ammonia corrodes copper- and zinc-containing alloys, and so brass fittings should not be used for handling the gas. Liquid ammonia can also attack rubber and certain plastics.

Ammonia reacts violently with the halogens. Nitrogen triiodide, a primary high explosive, is formed when ammonia comes in contact with iodine. Ammonia causes the explosive polymerisation of ethylene oxide. It also forms explosive fulminating compounds with compounds of gold, silver, mercury, germanium or tellurium, and with stibine. Violent reactions have also been reported with acetaldehyde, hypochlorite solutions, potassium ferricyanide and peroxides.

3.10- Ammonia Synthesis Promoted by Iron Catalysts

Although promoted iron catalysis for ammonia synthesis is still not entirely understood, there is strong evidence about structure and possible functioning mechanisms. The rate determining step for ammonia synthesis is most likely the adsorption and dissociation of nitrogen on the catalyst surface. Pure iron catalyst form is active only in the Fe(111) and Fe(211) conformations because of the presence of highly coordinated C7 sites that provide the strongest adsorption for nitrogen. The addition of Al, K and Ca promoter atoms drastically increases the activity of other Fe planes. It is believed that potassium acts as an electron donor that increases the electron density and thus provides a higher number of active sites on the surface. The presence of aluminum influences the morphology of the catalyst, increasing its porosity and free surface area. Since iron aluminate (FeAl₂O₄) is formed during the activation of the surface and allows growth of a Fe(111) adlayer, the catalytic activity increases additionally. A model of promoted iron catalyst takes all of the research efforts in account. It introduces a double layer structure on iron surface, active because of increase in surface free area due to oxygen compensated with aluminum atoms in the first layer, together with the increase of free adsorption sites because of potassium presence in the overlayer.

In despite of the intense and thorough studies performed since the discovery of ammonia catalyzed formation, the function of promoted iron surfaces is still not completely understood. Future experiments will most likely focus on studies of real catalyst crystals with catalytic history and efforts will be made for exploitation of these processes in a high vacuum and high temperature system, representing actual experimental conditions.

3.11- A Better Catalyst for Ammonia Production

"Ammonia is the fifth most abundantly produced chemical in the U.S. and ranks number two on the list of chemicals requiring the most energy to produce," said Zhen Song, the study's lead scientist. "Determining a more efficient way to synthesize ammonia could have a major impact on the ammonia production industry."

The Brookhaven scientists have uncovered details about the structure and reactivity of tiny particles of the metal ruthenium, which lead them to believe this metal could be more efficient in ammonia production than the catalysts currently used. The results are published in the June 26, 2004 issue of the Journal of the American Chemical Society.

Ammonia, a nitrogen/hydrogen compound used to make fertilizers, textiles, explosives, and many other products, is produced by combining nitrogen and hydrogen under high temperatures and pressures in the presence of a catalyst - usually made from iron. Ruthenium catalysts display five to 10 times higher reactivity rates under the same temperature and half the pressure, but are rarely used because they do not remain active long enough.

This problem is due to the surface, or "support," that ruthenium sits upon. Currently, the best type of support is "activated" carbon, a porous graphite with a layered, crystalline structure. However, the graphite is unstable during catalysis, tending to react with hydrogen to form methane gas, thus becoming slowly consumed.

Song and her colleagues studied how a graphite support affects the structure and reactivity of the ruthenium particles to try to understand why activated carbon - despite its drawbacks - is superior to other materials scientists have tested as ruthenium supports. Understanding these interactions may help them find a better support material.

First, they discovered that ruthenium can grow on a graphite surface "epitaxially" - mimicking the ordered structure of the surface below, forming flat crystalline particles. This makes graphite unique, Song said, since other surfaces don't encourage the same epitaxial growth.

They also determined the atomic structure of the flat ruthenium particles. The structure shows that the ruthenium particles have a high density of "active sites" - locations that allow them to participate in ammonia synthesis. This makes the flat particles better performers than the round ruthenium particles often grown on other types of supports.

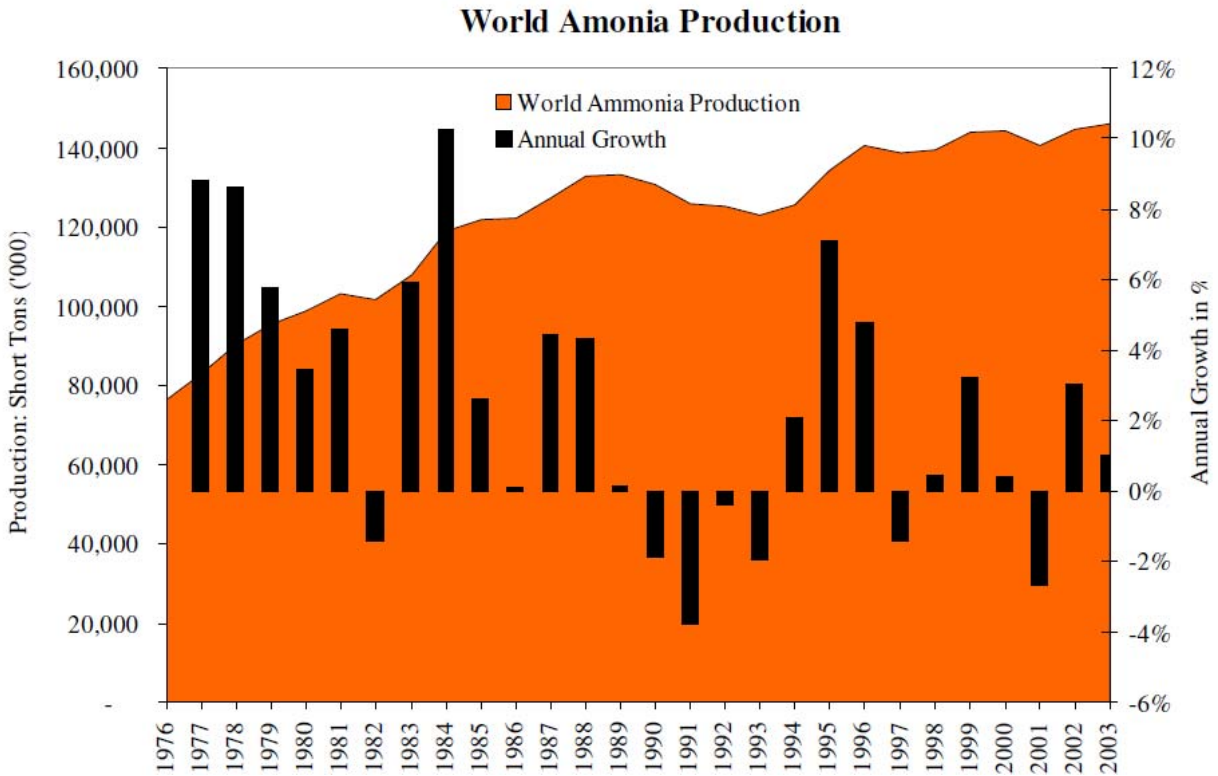
The flat particles have another key feature: They are built in layers. These layers form steps and terraces that are able to hold nitrogen, one of ammonia's components. From there, the nitrogen can participate in the ammonia synthesis reaction.

"These results tell us that scientists should look for a support that encourages the epitaxial growth of flat, layered ruthenium particles like these, in order to find an alternative to activated carbon," said Song. "Particles with these features are efficient catalysts."

The research group, led by Brookhaven chemist Jan Hrbek, plans to continue studying ruthenium catalysts. For example, they may investigate how to use additives, called promoters, to boost the ruthenium's effectiveness.

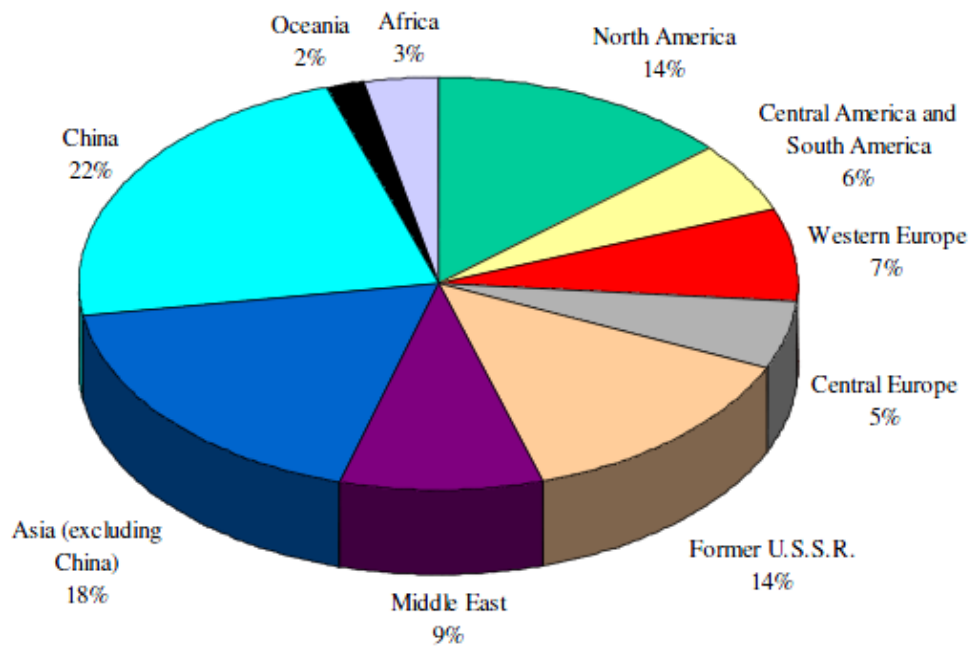
This research was funded by the Division of Chemical Sciences, Geosciences, & Biosciences within the U.S. Department of Energy's Office of Science.

3.12- World Ammonia Production

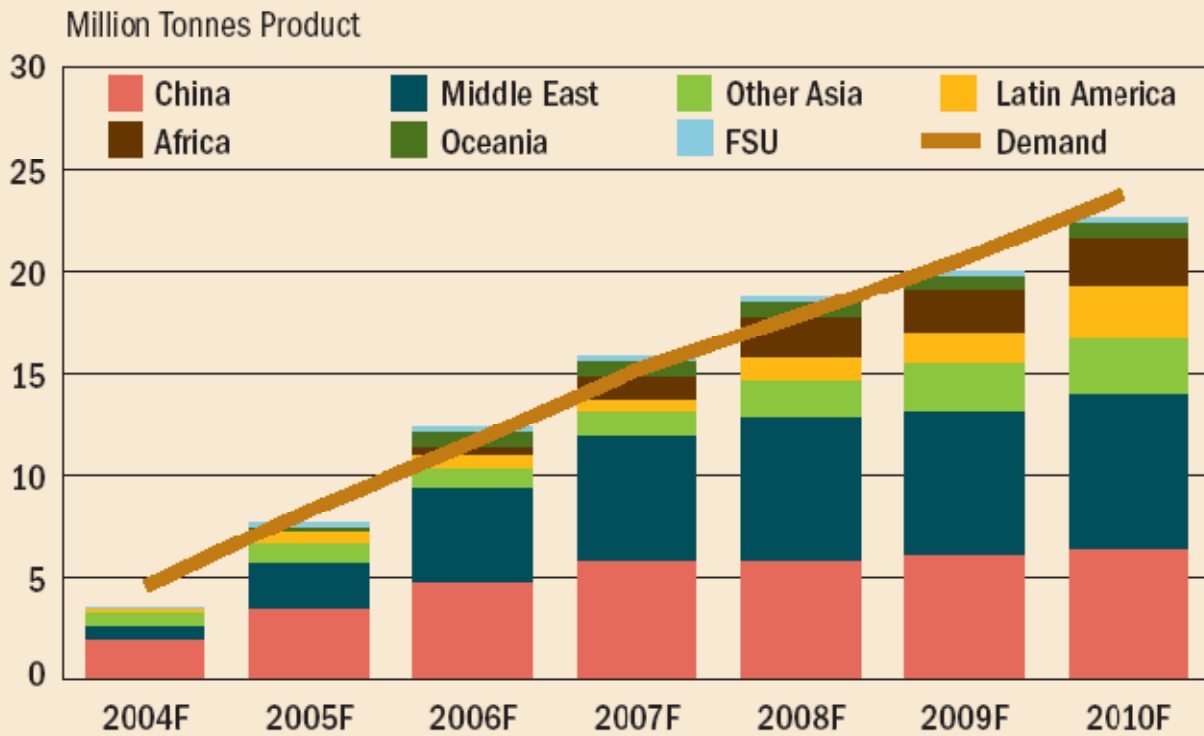


| Country | 1992 | 2002 | 2008 |
|-------------|------|------|------|
| China | 17% | 23% | 22% |
| Asia | 15% | 19% | 18% |
| North Am. | 19% | 16% | 14% |
| FSU | 21% | 15% | 14% |
| Middle East | 3% | 5% | 9% |
| Western Eu. | 11% | 8% | 7% |
| Latin Am | 3% | 5% | 6% |
| Central Eu. | 8% | 6% | 5% |
| Africa | 3% | 3% | 3% |
| Oceania | 0% | 0% | 2% |

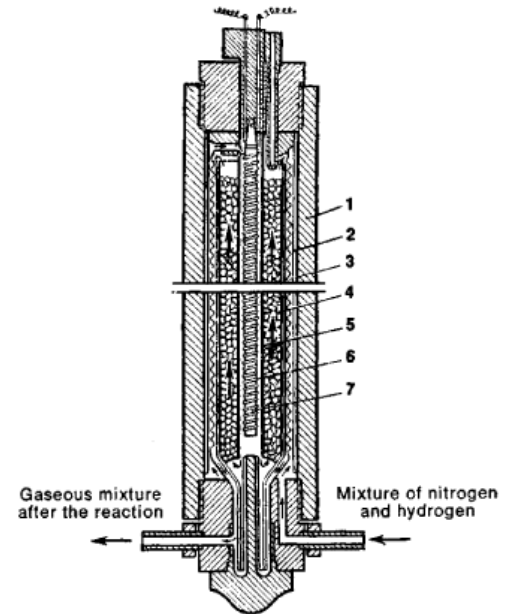
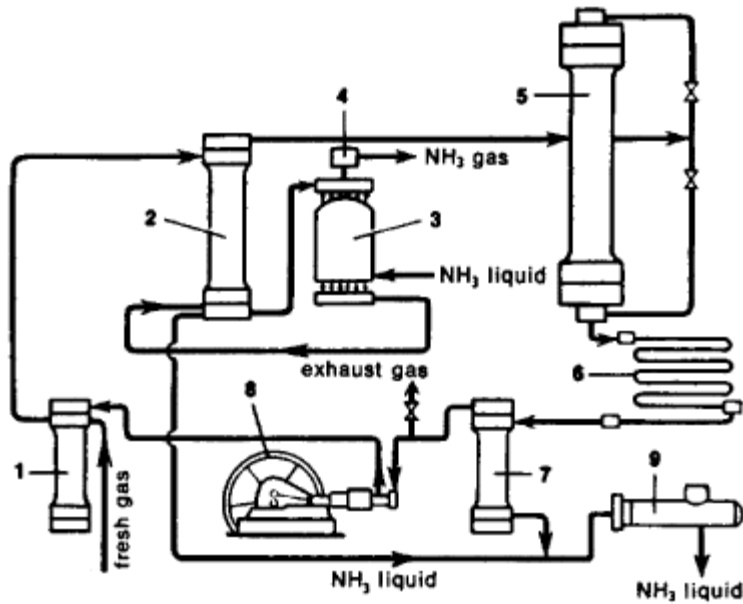
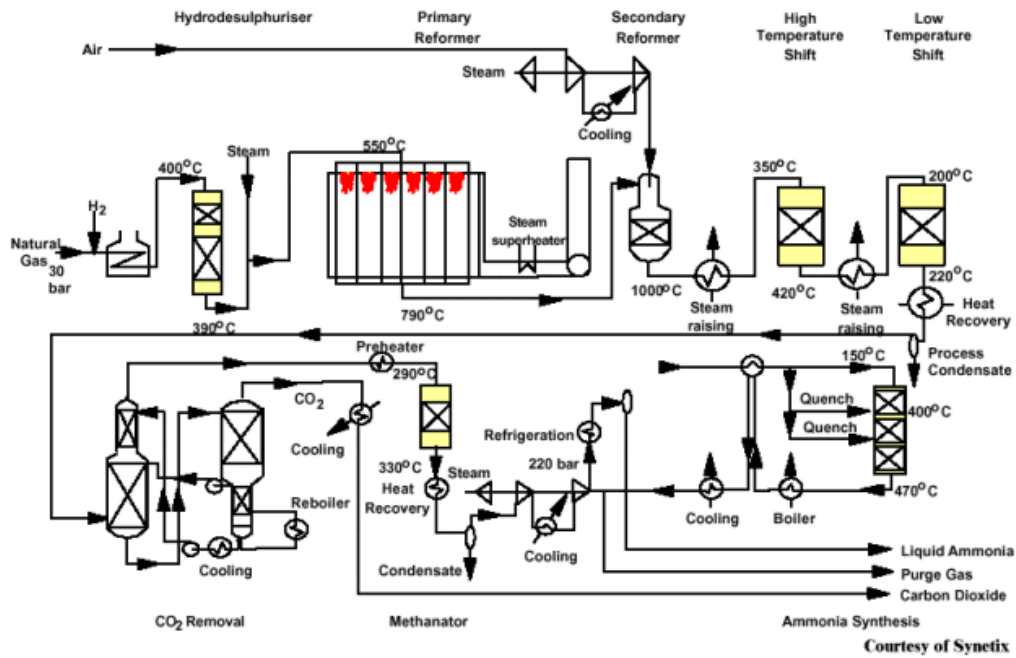
2008



New Ammonia Capacity vs Demand Cumulative Growth



3.13- Ammonia Production Scheme and Reactor



3.14- MODELING AND SIMULATION OF AMMONIA SYNTHESIS REACTOR

In this paper an industrial ammonia synthesis reactor has been modeled. The reactor under study is of horizontal type. This reactor which is under the license of Kellogg Company is equipped with three axial flow catalyst beds and an internal heat exchanger in accompany with a cooling flow. The achieved modeling is one dimensional and non-homogenous. Considering the sever effect of internal heat exchanger on reactor operation, it has been simulated by calculation of film heat transfer coefficients in its tube and shell and then, taking into account the shell thermal resistance and fouling coefficient, obtaining the overall heat transfer coefficient. So in the developed software, the heat transfer coefficient is first calculated using the conditions of the input flow to the exchanger and then the input flows to the first and second beds are calculated. The differential equations ave been solved using Rung Kutta 4 method and the results have been compared with the available industrial data. Finally the capability of the developed software for industrial application has been investigated by changing the reactor operation conditions and studying their effects on reactor output.

Introduction

Ammonia Synthesis is a very important process in chemical complexes. Ammonia is the initial chemical material for a variety of industries. It is used in production of chemical fertilizers, explosive materials, polymers, acids and even coolers. Simulation can play an important role to give an insight of the industrial units and hence simulation of Ammonia unit is very important to help us investigate the different operation modes of this unit and optimize that. Ammonia synthesis loop is the most important part of this unit which better understanding of its bottleneck can led us to make the operation yield higher than before.

Ammonia Synthesis Loop

In ammonia production unit, the synthesis loop is located after the syngas roduction and purification units. Ammonia synthesis process takes place in high pressure and hence high power multi cycle compressors are used to supply the required pressure. The Kellogg synthesis reactor incorporated in this loop is of horizontal type with three beds. To control the temperature between first and second beds, an internal heat exchanger has been used in which the input feed to the first bed and the output gas from the same bed have thermal exchange. In addition to the mentioned heat exchanger, the quench gas flow is also used for control of temperature. The input feed to the reactor, is first divided into two parts, before entrance. One part is considered as feed and the other part as quench gas. The feed, after entering the reactor, passes through the empty spaces of the beds as

well as the reactor walls and gets slightly heated. When reaching to the end of the reactor, it passes through the shell of the internal heat exchanger and its temperature reaches 400 °C. Tubes of the heat exchanger contain the output gas from the first bed. Quench gas is used to control the inlet temperature of the first bed. The required temperature for inlet of the first bed is 371 °C. Output gas, after warming up, is then entered to first catalytic bed. Figure 1 depicts the schematic diagram of a Kellogg horizontal reactor.

When the gas passes the first bed and the reaction is taken place, its temperature increases and reaches 496 °C. It then enters the tubes of the heat exchanger to cool down. Gas is then entered from top of the second bed. Temperature rises again as the reaction takes place in the second bed. No specific operation is carried out between beds two and three. In fact these two beds act as a single bed whose length is twice the length of each bed. The catalyst of this reactor is magnetic ferro oxide.

Mathematical Model

By modeling of the synthesis reactor, temperature, concentrations and pressure profiles are obtained. Of course testing of the model based on the above parameters is achieved at the end of each bed as industrial data are not usually available along the length of the bed. The following assumptions have been made for this modeling:

- a) One-dimensional Cartesian coordinate has been considered along with the bulk flow.
- b) Penetration of mass and heat is ignored, as the fluid velocity is very high in industrial scale.
- c) Density is constant
- d) Concentration and temperature on catalyst surface and bulk of gas are equal.
- e) The effects of penetration resistance in catalyst, temperature gradient and catalyst inside concentration have been incorporated in the equations by a coefficient.

For further information you can search sciencedirect.com or www.vurup.sk/pc

3.15- Latest Developments in Ammonia Production

Many Indian ammonia plants struggle with high feedstock prices. In order to survive in the competition from new plants in areas with low gas cost, many plant owners of existing plants have decided to revamp their plants to reduce the energy consumption and/or increase the capacity. New developments are needed in order to fulfill these needed in order to fulfill these needs of the market.

This article will highlight some of the developments made that are suitable to be implemented in revamp jobs. Furthermore, these developments are also important

for design of new very large capacity ammonia plants, and process schemes for a 4000 and 5000 MTPD ammonia plants will be covered, including an attractive option, which has been in full-scale commercial operation since January 2003, the proprietary and patented Haldor Topsoe Exchange Reformer (HTER). For further information you can search www.sciencedirect.com

References

- 1-** The Fertilizer Encyclopedia, Krishnamurthy, 2009
- 2-** Bradley David, A Great Potential, The Great Lakes as a Regional Renewable Energy Source, 2008
- 3-** Aleksander Abram and D. Lynn Forster, The Ohio State University, A PRIMER ON AMMONIA, NITROGEN FERTILIZERS, AND NATURAL GAS MARKETS, 2005.
- 4-** Yost, Don M. (2007). "Ammonia and Liquid Ammonia Solutions". Systematic Inorganic Chemistry. READ BOOKS. p. 132. ISBN 1-4067-7302-6.
<http://books.google.com/?id=qPGzhL3Y50YC&pg=PA132>.
- 5-** Palacios R, New Horizons in Nitrogen Fixation, 2010

Section 4: Urea Production

4.1- Urea

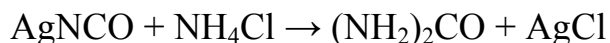
Urea or carbamide is an organic compound with the chemical formula $(\text{NH}_2)_2\text{CO}$. The molecule has two amine ($-\text{NH}_2$) groups joined by a carbonyl ($\text{C}=\text{O}$) functional group.

Urea serves an important role in the metabolism of nitrogen-containing compounds by animals and is the main nitrogen-containing substance in the urine of mammals. It is solid, colourless, and odorless (although the ammonia which it gives off in the presence of water, including water vapor in the air, has a strong odor). It is highly soluble in water and non-toxic. Dissolved in water it is neither acidic nor alkaline. The body uses it in many processes, most notably nitrogen excretion. Urea is widely used in fertilizers as a convenient source of nitrogen. Urea is also an important raw material for the chemical industry. The synthesis of this organic compound by Friedrich Wöhler in 1828 from an inorganic precursor was an important milestone in the development of organic chemistry, as it showed for the first time that a molecule found in living organisms could be synthesized in the lab without biological starting materials.

The terms urea and carbamide are also used for a class of chemical compounds sharing the same functional group $\text{RR}'\text{N}-\text{CO}-\text{NRR}'$, namely a carbonyl group attached to two organic amine residues. Examples include carbamide peroxide, allantoin, and hydantoin. Ureas are closely related to biurets and related in structure to amides, carbamates, carbodiimides, and thiocarbamides.

4.2- History

Urea was first discovered in urine in 1773 by the French chemist Hilaire Rouelle. In 1828, the German chemist Friedrich Wöhler obtained urea by treating silver isocyanate with ammonium chloride.



This was the first time an organic compound was artificially synthesized from inorganic starting materials, without the involvement of living organisms. The results of this experiment implicitly discredited vitalism: the theory that the chemicals of living organisms are fundamentally different from inanimate matter. This insight was important for the development of organic chemistry. His discovery prompted Wöhler to write triumphantly to Berzelius: "I must tell you that I can make urea without the use of kidneys, either man or dog. Ammonium

cyanate is urea." For this discovery, Wöhler is considered by many^[who?] the father of organic chemistry.

4.3- Physiology

Urea is synthesized in the body of many organisms as part of the urea cycle, either from the oxidation of amino acids or from ammonia. In this cycle, amino groups donated by ammonia and L-aspartate are converted to urea, while L-ornithine, citrulline, L-argininosuccinate, and L-arginine act as intermediates. Urea production occurs in the liver and is regulated by N-acetylglutamate. Urea is found dissolved in blood (in the reference range of 2.5 to 6.7 mmol/liter) and is excreted by the kidney as a component of urine. In addition, a small amount of urea is excreted (along with sodium chloride and water) in sweat.

Amino acids from ingested food which are not used for the synthesis of proteins and other biological substances are oxidized by the body, yielding urea and carbon dioxide, as an alternative source of energy. The oxidation pathway starts with the removal of the amino group by a transaminase, the amino group is then fed into the urea cycle.

Ammonia (NH₃) is another common byproduct of the metabolism of nitrogenous compounds. Ammonia is smaller, more volatile and more mobile than urea. If allowed to accumulate, ammonia would raise the pH in cells to toxic levels. Therefore many organisms convert ammonia to urea, even though this synthesis has a net energy cost. Being practically neutral and highly soluble in water, urea is a safe vehicle for the body to transport and excrete excess nitrogen.

In water, the amine groups undergo slow displacement by water molecules, producing ammonia and carbonate anion. For this reason, old, stale urine has a stronger odor than fresh urine.

4.4- In humans

The handling of urea by the kidneys is a vital part of human metabolism. Besides its role as carrier of waste nitrogen, urea also plays a role in the countercurrent exchange system of the nephrons, that allows for re-absorption of water and critical ions from the excreted urine. Urea is reabsorbed in the inner medullary collecting ducts of the nephrons, thus raising the osmolarity in the medullary interstitium surrounding the thin ascending limb of the loop of Henle, which in turn causes water to be reabsorbed. By action of the urea transporter 2, some of this reabsorbed

urea will eventually flow back into the thin ascending limb of the tubule, through the collecting ducts, and into the excreted urine.

This mechanism, which is controlled by the antidiuretic hormone, allows the body to create hyperosmotic urine, that has a higher concentration of dissolved substances than the blood plasma. This mechanism is important to prevent the loss of water, to maintain blood pressure, and to maintain a suitable concentration of sodium ions in the blood plasmas.

The equivalent nitrogen content (in gram) of urea (in mmol) can be estimated by the conversion factor 0.028 g/mmol. Furthermore, 1 gram of nitrogen is roughly equivalent to 6 gram of protein, and 1 gram of protein is roughly equivalent to 4 gram of muscle tissue. Subsequently, in situations such as muscle wasting, 1 mmol of excessive urea in the urine (as measured by urine volume in litres multiplied by urea concentration in mmol/l) roughly corresponds to a muscle loss of 0.67 gram.

4.5- In other species

In aquatic organisms the most common form of nitrogen waste is ammonia, while land-dwelling organisms convert the toxic ammonia to either urea or uric acid. Urea is found in the urine of mammals and amphibians, as well as some fish. Birds and saurian reptiles have a different form of nitrogen metabolism, that requires less water and leads to nitrogen being excreted in the form of uric acid. It is noteworthy that tadpoles excrete ammonia but shift to urea production during metamorphosis. Despite the generalization above, the urea pathway has been documented not only in mammals and amphibians but in many other organisms as well, including birds, invertebrates, insects, plants, yeast, fungi, and even microorganisms.

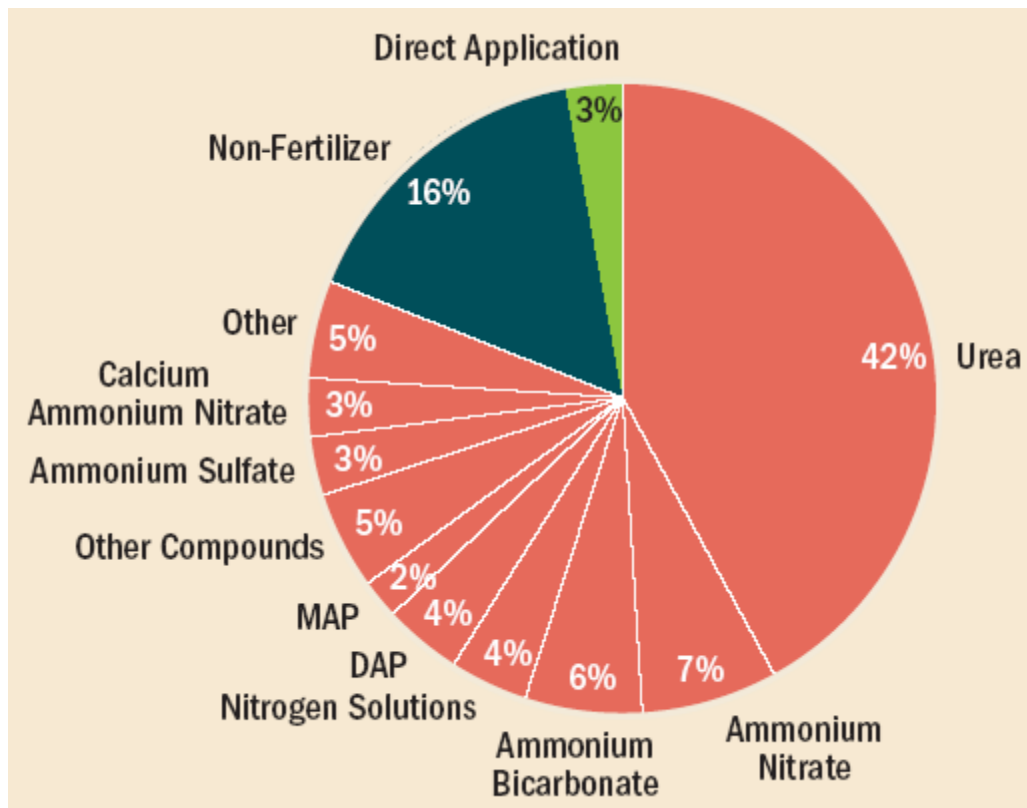
4.6- Urea Uses

Agriculture

More than 90% of world production of urea is destined for use as a nitrogen-release fertilizer. Urea has the highest nitrogen content of all solid nitrogenous fertilizers in common use. Therefore, it has the lowest transportation costs per unit of nitrogen nutrient.

Many soil bacteria possess the enzyme, urease, which catalyzes the conversion of the urea molecule to two ammonia molecules and one carbon dioxide molecule, thus urea fertilizers are very rapidly transformed to the ammonium form in soils. Among soil bacteria known to carry urease, some ammonia-oxidizing bacteria

(AOB), such as species of Nitrosomonas are also able to assimilate the carbon dioxide released by the reaction to make biomass via the Calvin Cycle, and harvest energy by oxidizing ammonia (the other product of urease) to nitrite, a process termed nitrification. Nitrite-oxidizing bacteria, especially, Nitrobacter, oxidize nitrite to nitrate, which is extremely mobile in soils and is a major cause of water pollution from agriculture. Ammonia and nitrate are readily absorbed by plants, and are the dominant sources of nitrogen for plant growth. Urea is also used in many multi-component solid fertilizer formulations. Urea is highly soluble in water and is, therefore, also very suitable for use in fertilizer solutions (in combination with ammonium nitrate: UAN), e.g., in 'foliar feed' fertilizers. For fertilizer use, granules are preferred over prills because of their narrower particle size distribution which is an advantage for mechanical application.



The most common impurity of synthetic urea is biuret, which impairs plant growth.

Urea is usually spread at rates of between 40 and 300 kg/ha but rates vary. Smaller applications incur lower losses due to leaching. During summer, urea is often spread just before, or during rain to minimize losses from volatilization (process wherein nitrogen is lost to the atmosphere as ammonia gas). Urea is not compatible with other fertilizers.

Because of the high nitrogen concentration in urea, it is very important to achieve an even spread. The application equipment must be correctly calibrated and properly used. Drilling must not occur on contact with or close to seed, due to the risk of germination damage. Urea dissolves in water for application as a spray or through irrigation systems.

In grain and cotton crops, urea is often applied at the time of the last cultivation before planting. In high rainfall areas and on sandy soils (where nitrogen can be lost through leaching) and where good in-season rainfall is expected, urea can be side- or top-dressed during the growing season. Top-dressing is also popular on pasture and forage crops. In cultivating sugarcane, urea is side-dressed after planting, and applied to each ratoon crop.

In irrigated crops, urea can be applied dry to the soil, or dissolved and applied through the irrigation water. Urea will dissolve in its own weight in water, but it becomes increasingly difficult to dissolve as the concentration increases. Dissolving urea in water is endothermic, causing the temperature of the solution to fall when urea dissolves.

As a practical guide, when preparing urea solutions for fertigation (injection into irrigation lines), dissolve no more than 30 kg urea per 100 L water.

In foliar sprays, urea concentrations of 0.5% – 2.0% are often used in horticultural crops. Low-biuret grades of urea are often indicated.

Urea absorbs moisture from the atmosphere and therefore is typically stored either in closed/sealed bags on pallets, or, if stored in bulk, under cover with a tarpaulin. As with most solid fertilizers, storage in a cool, dry, well-ventilated area is recommended.

Chemical industry

Urea is a raw material for the manufacture of many important chemical compounds, such as

- Various plastics, especially the urea-formaldehyde resins.
- Various adhesives, such as urea-formaldehyde or the urea-melamine-formaldehyde used in marine plywood.
- Potassium cyanate, another industrial feedstock.

Explosive

Urea can be used to make urea nitrate, a high explosive which is used industrially and as part of some improvised explosive devices.

Automobile systems

Urea is used in SNCR and SCR reactions to reduce the NO_x pollutants in exhaust gases from combustion from diesel, dual fuel, and lean-burn natural gas engines. The BlueTec system, for example, injects water-based urea solution into the exhaust system. The ammonia produced by the hydrolysis of the urea reacts with the nitrogen oxide emissions and is converted into nitrogen and water within the catalytic converter.

Other commercial uses

This section does not cite any references or sources. Please help improve this section by adding citations to reliable sources. Unsourced material may be challenged and removed. (May 2010)

- A stabilizer in nitrocellulose explosives
- A component of animal feed, providing a relatively cheap source of nitrogen to promote growth
- A non-corroding alternative to rock salt for road de-icing, and the resurfacing of snowboarding halfpipes and terrain parks
- A flavor-enhancing additive for cigarettes
- A main ingredient in hair removers such as Nair and Veet
- A browning agent in factory-produced pretzels
- An ingredient in some skin cream, moisturizers, hair conditioners
- 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 other salts
- A flame-proofing agent, commonly used in dry chemical fire extinguisher charges such as the urea-potassium bicarbonate mixture
- An ingredient in many tooth whitening products
- An ingredient in dish soap
- Along with ammonium phosphate, as a yeast nutrient, for fermentation of sugars into ethanol

- A nutrient used by plankton in ocean nourishment experiments for geoengineering purposes
- As an additive to extend the working temperature and open time of hide glue
- As a solubility-enhancing and moisture-retaining additive to dye baths for textile dyeing or printing

Laboratory uses

Urea in concentrations up to 10 M is a powerful protein denaturant as it disrupts the noncovalent bonds in the proteins. This property can be exploited to increase the solubility of some proteins. A mixture of urea and choline chloride is used as a deep eutectic solvent, a type of ionic liquid.

Urea can in principle serve as a hydrogen source for subsequent power generation in fuel cells. Urea present in urine/wastewater can be used directly (though bacteria normally quickly degrade urea.) Producing hydrogen by electrolysis of urea solution occurs at a lower voltage (0.37V) and thus consumes less energy than the electrolysis of water (1.2V).

Medical use

Urea-containing creams are used as topical dermatological products to promote rehydration of the skin. Urea 40% is indicated for psoriasis, xerosis, onychomycosis, ichthyosis, eczema, keratosis, keratoderma, corns and calluses. If covered by an occlusive dressing, 40% urea preparations may also be used for nonsurgical debridement of nails. Urea 40% "dissolves the intercellular matrix"^[9] of the nail plate. Only diseased or dystrophic nails are removed as there is no effect on healthy portions of the nail. This drug is also used as an earwax removal aid.

Certain types of instant cold packs (or ice packs) contain water and separated urea crystals. Rupturing the internal water bag starts an endothermic reaction and allows the pack to be used to reduce swelling.

Like saline, urea injection is used to perform abortions.

Urea is the main component of an alternative medicinal treatment referred to as urine therapy.

The blood urea nitrogen (BUN) test is a measure of the amount of nitrogen in the blood that comes from urea. It is used as a marker of renal function.

Urea labeled with carbon-14 or carbon-13 is used in the urea breath test, which is used to detect the presence of the bacteria *Helicobacter pylori* (*H. pylori*) in the stomach and duodenum of humans, associated with peptic ulcers. The test detects the characteristic enzyme urease, produced by *H. pylori*, by a reaction that produces ammonia from urea. This increases the pH (reduces acidity) of the stomach environment around the bacteria. Similar bacteria species to *H. pylori* can be identified by the same test in animals such as apes, dogs, and cats (including big cats).

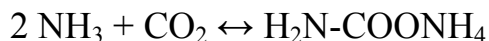
4.7- Urea Production

Urea is produced on a scale of some 100,000,000 tons per year worldwide.

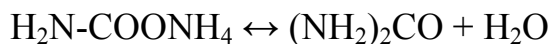
Industrial methods

For use in industry, urea is produced from synthetic 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. Such point sources of CO₂ facilitate direct synthesis of urea.

The basic process, developed in 1922, is also called the Bosch-Meiser urea process after its discoverers. 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. The process consists of two main equilibrium reactions, with incomplete conversion of the reactants. The first is an exothermic reaction of liquid ammonia with dry ice to form ammonium carbamate (H₂N-COONH₄):



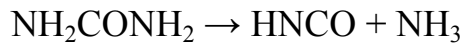
The second is an endothermic decomposition of ammonium carbamate into urea and water:



Both reactions combined are exothermic.

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.

Urea can be produced as prills, granules, pellets, crystals, and solutions. Solid urea is marketed as prills or granules. The advantage of prills is that, in general, they can be produced more cheaply than granules. Properties such as impact strength, crushing strength, and free-flowing behaviour are, in particular, important in product handling, storage, and bulk transportation. Typical impurities in the production are biuret and isocyanic acid:



The biuret content is a serious concern because it is often toxic to the very plants that are to be fertilized. Urea is classified on the basis of its biuret content.



Laboratory preparation

Ureas in the more general sense can be accessed in the laboratory by reaction of phosgene with primary or secondary amines, proceeding through an isocyanate intermediate. Non-symmetric ureas can be accessed by reaction of primary or secondary amines with an isocyanate.

Historical process

Historically urea was first noticed by Hermann Boerhaave in the early 18th century from evaporates of urine. In 1773, Hilaire Rouelle obtained crystals containing urea from dog's urine by evaporating it and treating it with alcohol in successive filtrations. This method was aided by Carl Wilhelm Scheele's discovery that urine treated by concentrated nitric acid precipitated crystals. Antoine François, comte de Fourcroy and Louis Nicolas Vauquelin discovered in 1799 that the nitrated crystals were identical to Rouelle's substance and invented the term "urea." Berzelius made further improvements to its purification and finally William Prout, in 1817, succeeded in obtaining and determining the chemical composition of the pure substance. In the evolved procedure, urea was precipitated as urea nitrate by adding strong nitric acid to urine. To purify the resulting crystals, they were dissolved in boiling water with charcoal and filtered. After cooling pure crystals of urea nitrate form. To reconstitute the urea from the nitrate, the crystals are dissolved in warm water, and barium carbonate added. The water is then evaporated and anhydrous alcohol added to extract the urea. This solution is drained off and allowed to evaporate resulting in pure urea.

4.8- Chemical Properties

Molecular and crystal structure

The urea molecule is planar in the crystal structure, but the geometry around the nitrogens is pyramidal in the gas-phase minimum-energy structure. In solid urea, the oxygen center is engaged in two N-H-O hydrogen bonds. The resulting dense and energetically favourable 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. The carbon in urea is described as sp^2 hybridized, the C-N bonds have significant double bond character, and the carbonyl oxygen is basic compared to, say, formaldehyde. Urea's high aqueous solubility reflects its ability to engage in extensive hydrogen bonding with water.

By virtue of its tendency to form a porous frameworks, urea has the ability to trap many organic compounds. In these so-called clathrates, the organic "guest" molecules are held in channels formed by interpenetrating helices comprising of hydrogen-bonded urea molecules. This behaviour can be used to separate mixtures, e.g. in the production of aviation fuel and lubricating oils, and in the separation of paraffins.

As the helices are interconnected, all helices in a crystal must have the same molecular handedness. This is determined when the crystal is nucleated and can thus be forced by seeding. The resulting crystals have been used to separate racemic mixtures.

4.9- Safety

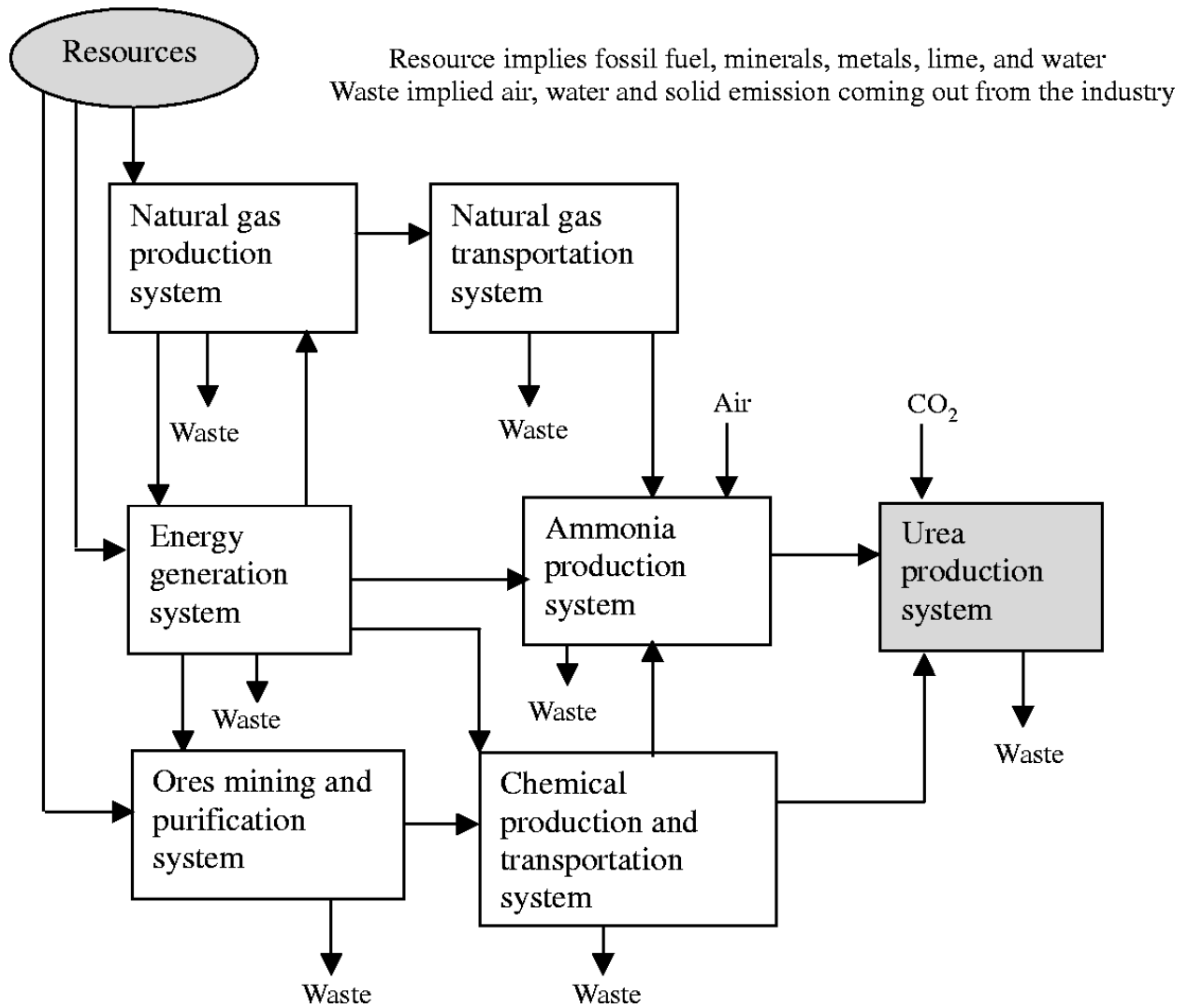
Urea can be irritating to skin, eyes, and the respiratory tract. Repeated or prolonged contact with urea in fertilizer form on the skin may cause dermatitis.

High concentrations in the blood can be damaging. Ingestion of low concentrations of urea, such as are found in typical human urine, are not dangerous with additional water ingestion within a reasonable time-frame. Many animals (e.g., dogs) have a much more concentrated urine and it contains a higher urea amount than normal human urine; this can prove dangerous as a source of liquids for consumption in a life-threatening situation (such as in a desert).

Urea can cause algal blooms to produce toxins, and its presence in the runoff from fertilized land may play a role in the increase of toxic blooms.

The substance decomposes on heating above melting point, producing toxic gases, and reacts violently with strong oxidants, nitrites, inorganic chlorides, chlorites and perchlorates, causing fire and explosion.

4.10- Urea Production Scheme



References

- 1- Krishnamurthy, The Fertilizer Encyclopedia, 2009
- 2- Palacios R, New Horizons in Nitrogen Fixation, 2010
- 3- www.dooyoo.co.uk (2009-06-19). "Lacura Multi Intensive Serum - Review - Excellent value for money - Lacura Multi Intensive Serum "Aqua complete"". Dooyoo.co.uk. <http://www.dooyoo.co.uk/skin-care/lacura-multi-intensive-serum/1264192/>. Retrieved 2010-12-28
- 4- Inorganic Chemicals » AMMONIUM CARBAMATE". Hillakomem.com. 2008-10-02. <http://www.hillakomem.com/tag/ammonium-carbamate>. Retrieved 2010-12-28.