

Urea, its history and applications

UreaKnowHow.com

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Preface

Where to start when writing the first process paper for UreaKnowHow.com ?

Why not at the origin of urea ? Who did discover urea and who invented the principles of the urea production process as we know it today ? This paper starts from there and describes also the possible applications of urea, because once we start to discuss the details of the urea process it will be too late to cover these aspects. And details we will discuss, many many details like fouling, corrosion, thermodynamics, different processes, construction details, reaction kinetics, operating procedures, maintenance issues, explosion risks, caking, emissions etc etc etc.

So please sit back, relax and travel back to 1773.

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1. History

Most literature sources state that Urea was first discovered in human urine by the French chemist **Hillaire Marin Rouelle** in 1773. Hillaire Marin was a neat and tactful person, an experimenter rather than a forceful teacher. He found potassium in "cream of tartar" and went on to isolate tartaric acid from unfermented grape juice. He found formic acid in ants and discovered urea, or possibly the hydrate of urea and sodium chloride in urine.



Picture: Hillaire Marin Rouelle (1718 - 1779)



The Dutch **Herman Boerhaave** [1668-1738] discovered urea possibly already in 1729. He confirmed the presence of iron in blood and was the first to separate out urea from urine, and to do so without adding chemical substances such as alcohol or nitric acid. Boerhaave was the founder of organic chemistry, of the chemistry of the carbon compounds. By systematizing existing knowledge and data, Boerhaave drafted a complete, all-embracing theory of medicine wherein all known facts received their proper place.

Picture: Herman Boerhaave

Urea was first synthesized from ammonia and phosgene, which was prepared by exposing carbon monoxide and chlorine gases to sunlight, by Humphry Davy's brother **John Davy** in 1812. But Davy did not recognize urea.

It was left for the German chemist **Friedrich Wöhler** to announce in 1828 the synthesis of urea after having slowly evaporated a water solution of ammonium cyanate.

Well over fifty different methods have since been devised for the synthesis of urea. It is of interest, however, that only two methods have attracted industrial attention, namely, the hydrolysis of cyanamide and the interaction of ammonia and carbon dioxide.

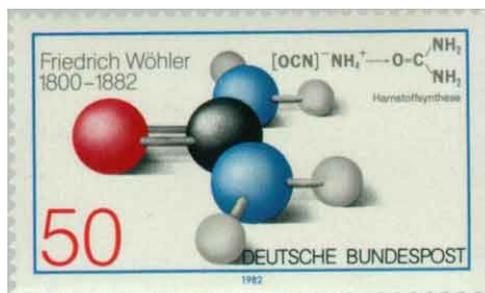
Starting from calcium cyanamide, numerous processes have been proposed, some yielding urea in a pure state and some giving a mixture of urea and the calcium salt of acid used for hydrolysis. The most developed process yielding pure urea is that proposed by **J. H. Lidholm**. This process comprises the addition of calcium cyanamide to water, either together with or followed by the addition of carbon dioxide usually under pressure and with violent agitation, to precipitate the calcium.

After settling, the cyanamide solution, containing 10 per cent or more of cyanamide and precipitated calcium carbonate, is filtered and evaporated to crystallize the urea.

A pilot plant operated by the Union Carbide Company at Niagara Falls to test the feasibility of the Lidholm process was described by McBride. This process consisted in mixing together in an efficient heater, calcium cyanamide and water in the presence of carbon dioxide gas, and in controlling both

the alkalinity of the solution by the rate of addition of calcium cyanamide and the pressure of the carbon dioxide over the solution.

Starting from ammonia and carbon dioxide, urea was synthesized in 1828 by Friedrich Wöhler and urea was the first organic compound to be synthesized from inorganic starting materials.



Picture: Friedrich Wöhler (1800-1882)

Friedrich Wöhler wrote in 1828:

"In a brief earlier communication, printed in Volume III of these Annals, I stated that by the action of cyanogen on liquid ammonia, besides several other products, there are formed oxalic acid and a crystallizable white substance, which is certainly not ammonium cyanate, but which one always obtains when one attempts to make ammonium cyanate by combining cyanic acid with ammonia, e.g., by so-called double decomposition. The fact that in the union of these substances they appear to change their nature, and give rise to a new body, drew my attention anew to this subject, and research gave the unexpected result that by the combination of cyanic acid with ammonia, urea is formed, a fact that is noteworthy since it furnishes an example of the artificial production of an organic, indeed a so-called animal substance, from inorganic materials....

....I will describe the behaviour of this artificial urea no further, since it coincides perfectly with that of urea from urine, according to the accounts of Proust, Prout and others, to be found in their writings, and I will mention only the fact, not specified by them, that both natural and artificial urea, on distillation, evolve first large amounts of ammonium carbonate, and then give off to a remarkable extent the stinging, acetic-acid-like smell of cyanic acid, exactly as I found in the distillation of mercuric cyanate or uric acid, and especially of the mercury salt of uric acid. In the distillation of urea, another white, apparently distinct substance also appears, with the examination of which I am still occupied. "

This 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."

This organic synthesis dealt a severe blow to a widespread belief called "vitalism" which maintained that organic chemicals could be modified by chemistry but could only be produced through the agency of a vital force present in living plants and animals. For many, then, Wöhler is considered the true father of organic chemistry.

Urea is found in mammalian and amphibian urine as well as in some fish. Birds and reptiles excrete uric acid, comprising a different form of nitrogen metabolism that requires less water.

Most organisms have to deal with the excretion of nitrogen waste originating from protein and amino acid catabolism. 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. In general, birds and saurian reptiles excrete uric acid, whereas the remaining species, including mammals, excrete urea.

Urea is highly soluble in water and is, therefore, an efficient way for the human body to expel excess nitrogen. Its high solubility is due to extensive hydrogen bonding with water: up to six hydrogen bonds may form - two from the oxygen atom and one from each hydrogen atom. Organisms synthesize urea from ammonia because ammonia (a common metabolic waste product) raises pH in cells to toxic levels. Therefore, urea synthesis is necessary even though it costs energy to produce. Urea is neither acidic nor basic, so it is a perfect vehicle for getting rid of nitrogen waste. Urea production occurs in the liver and is regulated by N-acetylglutamate.

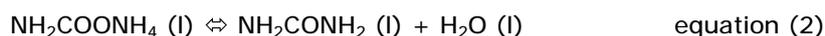
In 1868 urea was produced by heating ammonium carbamate in a sealed vessel. This provided the basis of the current industrial process for its production. The German chemist Alexander I. **Basaroff** (or was he Russian and named Basarow ?) discovered that ammonium carbamate would convert into urea at elevated pressure and temperature. In a Leipzig laboratory Basaroff obtained urea by heating the ammonia salt of carbonic acid in sealed tubes - that is to say from two molecules of NH_3 plus one of carbonic acid (CO_2).

2. Production

Large scale manufacture of urea in modern times has been based on synthesis from ammonia and carbon dioxide. This process as originally suggested by Basaroff was first translated into industrial manufacture by German chemists in I. G. Farben in about 1920. The development of the process continues to go ahead in different countries and many contributions to the process were made since then.

The raw materials carbon dioxide and ammonia first enter the autoclave, in which they react and form urea. The reacted mixture then flows out from the autoclave into a decomposer, in which portion of materials not converted into urea are decomposed and distilled off from the urea product in the solution. The urea solution is in a condition to be sent to recover the final product. The unconverted ammonia and carbon dioxide recovered from the decomposer can be used for recycle after certain treatment or be sent to by-product manufacture.

There are two main reactions involved in the synthesis of urea from carbon dioxide and ammonia; the formation of ammonium carbamate from carbon dioxide and ammonia, and the conversion of ammonium carbamate into urea. The reactions involved can be represented by the following equations:



At the temperature of 135 to 200 °C, the reaction as represented by equation (1) is almost instantaneous and complete, provided the pressure of the system is greater than the decomposition pressure of the ammonium carbamate at the system temperature. When the system is dry, the only product is ammonium carbamate if the proper relative proportion of the two constituents are used. In the presence of water, carbonates of ammonia are also formed. Water

and ammonium carbamate form a meta-stable system which evolves slowly into a complex mixture whose composition depends upon temperature and concentration.

The formation of carbamate is highly exothermic. The huge quantity of heat evolved in the formation of ammonium carbamate from carbon dioxide and ammonia necessitates the continual removal of heat in its preparation. At the point of temperature below the melting point of ammonium carbamate, 150 °C, the ammonium carbamate forms a compact covering adhering film on the wall of the vessel which conducts heat poorly and thus increases the difficulty of removing the released heat of reaction. Several means have been proposed to circumvent this difficulty. Above the melting point of ammonium carbamate, the problems resulting from the formation of a bad heat conducting film no longer exist, but they are replaced by serious problem of corrosion.

Since the reaction represented by equation (1) is an equilibrium reaction, a thorough knowledge for dissociation pressure of ammonium carbamate, equilibrium constants and free energies of ammonium carbamate synthesis is a "must" for the investigation of the process. Heat removal as discussed in the previous paragraph is very important in the process of manufacture. It is necessary to know about the quantity of heat formation of ammonium carbamate.

As to the reaction, represented by equation (2), the dehydration is never completed. The yield of urea involves many factors, such as molar ratio of ammonia to carbon dioxide, effect of water, packing density in batch process, autoclave pressure and liquid level in flow process, time of residence, etc. The reaction is assumed to proceed entirely in the liquid phase. The resulting product is a complex mixture of water, urea, unchanged ammonium carbamate and ammonium carbonates resulting from the action of ammonium carbamate on the water formed.

The reaction (2) is an endothermic reaction; however, the quantity of heat absorbed is much smaller than the heat evolved in the formation of ammonium carbamate from carbon dioxide and ammonia. In order to diminish the exothermic heat in the autoclave, it is preferable to introduce ammonia in the liquid state. Carbon dioxide can be introduced equally well as a gas or as a liquid, since its critical temperature is close to room temperature making its heat of vaporization very slight. The reaction mixture from the autoclave is discharged into a "decomposer," also called "distilling column" or "stripper" to decompose the ammonium carbamate and ammonium carbonates not converted into urea. 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 is commercially produced from two raw materials, ammonia, and carbon dioxide. Large quantities of carbon dioxide are produced during the manufacture of ammonia from coal or from hydrocarbons such as natural gas and petroleum-derived raw materials. This allows direct synthesis of urea from these raw materials.

For urea production, the ammonia was made available by the Haber process and Carl Bosch, a talented metallurgical engineer and BASF's future chairman designed and built an industrial-size installation that could contain the great pressures and high temperatures required in Haber's process for the production of ammonia.



Before long the scientific community was referring to the 'Haber-Bosch process'. The artificial fixation of nitrogen is considered one of the greatest innovations of the twentieth century and earned both men the acclaim of the international scientific community. The 'Haber-Bosch' process went on-stream in September 1913 and it is still the predominant method used. Many alternative techniques have been developed since but none have proved more effective.

Picture: Carl Bosch



The production process of urea, developed and patented (US patent 1,429,483) in 1922 as a continuous process, is called the **Bosch-Meiser** urea process after its discoverers.

Patented Sept. 19, 1922.

1,429,483

UNITED STATES PATENT OFFICE.

CARL BOSCH AND WILHELM MEISER OF LUDWIGSHAFEN-ON-THE-RHINE, GERMANY,
ASSIGNORS, BY MESNE ASSIGNMENTS, TO BADISCHE ANILIN & SODA FABRIK, OF
LUDWIGSHAFEN-ON-THE-RHINE, BAVARIA, GERMANY, A CORPORATION OF THE
GRAND DUCHY OF BADEN.

PROCESS OF MANUFACTURING UREA.

No Drawing.

Application filed July 9, 1900. Serial No. 395,149.

The patent describes an invention related to an improved method of manufacturing urea.

"We have found that, the production of urea from carbon dioxide and ammonia can be effected in a simple manner by forcing the mixture of the two gases in about the proportions required according to the equation into a vessel capable of withstanding the pressure and maintaining the melt of ammonium salts formed, at the temperature suitable for the transformation of ammonium-carbamate into urea say from about 130 to 140 degrees centigrade introducing as much additional heat as may be found necessary. The compression and conveyance of the mixed ammonia and carbon dioxide is rendered possible, according to the invention, by keeping the compressor and the pipe connections at a temperature sufficiently high to avoid the separation of liquid or solid ammonium carbamate, or carbonates. By this process the separation of ammonium carbamate in a solid, or liquid, state becomes unnecessary, and it is even possible to work continuously. In order to obtain this result, the reaction mass, after urea has been formed, is slowly discharged, while maintaining the pressure in the vessel, and the mass withdrawn is separated while lowering its pressure, into a solution of urea and a gaseous mixture of ammonia, and carbon dioxide, which mixture is again compressed and forced back into the vessel."

In fact one can read here the principles of a conventional total recycle urea plant as it is still in operation today.

All commercial synthetic urea now produced in the world is obtained through the abovementioned reaction of ammonia and carbon dioxide. Various investigators have made studies on the optimum operating conditions of the process and on combating corrosion. The simplest process is the once-through process without recycling any part of the unreacted gases. The earliest successful commercial process is the "Hot Gas Recycle Process" worked at the Oppau Plant of I. G. Farben. Reciprocating compressors were used in the Oppau Plant. These are unsatisfactory because their maximum operating temperature is very close to the temperature at which condensation and deposition of ammonium carbamate takes place. Total decomposition of carbamate into ammonia and carbon dioxide, followed by centrifugal compression of these gases at high temperatures, seem a very promising solution to the problem.

American development processes include du Pont's "solution recycle process", the Solvay process, Vulcan (or CPI Allied) and the Chemico process. European processes include Pechiney process from France, Inventa and Urea Casale process from Switzerland, Montecatini and Snamprogetti process from Italy and the Stamicarbon process from Netherland. Further there is the Toyo Koatsu, nowadays Toyo Engineering Corporation process from Japan.



Nowadays stripping technology seems to be standard and many processes use pool condensation in the synthesis section. The design plant capacities of 300 mtpd in the past now has developed to 3500 mtpd. In the future papers of UreaKnowHow.com more details about the different production processes will be discussed. Plus the Urea E-Library of UreaKnowHow.com contains this patent and all other urea related patents.

Today urea is a nitrogen-containing chemical product that is produced on a scale of some 140 million tons per year worldwide. For use in industry, urea is produced from synthetic ammonia and carbon dioxide. Urea can be produced as prills, granules, flakes, pellets, crystals, and solutions. More than 90% of world production is destined for use as a fertilizer. Urea has the highest nitrogen content of all solid nitrogenous fertilizers in common use (46.7%). Therefore, it has the lowest transportation costs per unit of nitrogen nutrient. Urea is highly soluble in water and is, therefore, also very suitable for use in fertilizer solutions (in combination with ammonium nitrate: UAN), e.g., in 'foliar feed' fertilizers.

3. Applications

Urea knows many applications, although the most widespread one is obviously agricultural.

Agricultural

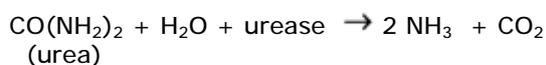
If properly applied, urea and fertilizers containing urea are excellent sources of nitrogen for crop production. After application to the soil, urea undergoes chemical changes and ammonium (NH_4^+) ions form. Soil moisture determines how rapidly this conversion takes place. When a urea particle dissolves, the area around it becomes a zone of high pH and ammonia concentration. This zone can be quite toxic for a few hours. Seed and seedling roots within this zone can be killed by the free ammonia that has formed. Fortunately, this toxic zone becomes neutralized in most soils as the ammonia converts to ammonium. Usually it's a few days before plants can effectively use the nitrogen. Although urea imparts an alkaline reaction when first applied to the soil, the net effect is to produce an acid reaction.

Advantages of Fertilizer Urea:

- Urea can be applied to soil as a solid or solution or to certain crops as a foliar spray.
- Urea usage involves little or no fire or explosion hazard.
- Urea's high analysis, 46% N, helps reduce handling, storage and transportation costs over other dry N forms.
- Urea manufacture releases few pollutants to the environment.
- Urea, when properly applied, results in crop yield increases equal to other forms of nitrogen.

Nitrogen inefficiency:

Urea breakdown begins as soon as it is applied to the soil. If the soil is totally dry, no reaction happens. But with the enzyme urease, plus any small amount of soil moisture, urea normally hydrolyzes and converts to ammonia and carbon dioxide. This can occur in 2 to 4 days and happens quicker on high pH soils. Unless it rains, urea must be incorporated during this time to avoid ammonia loss. Losses might be quite low in the spring if the soil temperature is cold. The chemical reaction is as follows:



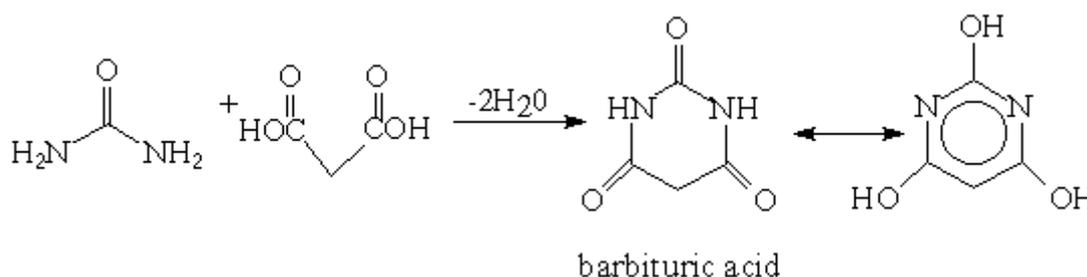
The problem is the NH_3 , because it's a gas, it will get easily lost.

Urea can also be readily nitrified—that is, converted to nitrate (NO_3^-)— and can be quite susceptible to denitrification or leaching.

A right application of urea as fertilizer is of great importance to increase its efficiency and reduce environmental problems. The industry is challenged nowadays to increase the nitrogen efficiency of urea in close co-operation with the farmers.

Pharmaceutical

Urea and malonic acid react to form barbituric acid.

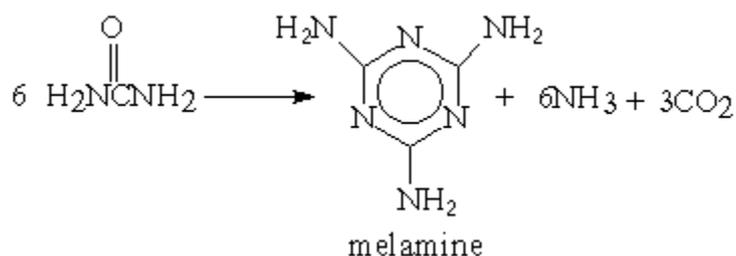


This was discovered by **Adolf Bayer** in 1864. But the barbiturates were not exploited as hypnotics until the early 1900's.

Urea is also used in the production of various acylureas and urethanes for use as sedatives and hypnotics.

Resins

Melamine is formed by the dehydration of urea.



Almost 100 years elapsed between **Liebig's** discovery in 1834 and a commercial process being developed. Melamine is primarily used in the production of melamine-formaldehyde resins which

have much greater hardness and stain resistance than urea-formaldehyde resins. Both melamine-formaldehyde and urea-formaldehyde have very varied uses including adhesives, laminates, moulding compounds, coatings and textile finishes.

Industrial Uses

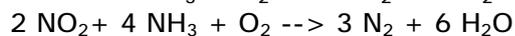
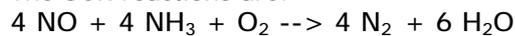
Urea has the ability to form 'loose compounds' with many organic compounds. The organic compounds are held in channels formed by interpenetrating helices comprising of hydrogen bonded urea molecules. This behavior can be used to separate mixtures and has been used in the production of aviation fuel and lubricating oils.

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

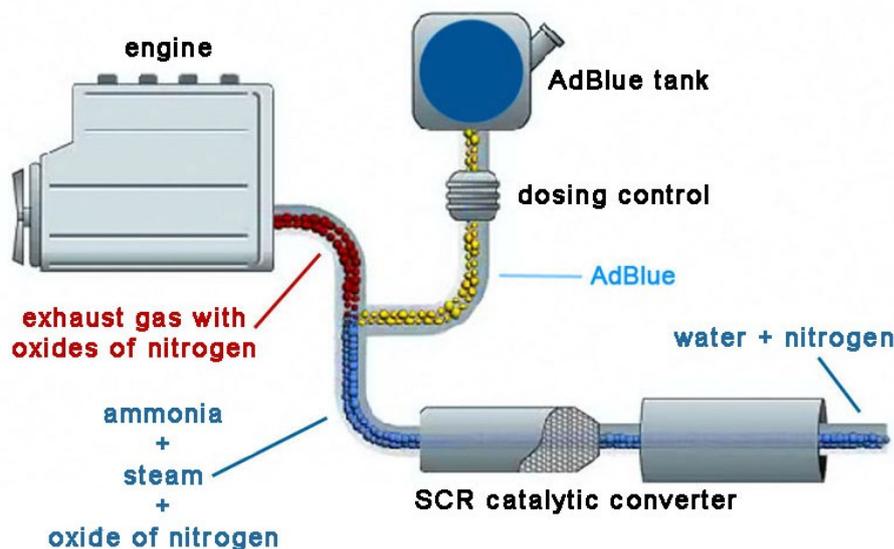
NO_x reduction

AdBlue is the registered trademark for AUS32 (Aqueous Urea Solution 32.5%) and is used in a process called selective catalytic reduction (SCR) to reduce emissions of oxides of nitrogen from the exhaust of diesel vehicles.

The SCR reactions are:



NH₃ is formed according the hydrolysis reaction of urea.



Picture: AdBlue application in automotive industry

As the name AUS32 would suggest, it is a 32.5% solution of high-purity urea in demineralised water that is clear, non-toxic and is safe to handle. However, it can be corrosive for some metals

and must be stored and transported with the correct materials. The AdBlue trademark is currently held by the German Association of the Automobile Industry (VDA), who ensure quality standards are maintained in accordance with DIN 70070 specifications.

AdBlue is carried onboard SCR-equipped trucks and buses in specially designed tanks and is dosed into the SCR system at a rate equivalent to 3-5% of diesel consumption. This low dosing rate ensures long refill periods and minimises the tank's impact on chassis space. On-highway SCR systems are currently in use throughout Europe, in Japan, Australia, Hong Kong, Taiwan, Korea, New Zealand and Singapore.

The United States Environmental Protection Agency's 2010 legislation will limit NOx to levels that will require North American trucks to be equipped with SCR post-2010. The trademark - AdBlue - will not be used in the US market. The current generic name for AUS32 is Diesel Emissions Fluid (DEF).



Picture: AdBlue installation at gasoline station in Norway

Some trucking industry OEM's have already developed branded SCR solutions, such as Daimler's BlueTec. All European truck manufacturers currently offer SCR equipped models, and the future Euro VI emission standard is set to reinforce the demand for this technology. SCR systems are sensitive to potential chemical impurities in the urea solution. Therefore, it is essential to maintain high standards of AdBlue quality and an ISO standard is being prepared to ensure this.

The use of SCR technology in Europe made it necessary to develop an AdBlue supply infrastructure. AdBlue is available in bulk or can be purchased by the litre at service stations.

Further commercial uses:

- A stabilizer in nitrocellulose explosives
- A component of fertilizer and animal feed, providing a relatively cheap source of nitrogen to promote growth
- An alternative to rock salt in the de-icing of roadways and runways; it does not promote metal corrosion to the extent that salt does
- An additive ingredient in cigarettes, designed to enhance flavour
- A browning agent in factory-produced pretzels
- An ingredient in some hair conditioners, facial cleansers, bath oils, and lotions
- A reactant in some ready-to-use cold compresses for first-aid use, due to the endothermic reaction it creates when mixed with water
- A cloud seeding agent, along with salts, to expedite the condensation of water in clouds, producing precipitation
- An ingredient used in the past to separate paraffins, due to the ability of urea to form clathrates (also called host-guest complexes, inclusion compounds, and adducts)



- A flame-proofing agent (commonly used in dry chemical fire extinguishers as Urea-potassium bicarbonate)
- An ingredient in many tooth whitening products
- A cream to soften the skin, especially cracked skin on the bottom of one's feet
- An ingredient in dish soap
- Along with Ammonium Phosphate, as a Yeast Nutrient, for fermentation of sugars into ethanol
- To make potassium cyanate
- A melt agent used in re-surfacing snowboarding halfpipes and terrain park features
- Laboratory use: Urea is a powerful protein denaturant. This property can be exploited to increase the solubility of some proteins
- Medical use: Urea is used in topical dermatological products to promote rehydration of the skin. If covered by an occlusive dressing, 40% urea preparations may also be used for nonsurgical debridement of nails. This drug is also used as an earwax removal aid. Like saline, urea injection is used to perform abortions. It is also the main component of an alternative medicinal treatment referred to as urine therapy
- Clinical diagnosis: blood urea nitrogen - 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
- Other diagnostic use: Isotopically-labeled urea (carbon-14 - radioactive, or carbon-13 - stable isotope) 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
- Textile use: Urea in textile laboratories are frequently used both in dyeing and printing as an important auxiliary, which provides solubility to the bath and retains some moisture required for the dyeing or printing process
- Ionic liquid: Choline chloride, in mixture with urea, is used as a deep eutectic solvent, a type of ionic liquid

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US patent 1,429,483

The Development of Modern Chemistry by Aaron John Ihde

Wikipedia

Mark Brouwer was born on July 6, 1966 in Groningen, The Netherlands. He graduated in 1988 at the Technical University of Eindhoven at the faculty of Chemical Engineering. His thesis was about the production of ethylene by partial oxidation of natural gas.

After University Mark joined Military Services, Dutch Royal Navy where he was working at the Prins Maurits Laboratory of TNO in Rijswijk. In this period he was involved in Process simulation studies on the absorption of poisonous gasses on active carbon.

In 1990 he joined DSM, working for the Ethylene Plant No.4 as a Process Engineer. In these seven years he was involved in the Basic Engineering of a debottlenecking project at Stone & Webster in London and in the implementation of the DSM Extraction Styrene project (from Conceptual Engineering upto the successful start up) .

In 1997 he joined Stamicarbon, the Licensing subsidiary of DSM as Licensing Manager Urea Revamps. Later he became Manager Stamicarbon Services responsible for all Stamicarbon's activities in existing urea plants, such as After Sales, Plant Inspections, Debottlenecking Projects, Reselling projects etc. In these nearly twelve years he did visit nearly one hundred urea plants worldwide and was involved in numerous revamp, relocation, debottlenecking and grass root projects.

End of 2008, Mark started up his own business: UreaKnowHow.com, the website where the urea industry meets.

