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Urea as a Hydrogen Carrier: A Perspective on its Potential for Safe, Sustainable and Long-term Energy Supply

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Abstract

Recently, there have been publications reporting the use of urea, as a source of hydrogen/fuel cell power. There have however been no reports that singularly assess the suitability of urea for this purpose. This article provides not only a perspective on the attributes of urea ($(NH_2)_2CO$) as a hydrogen carrier for fuel cells but also presents the findings of a review on the feasibility of utilising the enormous natural resource of urea that exists. Urea is a cheap and widely available commodity with well developed manufacturing infrastructure and a rapidly increasing volume of production. This offers rapid implementation of urea for application as a hydrogen carrier either directly or as a source of ammonia. Compared with other industrial chemicals previously considered, urea has the advantages of being non-toxic, stable, and therefore easy to transport and store. This report reveals that the natural resource of urea could be a solution to long-term future sustainable hydrogen supply and that the present status of scientific knowledge necessary to extract this natural resource is in the most part understood. It is considered realistic that these sustainable routes could be exploited if they are given sufficient focus of research attention.

1. Introduction

Alternatives to fossil fuels are required; to meet the global energy demand and to supply power for the basic service needs of poorer communities. For remote regions, this is likely to require energy creation close to the point of use due to the absence of a supply infrastructure.

Hydrogen powered fuel cells are identified as one attractive option as they offer the potential to be a reliable, mobile, non-polluting technology using an abundant and almost infinite resource. Present obstacles to the large scale application of hydrogen fuel cells include issues with the fuel, namely hydrogen production, storage, and transportation. These technological challenges associated with hydrogen containment and on-site production make its direct use prohibitive.[1] Numerous substances have been considered as suitable hydrogen carriers and though the synthesis and characterisation of many materials has been made, all so far considered have exhibited inherent problems.

Simple industrial chemicals are one promising group of energy vectors because they are generally cheap to produce and have the benefit of some form of established technological infrastructure for manufacture, storage and distribution. Hydrogen can be released from them by a number of well developed chemical techniques, usually requiring the control of pH and catalysts.[2]

This year we reported for the first time, experimental results on the steam reforming of urea[3] where we showed that a simple hydrogen rich synthesis gas could be produced using industrial nickel catalyst. A novel approach to produce hydrogen from the wastewater of a urea production plant was also reported in 2010. This modelled the feasibility of system design, also using a nickel-alumina catalyst bed.[4] In 2009 a study reported that hydrogen could also be produced from urea by electrolysis, using aqueous urea solutions replicating those found in urine.[5] Also in 2010, a direct urea fuel cell was reported[6] with the assertion that it is possible to develop urine fuel cells. Urea is therefore being considered as promising for both indirect hydrogen storage and for direct fuel cell supply, yet there is an absence of any single source of discussion on its merits. Present knowledge is found in many disparate areas of science and it is therefore with the aim of assessing the potential of urea as a future sustainable hydrogen vector energy source that this perspective review is made.

2. History and Properties

Urea ($(NH_2)_2CO$) is a non-flammable, relatively non-toxic, colourless, anisotropic and birefringent crystalline substance that is perhaps best known for its presence in urine. It was first isolated some time before 1727 by Herman Boerhaave though many texts mistakenly attribute the discovery to H.M.Rouelle in 1773.[7] In 1798-1799 urea was first obtained in crystalline form by Fourcroy and Vauquelin and ultimately synthesised from inorganic reagents in 1828 by F. Wöhler while heating what is now known to be its isomer: ammonium cyanate (NH_4^+ CNO^-). This had historical significance for it began the eventual demise of the theory of vitalism among scientists, showing that 'life process' chemicals were not distinct from other substances, as had previously been thought. Many textbooks define this discovery as marking the foundation of modern organic chemistry. Accessible accounts of Wöhler's work and its implications in a historical context are provided by Werner[8] and more recently Cohen.[9]

The reaction mechanics of Wöhler's synthesis, namely how the salt ammonium cyanate transforms into urea, are still not fully understood despite efforts being made by numerous researchers over the last century. This search described thirty years ago as 'a saga in reaction mechanisms'[10] continues to be appropriate today, as recent studies focused on ammonium cyanate had to be reassessed by the same research group five years later.[11,12] Work is apparently still in progress, with the theory now that solid state transfer to urea occurs by a proton (H^+) jump from ammonium (NH_4^+) to cyanate (NCO^-) along one of the salt's hydrogen bonds, followed by ammonia's nucleophilic attack on the carbon atom of hydrogen cyanate.[12]

Aside from this present uncertainty, methods of urea synthesis have been identified and applied both in the laboratory and in industry such that urea is now a widely used commodity. Because of this, its physical properties are known and available in standard literature (**Table 1**).

Table 1. Physical data of urea[13]

Property	Value
Molecular formula	$(NH_2)_2CO$
Synonyms	Carbamide, carbonyldiamide, isourea, B-I-K
Relative Molecular Mass (M_r)	60.06g/mol
Freezing/melting point	133°C
Boiling point	N/A (decomposes)
Density	$1.32 g/cm^3$
Flash point	Non-flammable

Urea is stable at room temperature and atmospheric pressure. In pure form it is crystalline in habit, though is easily shaped into granules and prills.[13] This fact, combined with its stability and non-flammability give urea favourability as a hydrogen carrier substance offering the potential for it to be easily transported and stored. Urea is however, hydrophilic and hygroscopic, being also soluble in alcohol, glycerol, and ammonia. This would necessitate dry containment for hydrogen supply applications.

3. Occurrence

Urea is produced synthetically on a commercial scale and is also naturally abundant as an in-vivo product of protein catabolism, where, due to its high solubility, it is present in bodily fluids and excreted in urine by mammals and all other animals except birds and saurian reptiles.[14,15,16,17] In mammals, urea is concentrated in the kidney prior to excretion as a means of water conservation; while those animals that do not have a kidney that can concentrate urine in this way excrete waste forms such as uric acid and allantoin. These nitrogenous wastes and other nucleic acids such as purines.[18] when acted on by micro-organisms and enzymes inside the body of higher animals degrade to urea thereby providing a further route to synthesis.

Plants are also found to contain urea, although the mechanisms of accumulation and transport are not fully understood. It is believed to be used as a nitrogen store, present through a combination of acquisition from the environment and by way of internal synthesis.[19]

An illustration of the potentially available global urea resource is given in **Figure 1**. The resource from human urine is in excess of 500 times the projected market demand (see **Section 5**), with the technology required to access it presently applied in other areas of science (see **Section 8**).

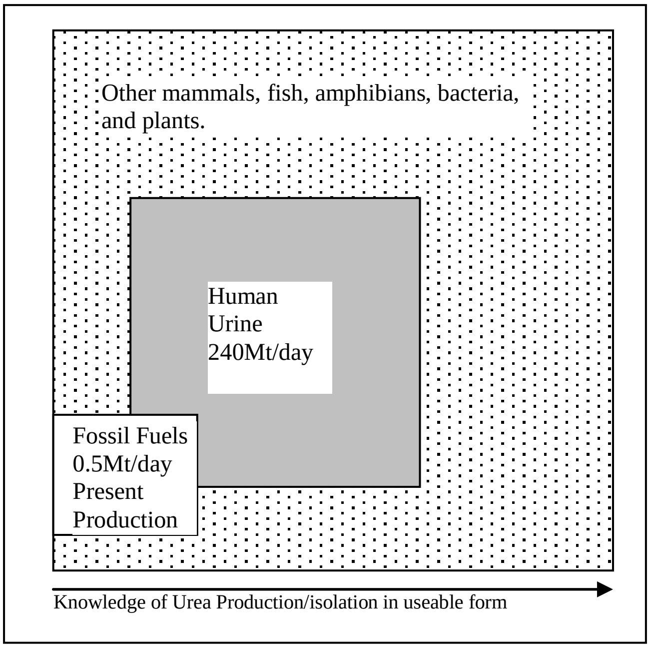

Figure 1. Urea resource produced per day in million of tonnes. Human urine resource estimated from average daily production of 35g multiplied by world population of 6.8 billion.

4. Urea in Comparison with Other Chemical Hydrogen Carriers

Urea has a gravimetric hydrogen content of 6.71 wt%, fulfilling present DOE targets for hydrogen storage in transport applications.[20] With the additional molecule of H_2 available when water is included from steam reforming the value becomes 7.95 wt% of stoichiometric urea-water solution, or 10.07 wt% of urea.[3] Table 2 shows a comparison between urea and previously considered hydrogen carrier chemicals. High flammability and toxicity are common to all, though it can be seen that urea does not share these associated disadvantages. Some, such as methanol, are cumulative poisons at low concentrations over long periods as might be encountered if utilised as a hydrogen carrier in small-scale and/or mobile fuel cells. Others, such as cyclohexane have reagents that are carcinogenic (benzene) or as with ethanol and methanol, generate high greenhouse gas emissions upon dehydrogenation.[21,22] These alcohols can be produced in small quantities sustainably from carbon-neutral bioresources and are best used as alternatives to petroleum for engine fuels where their benefits in reducing carbon emissions are proven.[2] Additionally there are concerns about the ethics of biomass for energy in general caused by deforestation and replacement of arable land to grow energy crops.[23]

Urea's stability at atmospheric pressure and temperature along with its lightweight and stable crystalline form make it easy to store and transport. Long-term human exposure studies have also indicated that it is non-allergenic and virtually free of side effects.[24] Toxicity studies have indicated that only with levels above several thousand mg/litre may it become toxic to mammals and birds, with low levels of ingestion permissible without ill effect.[24,25]

Urea is biodegradable and classified as having "no indication of concern for human health or the environment".[24] There has been some work attempting to assess the environmental fate of urea as an argument against using it as a method of atmospheric CO_2 sequestration and in the main as a potential cause for concern about its escalating agricultural use.[26] Causal links with anthropogenic sourced urea driving any ecosystem change have yet to be established however, with many other factors acknowledged as affecting algal bloom dynamics.[26] Where in-situ studies of urea influx on coastal waters and shorelines have been performed, results refute suggestions of harmful environmental disturbance.[27,28] Furthermore, when distribution of urea in coastal waters was examined, no evidence was found of land-derived urea being an important contributor to oceanic urea content, with the major source likely to be from in-situ production.[29]

One toxicity link with urea appears to be its decomposition to ammonia, enzymatically at room temperature or when heated:[30]

$$(NH_2)_2CO + H_2O \longrightarrow CO_2 + 2NH_3 \qquad \text{(R1).}$$

Spontaneous decomposition is possible but with half-life times, estimated to be from 40 years at 25°C for elimination, to ~ 10^{19} years for non-enzymatical hydrolysis.[31] This knowledge gives a measure of the proficiency of the urease catalyst.

Via the enzymatic route this can be controlled easily with numerous reversible and irreversible methods of urease inhibition. Microbial urease inhibitors are known along with a number of chemical elements and compounds[32].

Table 2 Comparison of physical properties, hydrogen content, toxicity and safety aspects of hydrogen carriers[33]

Substance	H_2 (wt %)	Safety Classifications[34]	Toxicity TLV	Flammability in air	Melting Point	Boiling Point
Ammonia (NH_3)	17.0	T,N,C	25ppm as TWA 35ppm as STEL	Auto-ignition temp 651°C. Explosive limits 15-28% vol%	-78°C	-33°C
Cyclohexane (C_6H_{12})	7.2	F, N, Xn	100ppm as TWA	Auto-ignition temp 260°C Explosive Limits 1.3-8.4 vol%	7°C	81°C
Ethanol (C_2H_5OH)	13.1	F	1000ppm as TWA	Auto-ignition temp 363°C Explosive limits 3.3-19 vol%	-117°C	79°C
Hydrazine (N_2H_4)	11.2	T,N,E,Carc,C	0.01ppm	Auto-ignition temp 24-100°C Explosive limits 1.8-100 vol%	2°C	114°C
Hydrogen (H_2)	N/A	F+	simple asphyxiant	Auto-ignition temp 500-571°C Explosive limits 4-76 vol%	N/A	-253°C
Methanol (CH_3OH)	12.6	F,T	200ppm as TWA 250ppm as STEL	Auto-ignition temp 464°C Explosive limits 5.5-44 vol%	-98°C	65°C
Methylcyclo-hexane (C_7H_{14})	6.2	F	400ppm	Auto-ignition temp 258°C Explosive limits 1.2-6.7 vol%	-126.7°C	101°C
Urea $(NH_2)_2CO$	6.7[b]	None	None established	Non-flammable	Crystalline solid. Decomposes at 133°C	

T = toxic, F = flammable, F+ = extremely flammable, N = dangerous for the environment, Xn = harmful, E = explosive; C = corrosive, Carc = carcinogen; TLV = threshold limit value, TWA = time weighted average (8h/day 40h/week), STEL = short term exposure limit (15 minutes); [b] 7.95wt % in aqueous solution;

Evolution of ammonia could be considered a highly favourable attribute since ammonia is very attractive as an energy vector either supplied directly into alkaline and solid oxide fuel cells[35,36] or as an irreversible hydrogen carrier, yielding hydrogen and inert nitrogen upon dissociation. Dissociation of ammonia, known as “cracking” or “splitting” has advantages over hydrocarbon reformation because the dynamics are fast and the reaction occurs in one single step without the need for oxygen or steam, making the process requirements simpler and relatively cheap:[37]

$$NH_3 \rightarrow 1/2N_2 + 3/2H_2 \qquad \Delta H^{\circ}_{298} = +\ 46\ \mathrm{kJ\ mol^{-1}} \qquad \text{(R2)}$$

Because the reaction kinetics and favourable energy requirements in comparison with methane reforming are advantageous for on-site supply, recent attempts have been made to bypass the toxicity of ammonia by storing it in the inert form of a metal ammine chloride.[38,39] It has not so far been acknowledged that urea is a naturally stable alternative. For utilisation of urea as an ammonia carrier, manipulation of urease may be required.

5. Production Status and Trends

Demand for urea is high with an increase of 3.8% per annum anticipated, giving an annual total demand of 174.6Mt by 2014.[40] Production plant capacity is expected to grow by 51.3Mt or 30% from 2009 levels to an estimated global production of 222Mt by 2014.[40] 55 new production plants are expected to open, with the major regions of production being Asia, Latin America and Africa. Due to the expansion in global production the supply/demand balance shows an anticipated rise in surplus from 3Mt/a in 2010 to 10Mt/a in 2014.[40]

Urea's main commercial application is as a slow release fertilizer. In the 1960s, urea represented 5% of global fertilizer consumption which had increased to ca.40% by the early 1990s[41] and is now estimated at >50%.[42]

Urea is now the primary means of NOx abatement in > 2.0 litre diesel engines where it is employed as a selective catalytic reductant.[43] Usually this involves an aqueous solution of the eutectic mixture at 11°C and 32.5wt%.[25] The values quoted for urea product growth are inclusive of non-fertilizer product applications. Non-fertilizer demand is anticipated to account for 13% of the total usage by 2014. New uses for urea are increasing and some present applications are shown in **Table 3**. These new markets, plus the potential for urea as a hydrogen carrier could provide the lever for future sustainable urea production.

Table 3. Present applications of urea

Use	Description
Slow-release fertiliser	Main commercial outlet. 85-90% of commercial application.[42] Agricultural grade flakes or prills.
Explosives additive	A propellant stabilizer in nitro-cellulose explosives.[44]
Reagent in catalytic reactions to reduce oxides of nitrogen.	Urea reacts with NO_x and is utilised for the catalytic and non-catalytic reduction of combustion gases to mitigate pollutant emissions.[25]
Pharmaceuticals/Medicine	Used to make emollient creams for treatment of dry skin due to its water-binding capacity and softening effects on the epidermis.[45,46] It is also used to detect the presence of pathogenic bacteria in the stomach.[47]
Animal feed additive	As an inclusion in cattle feed to aid the assimilation of proteins.[48]
Material in glue manufacture	Urea-formaldehyde and urea-melamine-formaldehyde (waterproof glue for marine plywood).[49]
De-icer	Urea is a non-corrosive alternative to sodium chloride as a de-icer.[50]
Cosmetics ingredient	In antiperspirants, a preservative in water-based soaps, and in moisturisers and skin creams.[51]
Cloud seeding agent	Due to its hygroscopic, non-toxic and non-corrosive properties.[52]
Petroleum processing	Urea has the ability to form clathrates and occlude hydrocarbons; used in petroleum refining to produce jet aviation fuel and for de-waxing of lubricant oils.[13]
A flame-proofing agent in dry fire extinguishers	Urea-K bicarbonate is a dry powder extinguisher for flammable liquids, ordinary combustibles, and electrical fires.[53]
Ingredient in dental products	Carbamide peroxide for bleaching.[54] Urea also has pH-elevation properties that make it effective at neutralising acidic plaque.[55]
Food additive	Formulation of alcoholic beverages, and gelatine.[56]
Dispersion and degradation of hydrocarbon oil spills	Stimulates the growth of bacteria which break-up the oil.[27,28,57]

6. Economics of Present Production

Present commercial urea production is energy intensive and its economic cost is linked to the price of its feedstock Natural Gas. Any consideration of environmental and economic factors must also include creation of the raw materials ammonia and carbon dioxide. Ammonia production is estimated to contribute ca.80% of the total manufacture cost for present urea production.[25] Transport costs are taken as nil since ammonia plants are sited adjacent to urea production. Current values of technical grade urea in the quarter up to April 2010 were €160 - €214/tonne.[58]

7. Environmental Aspects of Present Production

Due to stringent safety emissions legislation and the high commodity cost, direct losses of urea and ammonia to the environment from industrial production is relatively small.[59] The synthesis section of a modern urea plant will create wastewater in a ratio of 0.3:1 for every unit of urea produced.[42] On the level of present production plants creating 2000 tonnes urea/day, these large amounts of water must be treated to comply with local legislation and to moderate adverse environmental impact. Urea process water treatment systems therefore are able to reduce the effluent by desorption, distillation and stripping to create effluent NH_3 and urea concentrations of 5mg/litre and 1mg/litre respectively.[42]

Gaseous emissions for a urea processing plant are estimated to be CO_2 (746,797g), CH_4 (6,428g) and N_2O (10g), per tonne of urea produced.[25] These values include total production costs for natural gas processing and electricity consumption.

Airborne particulate emissions from urea production plants are potentially high because prilling generates very fine dust which is technically difficult and expensive to mitigate. Granulation dust emission is considerably higher at 5-40kg/tonne urea produced,[42] but its larger particle size decreases its health risk and increases its ease of abatement. Wet scrubbing is identified as the optimum particulate abatement method and efficiencies of 98% can be achieved.[42] Emissions of this kind (though effectively abated) are related to process shaping requirements for agricultural fertilizer products and so should not be relevant in the context of reagent purity grade used for application to a potential hydrogen economy. Where airborne urea particles are released, a half-life of less than a day is expected due to photochemical reaction with hydroxyl radicals resulting in ammonia and carbon dioxide.[25]

8. Alternative/Sustainable Routes of Urea Production

It has been described that urea is manufactured at present cheaply using fossil fuels, so attractively enabling rapid implementation for hydrogen supply infrastructure. As this does not offer long-term supply security and is environmentally damaging, this section identifies and assesses potentially sustainable production routes. These would also detach production from the need for adjacency to hydrocarbon reserves allowing global energy independence. Furthermore it would reduce overall processing as presently hydrogen has to be created and then re-formed into urea to be re-formed back to hydrogen again.

8.1 Urea from Urine

Large quantities of urea are produced to fertilise land for food production, yet at the same time, the natural quantities of urea produced by catabolism in urban areas, are flushed away through wastewater sewage systems; a process which then involves the additional expense of energy intensive methods of removing nitrates that would otherwise have completed a closed nitrogen cycle by being utilized in plant metabolism. The mammalian catabolic route of urea synthesis is both abundant and well understood yet there is little written about the scope for exploiting this natural route and obtaining urea from urine.

Medical texts quote that urea is excreted (quantified and termed as urea “clearance”) in urine at a rate of approximately 33-35g/day in a healthy adult, dependent on diet - with concentration increasing with increasing dietary protein intake.[60] For an estimated average adult, the urine excretion rate is 1.5litres/day[61] giving an approximate concentration of urea as 22-23g/litre. It can be assumed however that these values based on medical estimates will differ outside of the clinical environment due to dilution and contamination with other elements when mixed with flushing water in a modern sanitary system.[62] Of more importance is the fact that urea decomposes quickly outside of the non-sterile environment due to the ubiquitous presence of enzymatic micro-organisms. A study in 2003 identified that urine in a collection tank would be completely hydrolysed within little more than a day, and for a supply pipe completely filled with urine, ureolysis would be completed in about two minutes.[63]

Before attempts can be made to stabilize urine and extract urea, the urine must first be separated from faeces and any other components presently disposed of in wastewater. Separation will be easier if urine is not well mixed with other contaminants, and due to the extended residence times in wastewater, providing adequate mixing with urease containing bacteria, end of pipe treatments for urea collection would appear to be too challenging. Similarly, the collection, and preservation of urea from animal wastes would pose identical difficulties through mixing with other contaminants. A patent from 2005 however cites as one aspect of its invention the proposal of separating urine from livestock waste into a urea-rich fraction having the potential to be a saleable commodity.[64] The methodology of this patent is not detailed but involves the use of urease inhibitors to stop ureolysis and subsequent decomposition.

Urease inhibitors are not a new discovery. Several microbial urease inhibitors are known along with a number of chemical elements and compounds.[32] These microbes are widespread, and the high concentration of carbon in urine also accentuates their growth.[61]

Biological catalytic decomposition of a urea solution occurs at an optimum neutral pH but causes it to rise to 9.5 at which point ammonia evaporates from the mixture.[61] It is known that below pH 5 microbial urease is denatured.[63] The acidification of urine is therefore the major research method of urease inhibition. In tests, the addition of sulphuric or acetic acid could inhibit urea decomposition for over 100 days.[65]

Studies into the separation and stabilization of urine come mainly from the perspective of wastewater treatment. Most of this is driven by environmental concerns with the focus on sustainability, reducing waste, and mitigating nitrate build up in watercourses. There is also a focus on the possibility of utilizing nutrient components of separated urine for fertilizer applications, but not specifically urea. The preservation of pure urea is occasionally mentioned, but then only as a minor aspect and consequence of the main study.

Modern attempts at urine separation and stabilisation have yet to go beyond the research and development stage. Source separation “no-mix” toilets have been created and tested. In one project application the results were disappointing, with dilution and contamination of the urine occurring. This was attributed to a combination of inadequate system design and construction, plus inappropriate usage.[66]

In space station environments, urine can be acidified to inhibit urease activity then subjected to distillation and filtration.[67] Again this research was with the objective of volume reduction and hygienation rather than the isolation and extraction of urea. One recent study revealed that as a consequence of attempting to separate pharmaceutical pollutants from urine by the use of a nanomembrane, urea was found to permeate on the membrane in relatively high yields.[68]

The potential to extract urea in sufficient quantity from mammalian waste to offset some of the present commercial stock therefore seems a long way from reality. The resource is available, and the chemistry is in the most part understood, but it seems that not enough work is being done at present to adapt technology that is fit for purpose, and the required paradigm shift in modern waste removal seems to be too dramatic a step. A summary of these findings are illustrated in **Figure 2**. Drivers for change such as increasing prices of fossil fuels, depletion of resources, and uncertainty of supply, coupled with concerns about environmental damage caused by additions to the nitrogen budget, are however becoming increasingly prominent. If urea was shown to be a promising hydrogen carrier then this would undoubtedly generate interest in combining this knowledge to tap the huge waste resource.

Process Stage	1.Source Separation	→	2.Urease Inhibition	→	3.Urea Concentration
Solution	No-mix toilets for humans	→	Chemical, Microbial and Temperature	→	Solar, wind and battery/grid electrical
Status	Simple Technology Product Designed Product Implemented	→	Simple technology Currently applied in laboratories	→	Electrical heaters are a mature technology. Solar concentrators not known as being applied in this situation
Obstacles	Paradigm shift in waste disposal required.	→	Would need incorporating into no-mix toilet design due to rapid enzymatic decomposition of urea	→	Prolongs process stages.
Further Observations	Considerably greater resource from animals and plants. Animal sourced urea more challenging to separate. Absence of adequate knowledge on urea content in plants.	→	May require further sterilisation for safe handling to remove potential pathogens.	→	Solar concentrators, combined with urea's ease of transportation and storage make this combination highly attractive for remote applications.

Figure 2. Status of technology and process stages necessary for utilising the urea produced by animals and plants in preparation for steam reforming.

8.2 Urea from Bacteria

Arginine is a ubiquitous amino acid, found in most organisms, throughout all biological kingdoms.[69] Those that also contain the arginase enzyme are able to synthesise urea.

In ureotelic organisms (mainly mammals and marine fish) urea is created *in vivo* by the catalytic hydrolysis of the amino acid arginine in the presence of the enzyme arginase. This mechanism is part of the ornithine-urea cycle (or Krebs-Heinslet Cycle) which involves four other enzymes along with the intermediate amino acids citrulline and aspartate.[70] Arginase is the key enzyme in the stage of the cycle that creates urea.[69] Bacteria are able to catabolise arginine[71] and it has been shown that urea can also be created *in-vitro* using the arginase enzyme.[72] It therefore follows that if a cost effective and abundant source of arginine could be found then an alternative route of urea production is theoretically achievable (see **Figure 3**).

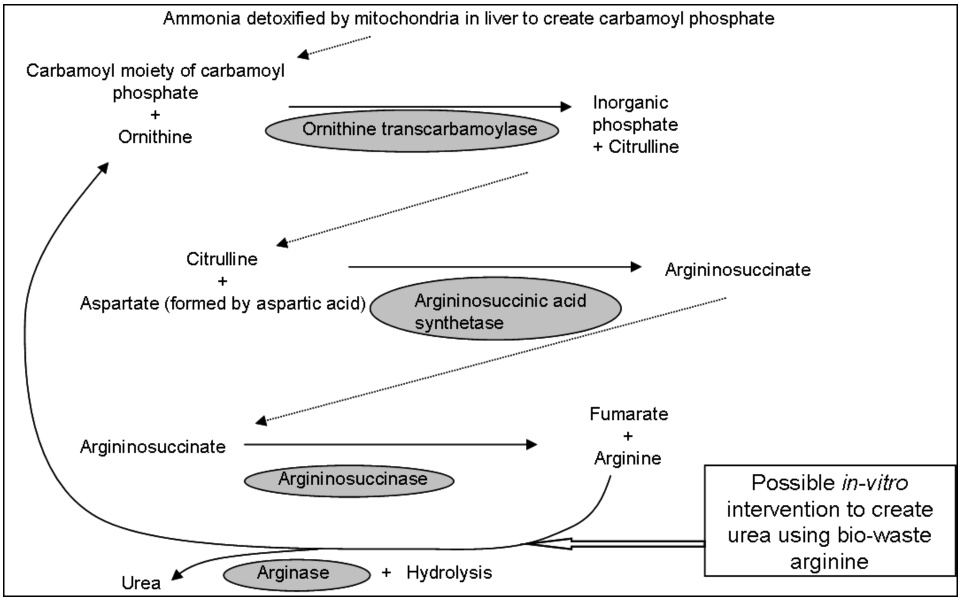

Figure 3. Ornithine-urea cycle in ureotelic organisms showing possible in-vitro mechanism for urea production.

One naturally-occurring source of arginine is in cyanophycin (Cyanophycin Granule polypeptide: CGP). Cyanophycin is an organic granule that is synthesised in and used as an energy store by cyanobacteria[73,74] and some heterotrophic bacteria[75] at relatively low temperature and light intensity. The cyanophycin synthelase enzyme has also been isolated and inserted into genetically modified recombinant bacteria. These have subsequently been tested on different ferment media[76] A patent was submitted by Elbahloul et al.[77] to make use of this micriobial synthesis using bio-refinery waste streams as a substrate for fermentation.

Biomass has ecological advantages since the CO_2 released by combustion is only that which the plant has captured during its lifetime. Theoretically therefore Biomass is “carbon-neutral”, and does not add to the atmosphere in the same way as fossil fuels. Moreover, there is presently a large volume of protein-rich waste streams that are generated with biofuel production and in established bio-refineries such as starch fractionation from wheat, sugar and potatoes and oil, proteins and nutraceuticals from soyabeans.[78,79] These amino-acid wastes have financial advantages since their calorific values are reportedly comparable with presently used petrochemical feedstocks, and furthermore they have in-built chemical functionality that could allow the circumvention of some or all of the process stages.[79] Using biomass in this way could be a more efficient use of inherent chemistry than for the production of power which is biomass’ present commodity outlet. Biological fermentation is one possible route of isolating these functional compounds for utilisation.

In Elbahloul’s study,[76] a 28wt% yield of cyanophycin was produced per dry cell matter within 24 hours using a potato starch waste stream of which an estimated 22,000 tonnes of amino acid are created every year. Present knowledge gaps occur on how to extract urea in useable form from bio-fuel ferment CGP, and also with the optimisation of substrate media and conditions. One interesting result from the study by Elbahoul et al. was that the ferment apparently synthesised CGP from amino acids other than arginine. This, and the opportunity to isolate other synthetase enzymes for insertion into genetically modified bacteria, is an area that requires further examination.

A study in 1984 also found that urea could be synthesised from arginine using inorganic montmorillonite clay particles as a shape selective catalyst.[80] This result does not appear to have been pursued since then.

9. Conclusions

Urea possesses many favourable attributes as a fuel cell energy vector to justify further study on its use for hydrogen supply and to fill the need of future global energy requirements. Compared with present hydrogen carrier chemicals, urea is stable, non-toxic and in most circumstances can be described as environmentally benign. The only controls required for adequate storage would be dry containment. A sealed container would be more than enough to store urea for a long time. Like the other simple chemical hydrogen vectors, urea is a well known and understood compound. A benefit of having half a century of commercial urea production means that there is a good understanding of knowledge to draw upon for working with urea as a process chemical. The transferability of this knowledge is definitely a boon.

Urea can be used as a direct fuel for fuel cells, and as a means of supplying both ammonia and hydrogen. Extra energy/process stages may be required for non-direct supply to fuel cells though dehydrogenation can occur naturally. Many of the advantageous aspects of the recently developed metal ammine storage tablets could also be said of urea as urea is a stable and dense ammonia/hydrogen carrier. In comparison, pure urea has a lower hydrogen weight percentage (6.7 wt%) but this value increases to 7.7wt% when steam reforming is considered.

Urea is a cheap and readily available substance. The resource of urea is high, with production increasing and an annual surplus expected for the near future based on fossil fuel synthesis. Present manufacture of urea releases quite high greenhouse gas emissions which is not sustainable. Also, with this manufacturing process, as with many other hydrogen carrier options, hydrogen is a reagent in the synthesis reaction meaning it is extracted from other substances to be made into urea to be released again. To overcome this problem, urea does have many varied natural production routes that have been combined and discussed in this review for the first time in the context of using them as an alternative source of urea for energy. Based on this initial assessment, it is considered realistic that these routes could be exploited if they are given sufficient focus of research attention.

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