The present invention is concerned with a method of generating energy from water and a composition comprising cyanoguanidine, the method comprising (a) reacting the composition with water to form ammonia and (b) oxidizing the ammonia formed in step (a) to form water and nitrogen thereby generating energy or (b') converting the ammonia formed in step (a) into nitrogen and hydrogen; and oxidising the said hydrogen to form water thereby generating energy. Thus, cyanoguanidine may be used as a transportation fuel (e.g. for cars, trucks and marine vehicles). Particularly effective conversion of cyanoguanidine to ammonia can be achieved when step (a) occurs in the presence of a catalyst comprising vanadium and zinc, particularly when the vanadium is vanadium pentoxide and the zinc is metallic zinc. The ammonia can be combusted in a internal combustion engine or an external combustion engine. The ammonia can also be oxidised in an ammonia fuel cell.
PRODUCTION AND USE OF CYANOGLUANIDINE AND CYANAMIDE

FIELD OF THE INVENTION

5 The present invention is concerned with novel methods of producing cyanoguanidine, which
is also known as dicyandiamide, and cyanamide. The present application is also concerned
with the use of cyanoguanidine and cyanamide as a fuel.

The present application also relates to a cyanamide-based composition, a method for
generating energy from a cyanamide-based composition, and a method for producing the
cyamide-based composition.

The present application also discloses methods and systems for production of calcium
cyanamide, hydrogen cyanamide, carbon monoxide, metal oxides, natural gas scrubbing,
coal scrubbing, and/or other products from rotary or plasma arc production of
cyanoamidine, also called dicyandiamide. The present application also discloses the
synthesis of a cyanamide-based composition using continuous and/or intermittent energy
sources when generating energy near sources of stranded natural gas or coal for reason to
synthesize a cyanamide-based composition. Furthermore, the present application also
discloses a method for producing the cyanamide-based composition, preferably
cyanoamidine, from "sour" natural gas or "polluted" coal.

BACKGROUND

25 Fossil fuels constitute the largest source of energy supply in the world. Their availability in
large quantities, high energy density, and relatively low cost makes fossil fuels the fuel of
choice for many applications for both industries and consumers. Nonetheless, an alternative
to fossil fuels as an energy source is highly desirable for safety reasons, for environmental
reasons, and to reduce the dependence of the industrialized world on oil imported from
relatively few oil-producing countries. In spite of these compelling arguments in favor of new
energy sources, no economical, safe and readily available fuel has been found to be a
viable alternative for fossil fuels, especially in automotive and portable power applications,
even though extensive research has been aimed at developing a fuel having the many
positive characteristics of gasoline without its drawbacks.

35 A new, alternative fuel should fulfill several requirements. The cost of the fuel should be
competitive with the cost of current energy sources. The fuel should have no undesirable
emissions. It should have a high energy density, as gasoline does, to avoid the need for
frequent refilling. The fuel should be easy to handle safely. Preferably, it should be non-
explosive and of low toxicity. Finally, it should be available through a distribution
infrastructure that can be readily expanded. There is therefore a need in the art for a fuel
having all of the above characteristics.
Current efforts directed to new fuels have not provided a fuel that is cost effective compared to gasoline. Furthermore, the effectiveness of any of the proposed alternatives as a source of energy appears problematic. For example, although hydrogen may be obtained from fossil or non-fossil sources, problems related to handling during transportation and to storage make hydrogen a poor choice for a consumer-oriented fuel. Other fuels, such as methanol, are toxic and flammable and still require a certain amount of fossil fuel, in the form of either natural gas or carbon monoxide, to be economically produced. Sources of hydrogen such as chemical hydrides, while easy and effective to use, require a recycle loop if it is desired to re-utilize the hydrides, as discussed in U.S. Pat. Nos. 5,804,329 and 6,534,033.

Del Duca (U.S. Pat. 3,403,053) first disclosed, in a table in that patent, the use of the "organic reactant" urea to yield the "fuel" ammonia that then participates in a reaction with oxygen to yield energy. Amendola (U.S. Pat. 7140187) proposed methods for production of the fuels ammonia and hydrogen from compositions containing urea. Amendola used the term "urea" to denote any one of the components of commercial urea, including urea, \( \text{NH}_2\text{CONH}_2 \), ammonium carbamate, ammonium carbonate, ammonium bicarbonate, ammonium formate, ammonium acetate, or a mixture of two or more of these components. Urea as a carrier of energy is limited in application by the safety issue of the decomposition of urea into ammonia and isocyanic acid when exposed to temperatures at or near the melting point of 133°C.

The problem encountered with urea compositions can be avoided by the use of other energy carriers that can react with water to form ammonia.

Graupner et al (WO2005/108289) proposed the use of guanidine (CH5N3) as an alternative fuel. Guanidine has also been proposed by Graupner et al (WO2008/15662) as a source for generating ammonia and hydrogen which in turn may drive a solid oxide fuel cell. A further proposal by Graupner et al (US2008/0307794) relates to the use of guanidine in a controlled water/ethanol composition to generate ammonia and carbon dioxide which is then delivered to a combustion chamber for combustion.

In a related proposal, Hultine et al (WO2009/056888) describe the manufacture of urea with ammonia obtained from reaction of nitrogen and hydrogen from electrolysis of aqueous metal chloride solution. A subsequent step of reacting the urea with ammonia produces guanidine.

Cyanoguanidine is a dimer of cyanamide, from which it can be prepared. Dicyanamide is used as a fertilizer and has also been used in the chemical industry, for example in paper and textile manufacturing, and in adhesives. Whilst it has low toxicity, the build-up of dicyanamide in the environment is to be avoided. Guethner (DE19707692A) proposed a method for the removal or decomposition of dicyanamide in solution.
SUMMARY OF THE INVENTION

The present inventors have found that the feasibility of guanidine as an alternative fuel is difficult.

The present inventors have found that, surprisingly, cyanoguanidine and cyanamide are viable alternative fuels, superior to guanidine in many ways.

Furthermore, the present inventors have developed a novel method of producing cyanoguanidine and/or cyanamide. In embodiments, the novel method includes heating metal oxide with carbon at elevated temperatures, suitably with a rotary arc, DC arc, plasma arc or similar, to produce metal carbide, for example calcium carbide. The method also includes reacting the resultant metal carbide with nitrogen to produce metal carbide, particularly calcium carbide to form a metal cyanamide, for example calcium cyanamide.

The cyanoguanidine and cyanamide produced by this method has a number of potential applications, not limited to use as a fuel. For example, the cyanoguanidine can be used as a fertilizer.

Cyanoguanidine (formerly 2-cyanoguanidine) is also known as dicyandiamide. It is a dimer of cyanamide. It has the following structural formula: NC-N=C(NH₂)₂.

Cyanamide is also known as hydrogen cyanamide. It has the following molecular formula: CN₂H₂. It can exist as two tautomers: NC-NH₂ and HN=C=NH.

As used herein the term "cyanamide-based compositions" means a composition comprising cyanamide, calcium cyanamide, cyanoguanidine or dicyanoguanidine and optionally one or more other compounds related to cyanamide, for example guanidine, urea and guanylurea.

Urea, guanidine, and guanylurea are related to calcium cyanamide because they are products of the partial hydrolysis of cyanoguanidine and urea is a product of the partial hydrolysis of hydrogen cyanamide.

Thus, cyanamide-based compositions are mixtures containing one or more compounds related to calcium cyanamide such as calcium cyanamide, hydrogen cyanamide (CN₂H₂), cyanoguanidine, dicyanoguanidine, guanidine, urea, and guanylurea.

A particularly preferred cyanamide-based composition is a composition containing cyanoguanidine. As noted above, the composition may also contain other compounds.

Accordingly, reference herein to "cyanamide-based composition" includes a reference to the preferred embodiment of "cyanoguanidine-containing composition".
Another particularly preferred cyanamide-based composition is a composition containing cyanamide. As noted above, the composition may also contain other compounds. Accordingly, reference herein to "cyanamide-based composition" includes a reference to the preferred embodiment of "cyanamide-containing composition".

Indeed, as will be clear from the subsequent discussions, the present invention is particularly concerned with cyanoguanidine-containing compositions and cyanamide-containing compositions.

The following discussion introduces the use of cyanoguanidine and cyanamide as fuels with reference to the relevant reactions and reaction products, the properties of cyanoguanidine and cyanamide and a comparison of cyanoguanidine and cyanamide with guanidine and urea.

The pH of dicyandiamide is near neutral and that of free base guanidine is pH 14. Free base guanidine is extremely caustic and, even if possible to manufacture in industrial quantities, safety issues associated with pH would have to be considered. The present inventors have found that even mostly dry and solid free base guanidine, when they were able to make it in small laboratory quantities, was very prone to instant reactions with either humidity or CO₂ from the atmosphere. Indeed, water vapor or CO₂ reacts with free base guanidine, this reaction resulting in the release of ammonia. On the other hand, the present inventors have found that dicyandiamide is exceptionally stable with toxicity similar to that of Vitamin C and is even less toxic than that of table salt.

Indeed, Ullmann's Encyclopedia of Industrial Chemistry (John Wiley, New York) Vol. A8 (Cyanamides article) states; "Dicyandiamide is essentially nontoxic, but it may cause dermatitis. The acute oral LD₅₀ of dicyandiamide for young, male albino rats is higher than 10 g/kg; therefore, the product is considered to be nontoxic. Albino rabbits tolerate single dosages of 10 g/kg of the product as an aqueous paste in contact with the closely clipped skin of the abdomen for 24 h with no evidence of systemic toxicity or skin irritation. Patch tests using the dry powdered material on 200 human subjects did not indicate sensitizing or primary irritant properties". Thus, cyanoguanidine has very low or no toxicity.

Dicyanamide has a melting temperature of 209°C and, as noted above, is widely used as a slow-release fertilizer. It is a non-corrosive and non-flammable solid at room temperature. Furthermore, dicyandiamide can easily be stored, for example in a covered shed. It can be safely transported, for example without the need of a closed container vessel. It is therefore far less dangerous to transport than either gasoline or diesel fuel.

As for cyanamide, it has a melting temperature of 44°C, is very mildly toxic to animals, and widely used as a fertilizer. It is given to humans to deter use of alcohol in Canada, the European Union, and Japan.
Thus, a first proposal described herein is that cyanoguanidine and/or cyanamide be used as a fuel and more specifically a transportation fuel (e.g. for cars, trucks, boats etc).

For example, a composition containing cyanoguanidine (C2N4H4) can be decomposed into ammonia and carbon dioxide in the presence of water as shown by the following overall equation:

\[(NH_2)_2C=NCN + 4H_2O \rightarrow 2CO_2 + 4NH_3\]

Upon reaction to form ammonia, a one-half volume of carbon dioxide will be produced for every volume of ammonia, allowing the product to be immediately used as a fuel. Based on the amount of ammonia released after hydrolysis, cyanoguanidine has an energy density approximately 1.4 times higher than a dry urea composition.

The following information compares the ammonia-containing properties of previously proposed alternative fuels with cyanoguanidine and cyanamide (the weight of additional water for decomposition not being considered because said water is readily obtained in adequate quantities by condensation from the exhaust of systems combusting ammonia and or hydrogen products obtained from the hydrolysis of compositions containing cyanoguanidine):

- Solid free-base guanidine (FBG) ammonia content = 51/59 = 0.86
- Urea ammonia content = 34/(60) = 0.57
- Cyanamide ammonia content = 34/42 = 0.81
- Dicyandiamide (cyanoguanidine) ammonia content = 68/84 = 0.81

Thus, cyanoguanidine and cyanamide have comparatively high ammonia content, on a par with guanidine.

Other cyanamide-based compositions react in the presence of water in a similar manner to cyanoguanidine.

Calcium cyanamide (the calcium form of cyanamide) is a convenient and accessible form of cyanamide. Calcium cyanamide can be made, in a batch process, from a metal oxide and carbon at high temperatures to form calcium carbide followed by subsequent milling of the carbide to a fine powder and heating in a nitrogen atmosphere to form calcium cyanamide.

Calcium cyanamide can also be produced from calcium compounds and urea (Weber et al., U.S. 5753199). Calcium cyanamide can also be made by passing partially nitrogenerated carbide formed in a turbulence reactor to a rotating kiln where it remains until the desired nitrogeneration degree is achieved (Fischer et al., U.S. 2,917,371).
Whilst these conventional methods of producing cyanamide are sufficient to permit the use of cyanamide and cyanoguanidine as described herein, the present inventors also describe herein a novel method of producing cyanamide and cyanoguanidine.

More generally, regardless of whether the conventional or novel method of manufacture is used, cyanamide-based compositions (i.e. especially cyanoguanidine-containing compositions and cyanamide-containing compositions) can be produced in a sustainable manner because the raw materials are electrical energy, carbon, nitrogen, and water.

For example, in embodiments described herein the metal oxide required for the synthesis of the carbide is recycled from the metal hydroxide produced in later production steps, so it is not consumed in the production process. Nitrogen can be extracted from the air at low cost. Carbon in the form of charcoal can be created by pyrolysis of biomass or from methane produced from methanogenensis using agricultural or domestic waste products. Using wind power or other sustainable energy sources, the cyanamide-based composition can be produced and delivered at a price which can allow it to be competitive with gasoline or diesel fuel.

These sources of carbon and electricity are discussed in more detail below.

While there is a growing concern about supplies of petroleum for future use as transportation fuels, there are still substantial known and established sources of natural gas that is "stranded" in the sense that it is not economical to transport this gas from its source to potential markets. Such source sites include regions around and in the Caspian Sea and the North Sea. There is also a substantial supply of hydrocarbons in waste plastic, including tire-waste, which presently finds no economic conversion to transportation fuel and instead is polluting the World Environment, especially the Pacific Ocean. There is a substantial amount of biomass from agriculture and from silviculture going to waste that might be converted to biochar and then made available as a source of carbon for possible conversion various chemicals, including conventional and novel transportation fuels. (See G.-D. Li, Q.-G. Liu, Z.-Y. Liu, Z. C. Zhang, C.-Y. Li, and W.Z. Wu "Production of Calcium Carbide from Fine Biochars" Angew. Chem. Int. Ed. (2010) 49, 8480-8483 and therein). Indeed, as discussed herein, the source of carbon that can be used in the production of cyanamide and/or cyanoguanidine can be selected from the group comprising hydrocarbon gas, especially methane, coal and charcoal, wherein the hydrocarbon gas, especially methane can be obtained from waste treatment plants, landfills, sewers, and anaerobic digestion of plant and/or animal waste. In short, there are ample sources of carbon for conversion to alternative transportation fuels.

As a source of electricity, there is also some "stranded" electrical energy, such as the stranded wind generated electrical energy in the Columbia River Gorge that goes to waste when at various times its amount exceeds what the existing electrical power grid can then
handle. Vastly more electrical energy could be generated at low cost from wind energy at the World's best wind energy sites, such as those in the Aleutian Archipelago, the Hebrides, and Terra del Fuego, if only there were a way to market it economically.

5 Regarding the methodology for producing cyanoguanidine, this can be achieved via the intermediate cyanamide (itself the subject of proposals of the present application as described herein). The synthesis of cyanamide and then cyanoguanidine is described in more detail below.

10 Since the 19th Century there has been a widely practiced conversion of carbon from various sources and CaO (quicklime) from limestone to CaC$_2$ (calcium carbide), i.e.,

$$3 \text{C} + \text{CaO} \rightarrow \text{CaC}_2 + \text{CO}, \quad (1)$$

15 in an electric arc at temperatures above 2000°C. Li et al. (see above) assert that this process has not changed much since 1892 (citing J. Lacson, U. Lochner, and G. Toki, Chemical Economics Handbook (SRI International, Menlo Park, CA, 2001) pp. 1-48 and J. T. Morehead and G. De Chalmont, J. Am. Chem. Soc. (1896) 18, 311-331) and has a heat of reaction of about 445.6 kJ/mole but typically requires 4000 kWh/t of CaC$_2$ = 923 kJ/mole in the prior art. They report a process, which uses 0.022 mm (also known as "1 mil") particle sizes for both CaO and the biochar carbon source, uses combustion of the carbon source (also known as "autothermal") heating to temperatures up to 500°C less than used in the traditional electric arc process, and, on the basis of an Aspen Plus® computer simulation, is projected to achieve better energy efficiency.

25 Actually, there has been some advance in the art of electric arc driving of Reaction (1) since 1892. In 1979 C. S. Kim, R. F. Baddour, J. B. Howard, and H. P. Meissner reported (Ing. Eng. Chem. Process Des. Dev. (1979) 18, 323 - 328) the replacement of the prior art DC arc with a rotating-arc type furnace. They used this to react finely divided CaO with methane, ethylene, and bituminous coal. Also, A. F. Diaz, A. J. Modestino, J. B. Howard, J. W. Tester, and W. A. Peters reported rotating arc conversion of MgO in "Magnesium Carbide Synthesis from Methane and Magnesium Oxide - A Potential Methodology for Natural Gas Conversion to Premium Fuels and Chemicals" in Proceeding of the U.S. DoE Coal Liquefaction and Gas Conversion Contractors' Review Conference (8/29-31/1995), which is available at:


30 Specifically, they disclosed rotating arc conversion above 2100 K of MgO to MgC$_2$ and to Mg$_2$C$_3$ by reaction with methane:

$$3 \text{CH}_4 + \text{MgO} \rightarrow \text{MgC}_2 + 6 \text{H}_2 + \text{CO}, \quad (2)$$
and

\[ 5 \text{CH}_4 + 2 \text{MgO} \rightarrow \text{Mg}_2\text{C}_3 + 10 \text{H}_2 + 2 \text{CO} \]  

(3)

in addition to

\[ 3 \text{CH}_4 + \text{CaO} \rightarrow \text{CaC}_2 + 6 \text{H}_2 + \text{CO} \]  

(4)

They were enthusiastic about Reaction (3) because of the possibility to do

\[ \text{Mg}_2\text{C}_3 + 4 \text{H}_2\text{O} \rightarrow 2 \text{Mg(OH)}_2 + \text{C}_3\text{H}_5 \]  

(5)

and to use methylacetylene/propadiene to make conventional hydrocarbon fuels. Of course, calcium carbide has long been used to produce acetylene for fuel and as a source of other chemicals by reaction with water;

\[ \text{CaC}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{C}_2\text{H}_2 \]  

(6)

The corresponding reaction with magnesium carbide,

\[ \text{MgC}_2 + 2 \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{C}_2\text{H}_2 \]  

(7)

could be used for the same purpose.

Calcium carbide has also been used since 1895 in the Frank-Caro Process to make calcium cyanamide, a common nitrogen fertilizer, in an electric arc furnace at about 1000°C;

\[ \text{CaC}_2 + \text{N}_2 \rightarrow \text{CaCN}_2 + \text{C} \]  

(8)

The CaCN\(_2\) may be reacted with water and CO\(_2\) to obtain cyanamide (H\(_2\)NCN)

\[ \text{CaCN}_2 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{NCN} \]  

(9)

Two cyanamide molecules may be combined to form dicyandiamide, which is also known as 2-cyanoguanidine, by well-known art;

\[ 2 \text{H}_2\text{NCN} \rightarrow (\text{H}_2\text{NCN})_2 \]  

(10)

Reaction (10) can occur in a basic aqueous solution, such as water plus CaO, in which one cyanamide molecule loses a proton, then bonds to the C of a second cyanamide molecule, and then regains a proton on coming out of solution as a solid.
In fact, Reaction (10) occurs so easily that it limits the shelf-life of the monomer (i.e., of cyanamide) at temperatures above 20°C rather severely and, for the dry solid possess a potential danger of violent dimerization (Cameron, “Cyanamides” Kirk-Othner Encyclopedia of Chemical Technology, John Wiley & Sons, New York, published on-line 17 Sept 2010).

However, Weiss taught in U.S. Patent 4,477,421 that cyanamide can be substantially stabilized against dimerization by addition of a fraction of a weight percent of divalent magnesium and Cameron (see above) notes that it is stabilized against dimerization by control of the pH, e.g., with sodium phosphate.

Thus, the common method of making calcium carbide is to heat CaC\textsubscript{3} and coke in an electric arc furnace at temperatures of ~2000°C. This process has been relatively unchanged since its invention in 1888. The calcium carbide is then converted to calcium cyanamide by heating at ~1000°C in nitrogen. Because cyanamide or cyanoguanidine provides almost the same amount of ammonia per unit mass as free base guanidine (see above, 81% vs 86%) and a much higher amount per unit mass than urea with one mole of water (see above, 81% vs 57%) the present inventors believe it advantageous to avoid the additional processing steps into either free base guanidine, guanidine salts or urea and use the cyanamide, and to then easily convert the cyanamide to the dimer of cyanamide: cyanoguanidine, for example for use directly as a transportation fuel or fertilizer.

In the proposed method of producing cyanoguanidine and/or cyanamide, the metal oxide and carbon are reacted together at an elevated temperature (e.g. about 2000°C), suitably in an electric arc reactor, to form metal carbide, the metal carbide, still hot from the carbide reaction, is then reacted with nitrogen to form metal cyanamide. The present inventors have found that the reaction of the hot metal carbide with nitrogen, i.e. utilising the heat energy already present in the metal carbide from the oxide-carbon reaction, makes for an efficient and effective process, permitting the formation of metal cyanamide in good yield.

Furthermore, the present inventors have observed that the use of an electric arc, especially a rotary arc, is particularly effective at pulverising, breaking down or comminuting the solid material introduced into the reactor. This means that a subsequent grinding step (as per the conventional process) is not required prior to reaction with nitrogen.

Whilst cyanamide has been used as a binder for fuel in gun propellants and rocket fuels, to the best of the inventors' knowledge, it has not been used in transportation fuels.

As for the release of energy from cyanamide, it has long been known that one can react cyanamide with a water to form ammonia and carbon dioxide in two steps;

\[ \text{H}_2\text{NCN} + \text{H}_2\text{O} \rightarrow (\text{NH}_2)\text{CO} \quad (11) \]

\[ (\text{NH}_2)\text{CO} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2. \quad (12) \]
However, the mixture of ammonia and carbon dioxide was not thought previously to be a viable fuel. Of course, carbon dioxide-free ammonia (e.g. obtained from the Haber-Bosch process) has been used as a transportation fuel when petroleum based fuels were in short supply, especially in Axis Power occupied areas during World War II.

As noted above, a mixture of carbon dioxide and ammonia is not thought to be suitable as a fuel and indeed a 33% mixture of carbon dioxide in ammonia would have a severe problem for use as a transportation fuel because the Reaction

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

(13)

to make ammonium carbamate is exothermic. Any ammonium carbamate spontaneously produced would tend to plug up the plumbing of the system using the ammonia. Preferably, to reduce or eliminate the potential of plugged fuel lines from the very rapid formation of ammonium carbamate all fuel lines should be maintained at a temperature greater than 58°C, or more preferably, maintained at or near 100°C so that no formation of ammonium carbamate takes place. Furthermore, with the potential of water or steam being present within a mixture of ammonia and carbon dioxide gases the same requirements for the formation of ammonium carbonate within fuel lines apply. Nevertheless, even with these precautions, the mixture of carbon dioxide and ammonia arising from the two step hydrolysis of cyanamide has not been regarded as feasible as a fuel and neither cyanamide nor cyanoguanidine has been used as such.

With regards to comparing the generating energy from clean coal by burning and generating energy from cyanoguanidine, the following observations can be made.

All of the carbon within coal or within cyanoguanidine appears as C02, however the important points are the work extracted from the conversion of carbon to C02 and the form in which the C02 is released can make a significant difference for the potential capture of the C02. The interesting combination is using excess or stranded renewable energy and coal to produce cyanoguanidine.

Four carbon atoms are consumed in the production of one molecule of cyanoguanidine. Two of these are incorporated into the cyanoguanidine molecule and two are released as pure CO (undiluted by nitrogen etc.) during the formation of a calcium carbide molecule (an additional carbon atom is recycled through the process). The CO can be burned to release energy, or could be reduced back to carbon plus water by use of hydrogen (produced from the renewable energy by electrolysis) via the Bosch Reaction (see http://en.wikipedia.org/wiki/Bosch_reaction). With this process all of the carbon consumed is incorporated into the cyanoguanidine.

When the cyanoguanidine is decomposed ammonia and C02 are released before any combustion. This means that the mixture contains only ammonia and C02 (no nitrogen or
oxygen etc.) and the $\text{CO}_2$ can be separated without too much difficulty and sequestered (e.g. consumed by algae, injected into rock formations, etc.). Also, while the typical efficiency of a coal-burning power plant is ~33%, ammonia can be used to power a solid oxide fuel cell combined with a steam turbine with efficiency of ~70%. So even if all the $\text{CO}_2$ from the decomposition of the cyanoguanidine is released to the atmosphere, the present inventors have obtained twice the energy from the same amount of carbon at the point of use (more total energy is required when the renewable energy is considered) and an abundant, but much maligned resource (coal) has been used to replace petroleum in a manner potentially completely sustainable.

Regarding the use of coal as a carbon source, the present inventors propose that iron pyrite (iron sulphide) can be removed by known floatation methods. The powdered coal can then be dried. The coal, together with any remaining impurities, can then be reacted with a metal oxide (e.g. calcium oxide) to form the desired metal carbide (e.g. calcium carbide).

As noted above, it is a particular feature of embodiments of the present invention that a rotary arc reactor is used. Thus, in those embodiments, the coal, suitably dried powdered coal as discussed above, can be injected into the rotary arc reactor.

The present inventors have found that the impurities will be released into the CO gas stream (CO being the reaction product of calcium oxide and carbon) and can be condensed out into potentially valuable commodities.

Even if remaining impurities combine with calcium oxide, they can be separated out at the hydrogen cyanamide synthesis step.

In practice, a key issue is having the coal together with excess energy. With this in mind, as wind power generation increases, the present inventors propose that situations such as stranded wind power in the Western United States together with coal from, for example, Wyoming may become rather common sources of cyanoguanidine synthesis.

Additionally, the United Kingdom, Norway, Ukraine, Germany and China have large, even huge reserves of coal. Very often, the issue is whether the coal is "clean." Inventors teach how to clean coal, separate valuable commodity elements, all in a manner that allows for an efficient method of synthesizing cyanoguanidine.

Because "coal" is not a precisely defined material; there are many commodities that are loosely referred to as "coal"; the thesis by Kim from MIT ("Formation of $\text{CaC}_2$ from $\text{CaO}$ and "Nascent" Carbon Species In A Rotating Arc Reactor", Chi Sang Kim, Massachusetts Institute of Technology, May 1977) specified the exact mine and seam that they got their material from.
A US Bureau of Mines report has noted that the margins of coal seams, which are often collect as "boney piles" at mine sites because the coal is too dirty for normal markets, contain high concentrations of such elements as Zn, Cu, Ga, and Ge that can assay out at more than $1000/tonne. What they lacked was an economic process to sort out the jumbled mix.

The present inventors propose that almost all the impurities will come out of the rotary arc reactor as gasses together with the CO and that very little of them will remain in the reactor as solids with the CaO, the CaC₂, and the CaCN₂. The reason for this is that the region of the arc is both rather hot, ~ 2000°C, and subject to a very strong electric field. The strong electric field will enhance the thermal breaking of chemical bonds that are ionic, i.e., between atoms of different elements. The reason that CO escapes from the arc region intact is that it has both a very strong (triple) bond energy and a very small electrostatic dipole moment. Molecules of elements form bonds with no dipole moment at all, so these are not much affected by the electric field. Molecules of elements are subject to thermal breaking, but the present inventors believe that as these molecules exit the rotary arc and cool many of these will reform as molecules of elements after they exit the region of the arc. Depending on the source of coal, the concentration of impurities within the coal that is blended with calcium oxide and introduced as a feed into the rotary arc, the present inventors believe that these molecules, by and large, do not react with the CaO, CaC₂, and CaCN₂ that remains in the arc region.

The most important mineral left in the arc region is CaS. This has a high melting point (~2525°C) and is known to form when coal dumps burn. However, the CaS bond has a very large dipole moment. The present inventors believe that the majority of the CaS does not persist in the arc region and that instead the sulfur comes out as either elemental sulfur or as sulfur dioxide when combined with oxygen entrapped within coal particles or as sulfuric acid when the flotation coal is not completely dried.

As for mercury that may be present in the coal commodity, the present inventors observe that nearly all of the mercury within the coal commodity will come out of the rotary arc region as a Hg-gas and can be easily separated from the CO, which is the predominant gas.

Should silica be introduced within the coal feed, the melting point of silica is well below 2000°C. It might be extracted out of the arc region either as a gas or as a liquid and is not a major problem unless the reaction temperature falls below 1500°C.

The key differences, leading to lower costs, using the proposed method including a rotary arc reactor when compared with the conventional production of CaCN₂ are shown below:

Conventional Process: Uses expensive energy; Batch Production of CaC₂; Grinding of CaC₂ required; Batch process for CaCN₂; Heating of CaC₂ to form CaCN₂; ~ 5 hr reaction time; Energy added for CaCO₃ to CaO reaction.
Proposed Rotary Arc Reactor Process: Can use low-cost "stranded" energy; Continuous production of CaC₂; No grinding needed; Continuous process for CaCN₂; No heating required (uses hot CaC₂ from the rotary arc reactor); Seconds to minutes reaction time;

Waste heat drives CaCO₃ to CaO reaction.

The net hydrolysis reaction for cyanoguanidine (CG) and the enthalpies of formation (kJ/mol) at 298K are as follows:

\[
\text{CG (s) + 4H₂O (l)} \rightarrow 2\text{CO}_2 (g) + 4\text{NH}_3 (g) \\
24.9 \quad 4 (-285.8) \quad 2 (-393.5) \quad 4 (-45.9) \\
\Delta H = 147.7 \text{ kJ/mole}
\]

The reaction for the combustion of the resulting ammonia and the enthalpies of formation (kJ/mol) at 298K are:

\[
4\text{NH}_3 (g) + 3\text{O}_2 (g) \rightarrow 6\text{H}_2\text{O} (l) + 2\text{N}_2 \\
4 (-45.9) \quad 3 (0) \quad 6 (-285.8) \quad 2(0) \\
\Delta H = -1531.2 \text{ kJ/mole}
\]

The reaction for CG decomposition requires \((147.7/1531.2 = 0.096)\) 9.6% of the heat released by the combustion of ammonia, so there is ample waste heat to drive the CG decomposition as long as the efficiency of the engine is less that 90%. The output of the reactor is a gaseous mixture of ammonia and carbon dioxide.

It is noted that there is a significant challenge in using ammonia in diesel engines because the autoignition temperature of ammonia (~650°C) is much higher than the autoignition temperature of diesel (~225°C). There has been significant work on ammonia-fueled engines presented at several annual "Ammonia Alternative Fuel Conferences" (http://www.energy.iastate.edu/Renewable/ammonia/index.htm). The present inventors are working with Hydrogen Engine Center (HEC) in Algona, Iowa have developed a spark-ignition Otto cycle engine that runs on 100% ammonia.

A 2011 research paper by Reiter and Kong, "Combustion and emissions characteristics of compression-ignition engine using dual ammonia-diesel fuel", published in the journal Fuel, reported experimental results on the use of ammonia in a standard 4-cycle diesel engine (John Deere 4045 turbocharged engine). The ammonia was injected into the engine manifold and varying amounts of diesel were injected into the cylinder to ignite the ammonia. The engine was run with the ammonia providing up to 80% of the energy supplied to the engine. The paper also includes a good summary of prior work and extensive experimental work on emissions including nitric oxide and soot.
Sandia National Laboratories have designed an interesting free piston diesel engine that can use multiple fuels and provides the output directly as electrical energy. The present inventors understand that some vessels use electric motors to provide propulsion and for those designs this type of engine would be advantageous. To inventor's knowledge, this is the only work that uses ammonia in a 2-cycle diesel engine. The compression ratio is 48:1 to achieve the temperatures necessary for ignition of ammonia. They also report on page 18 of the Sandia paper labeled "Sandia linear engine 2001" that the levels of ammonia and NOx in the exhaust and suggest that they can be reduced using a zeolite catalyst in the exhaust to promote an SCR-type reaction. The present inventors acknowledge the Sandia paper labeled "Sandia linear engine 2001" and applaud the efforts of Peter Van Blarigan, Sandia National Laboratories, Livermore, CA 94550, for his work in this field.

Interesting work on the use of ammonia in diesel engines was performed in the 1960s under a military contract related to a Fuel Depot concept where ammonia would be produced on a nuclear-powered vessel for military use in remote areas. A paper titled "Combustion of Anhydrous Ammonia in Diesel Engines" (SAE paper 670947) by Pearsall and Garabedian outlined several experimental approaches tested in a modified combat tank engine. They used ammonia injected into the manifold and ignited with a small amount of diesel fuel (similar to the Reiter and Kong paper), they used spark ignition with ammonia injected into the manifold and they tried direct injection of liquid anhydrous ammonia. The spark ignition results at compression ratios of 18.6:1 and 16:1 were quite favorable but were limited by the pressure capability of the available spark plugs. They observed:

"Horsepower output is greater with spark ignition than with either pilot ignition or straight diesel operation. It is possible to obtain supercharged diesel output with unsupercharged ammonia fuel spark ignition"

Their work with direct injection of ammonia was not satisfactory. The spark ignition method seemed to provide the best results and did not require any diesel fuel. Their main conclusion follows:

"The results of this investigation have shown that it is feasible and practical to convert and operate a compression ignition engine with anhydrous ammonia fuel. ... It should be a spark ignition engine utilizing a high energy ignition source, such as magneto. It should have a relatively high compression ratio of the order of 12:1 to 16:1."

The paper by Reiter and Kong, mentioned above, presents detailed results on NO and soot levels. The NO levels are several times higher than those from 100% diesel, and the soot levels are dramatically lower than with diesel fuel. The paper from Sandia Laboratories suggests the use of a zeolite catalyst to reduce both the NOx and ammonia levels in the exhaust.
The temperature of the exhaust will be lowered because heat needs to be extracted to run the cyanoguanidine hydrolysis reaction so the Selective Catalytic Reduction could be implemented.

5 The above discussion sets out the benefits that can be realised in embodiments of the invention and in particular highlights the advantages of using cyanoguanidine and/or cyanamide as a transportation fuel; and of the novel manufacturing process for cyanoguanidine and cyanamide whereby a rotary arc reactor or similar is used to generate metal carbide and subsequently react the hot metal carbide with nitrogen.

10 In one aspect, the present invention proposes an improved method for providing a cyanamide-based composition. Current methods used to produce calcium cyanamide and hydrogen cyanamide are essentially over 100 years old. The formation of calcium carbide by current methods follows the equation:

\[ \text{CaO} + 3\text{C} = \text{CaC}_2 + \text{CO} \quad \Delta H_{\text{298K}} = +446 \text{ kJ} \]

The improved method proposed herein comprises reacting a metal oxide and a source of carbon to produce a metal carbide and then reacting the metal carbide with nitrogen wherein the metal carbide is still hot from the metal oxide-carbon reaction.

In embodiments the method comprises: (a) using a source of energy to react a metal oxide with a source of carbon to produce a finely divided metal carbide at an elevated temperature and immediately reacting the hot finely divided metal carbide with nitrogen gas to form the metal cyanamide together with unreacted metal carbide via the following equation (using calcium as an illustration and also a preferred metal):

\[ \text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C} \quad \Delta H_{\text{100K}} = -295 \text{ kJ} \]

(b) reacting the mixture with water to decompose the metal carbides into acetylene and acetylene-related compounds and metal hydroxide (c) combusting the acetylene and acetylene-related compounds to release energy (d) separating the metal cyanamide for use in the composition and separating carbon and metal hydroxide for recycling in the production process.

35 A related proposal is an improved method for providing a cyanamide-based composition. The method comprising: (a) using a source of energy to react a metal oxide with a source of carbon to produce a finely divided metal carbide at an elevated temperature and immediately reacting the hot finely divided metal carbide with nitrogen gas to form the metal cyanamide together with unreacted metal carbide (b) reacting the mixture with water to decompose the metal carbides into acetylene and acetylene-related compounds and metal hydroxide (c) combusting the acetylene and acetylene-related compounds to release energy (d) reacting the mixture with carbon dioxide and water in acidic solution to form hydrogen
cyanamide and calcium carbonate (e) separating the hydrogen cyanamide for use in the composition.

Another related proposal is an improved method for providing a cyanamide-based composition. The method comprising: (a) using a source of energy to react a metal oxide with a source of carbon to produce a finely divided metal carbide at an elevated temperature and immediately reacting the hot finely divided metal carbide with nitrogen gas to form the metal cyanamide together with unreacted metal carbide (b) reacting the mixture with water to decompose the metal carbides into acetylene and acetylene-related compounds and metal hydroxide (c) combusting the acetylene and acetylene-related compounds to form energy (d) reacting the mixture with carbon dioxide and water in acidic solution to form hydrogen cyanamide and calcium carbonate (e) separating the hydrogen cyanamide (f) reacting the hydrogen cyanamide in basic solution to form cyanoguanidine (g) separating the cyanoguanidine for use in the composition.

Thus, the method includes reacting the metal carbide with nitrogen after metal carbide formation without any intervening substantive process steps. As noted below, this does not preclude partial cooling of the metal carbide. This can be achieved by introducing nitrogen into the reactor at a location downstream of the metal carbide formation zone/section. For example, a reactor can be provided with a first section for the formation of metal carbide, and a second section wherein the hot metal carbide product is contacted with nitrogen. In practice, the first and second section may be regions or zones in the same chamber. For example, as illustrated herein, the second section (i.e. the nitrogen-metal carbide reaction region) can be located below the first section (i.e. the carbon-metal oxide region). In such an arrangement, the metal carbide particles can conveniently move from the first to the second section under the action of gravity. Alternatively or additionally, the metal carbide particles can be moved along or through the reactor by a gas flow.

It is therefore a contribution of embodiments of the present invention that the metal cyanamide is formed directly in step (a) above, in contrast to the conventional (Frank-Caro) approach whereby reaction of the metal carbide with nitrogen occurs in a separate step.

In particular, it is a characteristic of embodiments of the method that the heat required to bring about the reaction of nitrogen with the metal carbide is derived at least in part from the thermal energy imparted to the metal carbide in the metal oxide-carbon reaction. That is, the metal carbide is already hot when it is contacted with nitrogen. Again, this is in contrast to the conventional (Frank-Caro) approach whereby "cold" metal carbide is the starting material, thereby requiring significant heating prior to mixing with nitrogen.

The metal oxide is suitably calcium oxide or magnesium oxide.

Suitably the reaction is a continuous reaction, i.e. metal carbide and metal cyanamide production operates as a continuous process. Suitably the reactor is a continuous reactor,
i.e. is configured or adapted to permit the reaction to operate as a continuous process. Thus, suitably the reactor is a continuous flow reactor.

Regarding the elevated temperature in the metal oxide-carbon reaction, it is desirable to have the reaction equilibrium constant K>1 for the endothermic reactions so that a reasonable yield is obtained. Nevertheless, it is preferred not to go significantly higher in temperature so as to increase delta H for the reactions and to require more input energy (because of the difference in heat capacities of reactants and products). For the specific reaction of carbon with CaO, K>1 at 1900°C and for the reaction of methane with CaO, K>1 at 1200°C.

Naturally, the reaction should proceed fast enough so that it is nearly complete by the time the reactants pass through the relevant region of the reactor, suitably the arc. In the case of an arc reactor, the temperature can be controlled via control of the arc power.

In practice, the skilled reader is able to select appropriate arc power to achieve acceptable conversion of the reactants, taking account the size and geometry of the reactor.

A typical temperature range is 1000°C to 2500°C, preferably 110°C to 2200°C, more preferably 1150°C to 2100°C, more preferably 1200°C to 2100°C, more preferably 1400°C to 2100°C, more preferably 1600°C to 2100°C, more preferably 1800°C to 2100°C. A particularly preferred temperature range is 1900°C to 2100°C, especially 1950°C to 2050°C, with about 2000°C being particularly effective, especially for the reaction of methane and calcium oxide.

As noted above, it is preferred that the elevated temperature is provided by an electric arc reactor, suitably a rotating arc reactor. Nevertheless, other methods of supplying intense localized heat may also be used. A non-rotating arc would work, for example. Similarly, a solar furnace could be used to heat the carbon and metal oxide to produce a melt that yields metal carbide, by passing the carbon/metal oxide mixture through the focal point of a solar furnace. A microwave arc/plasma could also be used.

As regards the provision of a rotary arc, the rotation can be achieved for example by magnetic coils associated with the reactor or by permanent magnets located so as to provide a vertical magnetic field, for example located at each end of the arc chamber.

Regarding the delivery of the carbon source (e.g. methane) and the metal oxide, this can be achieved by entraining the metal oxide in a gas flow, for example in a methane or other hydrocarbon gas flow. Entraining the metal oxide in the gas flow can be achieved by using a vibratory feeder. In such an arrangement, the combination of carbon source and metal oxide can be delivered to the reactor, specifically the arc chamber, via a single inlet port. Alternatively or additionally the carbon source and the metal oxide can be delivered via different inlet ports, for example one inlet port for the carbon source (e.g. methane) and one
for the metal oxide. Nevertheless, the delivery of the two components should suitably be simultaneous.

The delivery rates of the components (carbon source and metal oxide) can be selected with the energy output of the reactor in mind so as to ensure that there is sufficient energy input to achieve the desired reaction. For example, in the case of methane and calcium oxide, the following calculations can be made so as to ensure that the total energy input from the arc for a set time period, say 1 minute, exceeds the delta H of the reaction for the amount of reactants that pass through, assuming a stoichiometric ratio of the carbon and the CaO. In the reaction of CaO with methane, the delta H of reaction is 7.2 E5 Joules/turn of the reaction. At 25 kWarc power, 7.2 E5 Joules are delivered in 28 sec. So in 1 minute, (60/28) moles of CaO is the maximum amount that could theoretically be reacted which equals 124 grams. The amount of methane is (3 moles)\(^*\) (60/28)\(^*\) 22.4 liters/mole = 48 liters assuming 1 atm pressure and 0 °C. Inevitably, as the reaction is not 100% efficient the maximum rate can be multiplied by a factor of, say, 0.9.

As noted above, the heat energy of the metal carbide arising from the formation (e.g. in the arc chamber) of the metal carbide is utilised in the reaction with nitrogen. Nevertheless, some cooling of the metal carbide can be accommodated and/or may be desirable. For example, cooling may occur as a result of the metal carbide moving from the "active" hotter region of the arc chamber, to the "passive" region of the arch chamber which is at a lower temperature. In embodiments, the arc chamber and hence the metal carbide formation reaction is at a temperature indicated above, for example 1800°C to 2100°C, and cooling then occurs such that the reaction of metal carbide and nitrogen occurs at, for example, 900°C to 1100°C. Indeed, in embodiments the reaction of metal carbide and nitrogen occurs at 980°C to 1020°C, preferably about 1000°C.

The size of the metal carbide particles is suitably less than 200\(\mu\text{m}\), preferably in the range of 0.1 \(\mu\text{m}\) to 100\(\mu\text{m}\), preferably 0.1 \(\mu\text{m}\) to 1.5\(\mu\text{m}\).

The present inventors have found that the reaction of metal carbide and nitrogen occurs particularly effectively if the metal carbide is maintained in a fluidized state. This can conveniently be achieved by feeding the nitrogen into the reactor so that it passes through the metal carbide, for example to produce a fluidized bed. Suitably the reactor comprises a fluidized bed region, including means for introducing the nitrogen through the bed.

Following the formation of metal cyanamide, preferably cyanoguanidine is formed from the metal cyanamide.

Typically, after formation of the metal cyanamide, the metal cyanamide is cooled.

The metal cyanamide can be mixed with water, suitably to form a slurry. Typically this will result in the formation of acetylene. The evolution of acetylene is preferably monitored.
 Optionally the mixture is cooled, for example to about room temperature.

The mixture can then be contacted with carbon dioxide (suitably after evolution of acetylene has stopped). This can be achieved by delivering the carbon dioxide into the slurry, e.g. bubbling carbon dioxide into the slurry. Contact with carbon dioxide suitably occurs for at least 1 hour, preferably at least 4 hours, for example about 8 hours.

Insoluble material can be removed by filtering. The filtered (insoluble) material may include CaCO₃, Ca(OH)₂ (from the decomposition of unreacted calcium carbide), and carbon. These materials can be recycled to generate the CaO and a portion of the required carbon used as input materials. The filtrate can be evaporated to dryness to isolate cyanoguanidine.

As discussed above, the source of carbon can come from several sources. The carbon source can be in the form of elemental carbon in the form of carbon black, charcoal, coal, graphite, or similar form. The carbon source can also be in the form of a carbon compound such as methane, propane, butane or a similar organic compound. The carbon compound can also be in the form of a hazardous waste or toxic compound that requires a safe disposal. For such hazardous waste the high temperatures completely destroy the hazardous compounds while providing a useful product. The source of carbon can also be a combination of one or more of the above mentioned carbon sources. It is particularly advantageous to use a portion of the carbon liberated during the formation of calcium cyanamid to reduce the amount of carbon consumed in the production process.

Thus, embodiments described herein generally relate to systems and methods of rotary or plasma arc synthesis of nitrogen-based fuel compositions, preferably cyanoguanidine fuel compositions and, more preferably, to the improvement of the production of cyanoguanidine fuel compositions. Embodiments described herein also have novel components that generally relate to rotary or plasma arc nitrogen-based fuel production systems and to the improvement of the production of cyanoguanidine fuel compositions that also serve to substantially “scrub” unwanted contaminants, such as the elements sulfur or mercury, from coal or remove unwanted gas, such as hydrogen sulfide, from well head “sour” natural gas. Such rotary or plasma arcs methods for the synthesis of nitrogen-based fuel compositions can be obtained by using the systems and methods described herein.

In certain embodiments, the invention provides a system for providing power to one or more rotary or plasma arcs, comprising: a continuous and/or intermittent power source; a transformer coupled to the intermittent power source, the transformer being configured to transform power from the intermittent power source to power with appropriate operating parameters for the rotary or plasma arcs; and a tap controller coupled to the transformer, the tap controller being configured to monitor and control the transformer so that a constant voltage is provided to the rotary or plasma arcs from the transformer regardless of the load of the rotary or plasma arcs and the power output provided by the intermittent power source.
In yet further embodiments, a novel method for removing elements or molecules from non-scrubbed natural gas or low quality coal that is known to contain toxic elements or molecules is performed using the methods, systems, and rotary or plasma arc synthesis of nitrogen-based fuel or fuels described herein.

The product of the method, namely the cyanamide-based composition, when combined with water represents a suitable alternative to fossil fuels. The composition has a high specific energy and energy density, and can be environmentally friendly and easy to handle. As discussed above, cyanoguanidine and calcium cyanamide have been used in fertilizers, so spills of cyanamide-based compositions would present a small environmental hazard.

Accordingly, at its most general a further proposal is a method for generating energy from water and a cyanamide-based composition. The method comprises: (a) reacting the composition with water to form ammonia; and (b) oxidizing the ammonia formed in step (a) to form water and nitrogen thereby generating energy.

In a related proposal, the method comprises: (a) reacting the composition with water to form ammonia; (b) converting the ammonia formed in step (a) into nitrogen and hydrogen; and (c) oxidizing the hydrogen formed in step (b) to form water thereby generating energy.

Another proposal is a method for using cyanamide-based compositions for temporarily storing electrical energy in the form of chemical energy for the purposes of load-levelling in electrical generation and transmission networks or for temporarily storing electrical energy in the form of chemical energy when adequate capacity on electrical transmission lines is lacking. In embodiments the method comprises (a) use of electrical energy, nitrogen, a metal oxide and a carbon source to produce a cyanamide-based composition (b) storing the cyanamide-based composition (c) combining the cyanamide-based composition with water to generate ammonia (d) using the ammonia to generate electrical energy when needed (e) supplying that electrical energy to the transmission line.

Another proposal is a method for using cyanamide-based compositions for temporarily storing electrical energy in the form of chemical energy for the purposes of load-levelling in electrical generation and transmission networks or for temporarily storing electrical energy in the form of chemical energy when adequate capacity on electrical transmission lines is lacking. The method comprising (a) use of electrical energy to produce a cyanamide-based composition (b) transporting the cyanamide-based composition to remote locations where electrical energy is required (c) combining the cyanamide-based composition with water at the remote locations to generate ammonia (d) using the ammonia to generate electrical energy where and when needed (e) supplying that electrical energy to a transmission line.

Calcium cyanamide, hydrogen cyanamide, and cyanoguanidine are valuable chemicals with uses other than the generation of energy, so that a portion of the production of these
chemicals produced using the methods described above can be sold on the open market as a source of revenue.

Furthermore, the present inventors have observed that:

Cyanamide and dicyandiamide can be used as a transportation fuel, preferably in their molten states, for example by injection into a Diesel engine’s cylinder when the piston is near top-dead-center, to burn according to the reaction,

\[ 2 \text{H}_2\text{NCN} + 3 \text{O}_2 \rightarrow 2 \text{H}_2\text{O} + 2 \text{CO}_2 + 2 \text{N}_2 \] ; (14)

Cyanamide and dicyandiamide can be made from sources of carbon, hydrogen, and nitrogen more efficiently than in the prior art by, as discussed above, combining the steps for producing alkali earth carbide and for producing alkali-earth cyanamide into one manufacturing step or by combining all three steps into one manufacturing step; for example, the sum of Reaction (4), (8) and (9) is

\[ 3 \text{CH}_4 + \text{N}_2 + \text{H}_2\text{O} + \text{CO}_2 + \text{CaO} \rightarrow \text{H}_2\text{NCN} + \text{CaC}_3 + \text{CO} + \text{C} + 6 \text{H}_2 \] ; (15)

after the products are removed from the furnace where Reaction (15) is performed, the CaO and the CO2 needed for the source can be obtained by recycling the CaC03 product with heat,

\[ \text{CaC}_3 \rightarrow \text{CaO} + \text{CO}_2 \] (16)

the products CO and C can be burned in air, which may be represented as "4 N2 + O2"

\[ 2 \text{CO} + 2 \text{C} + 3 \left(4 \text{N}_2 + 0_2 \right) \rightarrow 4 \text{CO}_2 + 12 \text{N}_2 \] ; (17)

and the nitrogen can be separated from the product of Reaction (17) can be used to supply that needed as a source for Reaction (15).

The portion of the remaining nitrogen from Reaction (17) might be reacted via the Haber-Bosch Process with the hydrogen product of Reaction (15) to form ammonia,

\[ 6 \text{H}_2 + 2 \text{N}_2 \rightarrow 4 \text{NH}_3 \] , (18)

which might be combined with a portion of the carbon dioxide product of Reaction (17) to form urea via the Bosch-Meiser Process

\[ 4 \text{NH}_3 + 2 \text{CO}_2 \rightarrow 2 \text{CON}_2\text{H}_4 + 2 \text{H}_2\text{O} \] , (19)
or otherwise converted to a product with good logistical and transportation characteristic and a large market value; alternatively one might form the H2NCO in two steps, the first being

\[
3 \text{CH}_4 + 2 \text{N}_2 + 2 \text{CaO} \rightarrow 2 \text{CaCN}_2 + \text{CO}_2 + 6 \text{H}_2, \quad (20)
\]

after which the solid product is separated from the gaseous products, the gaseous products are separated into hydrogen and carbon dioxide (as may be done with a hydrogen passing membrane of known art) preferably one using a mischmetal alloy (see Wu et al.) and most preferably an amorphous mischmetal-transition-metal alloy (see Van Vechten et al.), the carbon dioxide is combined with an equal amount more carbon dioxide (obtained by heating calcium carbonate) in a separate reaction vessel with the solid product and water to perform Reaction (9) to produce the cyanamide and calcium carbonate, this calcium carbonate is then heated (Reaction (16)) to regain the CaO and the needed carbon dioxide, and the elemental hydrogen is put to some of many good uses known in the art, including the production of ammonia.

The need of electrical energy to power an electric arc as a source of energy needed to make the cyanamide or dicyandiamide is not a disadvantage especially if the energy used is stranded electrical energy; for example gas well platforms in the North Sea are excellent sites for wave and wind energy converters; and the mixture of ammonia and carbon dioxide produced by reacting cyanamide or dicyandiamide with water can be useful in cases where the formation of ammonium carbamate will not plug up the system. Similarly, the mixture of ammonia and carbon dioxide produced by reacting cyanoguanidine or cyanamide with water or steam with a catalyst, that may be a mixture of metallic zinc and vanadium pentoxide, to form ammonia and carbon dioxide being used as a fuel can be useful in cases where the formation of ammonium carbamate and/or ammonium carbonate will not plug up the system.

A mixture of metallic zinc and vanadium pentoxide greatly enhances the hydrolysis of dicyandiamide in water at temperatures greater than 175 °C.

Indeed, a further proposal is that a catalyst comprising vanadium and zinc should be used in the hydrolysis of cyanoguanidine. Thus, an aspect of the present invention is a method of hydrolysing cyanoguanidine wherein cyanoguanidine is reacted with water in the presence of a catalyst, the catalyst comprising vanadium and zinc. Suitably the zinc is metallic zinc.

Suitably the vanadium is provided as vanadium in the +5 oxidation state, for example vanadium pentoxide.

The present inventors have observed that as a result of the reaction between cyanoguanidine and water in the presence of the catalyst, the oxidation state of some or all of the vanadium may change. For example, some or all of the vanadium may be reduced to vanadium in one or more of the +2, +3 and +4 oxidation states. Without wishing to be bound by theory, the present inventors consider that the zinc may be acting to reduce the vanadium +5 in-situ. Indeed, in particular, the present inventors consider that the "active"
form of the catalyst may comprise vanadium in the +3 oxidation state, this observation arising from the characteristic dark green colour of V +3.

According to experiments conducted by the present inventors, there is a synergistic effect arising from the use of vanadium (e.g. vanadium pentoxide) and zinc. The present inventors have observed increased conversion of cyanoguanidine as compared to vanadium or zinc alone.

A yet further proposal is that cyanoguanidine be used in selective catalytic and non-catalytic reduction (SCR and SNCR) methods and apparatus. Specifically, the proposal for SCR is that cyanoguanidine be used, suitably in the exhaust stream of vehicles and the like, to convert nitrogen oxides (NOx) into N₂ and water. As for SNCR, the proposal is that cyanoguanidine be used, suitably in the flue gas of a power plant, boiler or similar, to reduce, ameliorate or remove nitrogen oxide (NOx) emissions.

Conventionally, urea is used in SNCR and SCR reactions to reduce the NOx pollutants in exhaust gases from combustion from diesel, dual fuel, and lean-burn natural gas engines. For example, a water-based urea solution can be injected 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.

In embodiments, cyanoguanidine is injected into the engine exhaust gases in molten form as opposed to urea which is carried in a concentrated solution and because it carries several times the amount of ammonia available in the same mass of urea solution. The present inventors have observed that molten urea has drawbacks because it rapidly decomposes at its melting point with the release of ammonia and isocyanic acid. Cyanoguinidine has a higher melting point than urea (209 °C as compared to 135 °C) but cyanoguinidin does not decompose until it reaches a higher temperature. Using either engine heat or an electric heater, the cyanoguinidine could be metered into the exhaust.

Thus, the present invention provides a method (suitably a SCR method) of reducing the NOx content of engine exhaust, the method comprising the step of introducing (e.g. injecting) cyanoguanidine into the exhaust gases.

The present invention provides a method (suitably a SNCR method) of reducing the NOx content of flue gases, the method comprising the step of introducing (e.g. injecting) cyanoguanidine into the flue gases.

In embodiments, features from specific embodiments may be combined with features from other embodiments. For example, features from one embodiment may be combined with features from any of the other embodiments.
In further embodiments, additional features may be added to the specific embodiments described herein.

The following paragraphs define aspects and optional features of the present invention:

1) A method to produce transportation fuel by: a) mixing a source of carbon with calcium oxide and nitrogen gas with a practical minimum of free oxygen; b) subjecting this combination to an electric arc to produce a mixture of gaseous and solid products; c) reacting the products with water to eliminate calcium carbide with the released acetylene gas burned to supply energy and the remaining solid, consisting of calcium cyanamidate and other products passed to a reaction vessel; d) reacting the calcium cyanamidate according to the Frank-Caro Process, thereby obtaining cyanamide and calcium carbonate; e) using heat to convert the calcium carbonate to calcium oxide for use in step a); f) separating the cyanamide product from water and other products; and g) marketing the cyanamide as a fuel that has a melting temperature of about 45°C and is only mildly toxic.

2) The method of paragraph 1) further comprising the conversion by known art of cyanamide to dicyandiamide and marketing of this as a non-toxic solid with a melting temperature of 209°C as a transportation fuel.

3) The method of any one of the preceding paragraphs wherein the cyanamide is reacted with water to form ammonia and carbon dioxide, the ammonia being used as a fuel.

4) The method of any one of the preceding paragraphs wherein the ammonia is separated into nitrogen and hydrogen by either electrolysis or thermal cracking and the hydrogen is used as fuel.

5) The method of any one of the preceding paragraphs wherein a mixture of dicyandiamide and calcium hydroxide is reacted with water to form ammonia and calcium carbonate, the substantially pure ammonia being used as a fuel either as ammonia or as hydrogen after separation to nitrogen and hydrogen by either electrolysis or thermal cracking.

6) The method of any one of the preceding paragraphs wherein the cyanamide is combined with oxygen and burned to produce heat.

7) The method of any one of the preceding paragraphs wherein a mixture of cyanamide and a combustion enhancer is combined with oxygen and burned to produce heat.

8) The method of any one of the preceding paragraphs whereby the combustion enhancer is hydrogen, an alcohol, a fossil fuel, or a mixture of these.

9) The method of any one of the preceding paragraphs wherein a mixture of dicyandiamide and a combustion enhancer is mixed with oxygen and burned to produce heat.
10) The method of any one of the preceding paragraphs wherein the combustion enhancer is hydrogen, an alcohol, a petroleum-based fuel, or a mixture of these.

5 11) The method of any one of the preceding paragraphs wherein a mixture consisting of cyanamide, dicyandiamide, and a combustion enhancer is mixed with oxygen and burned to produce heat.

12) The method of paragraph 11) whereby the combustion enhancer is hydrogen, an alcohol, a petroleum-based fuel, or a mixture of these.

13) The method of any one of the preceding paragraphs wherein the electric arc is a rotating-arc.

15 14) The method of any one of the preceding paragraphs wherein the electric arc is a DC arc.

15) The method of any one of the preceding paragraphs whereby the nitrogen is injected downstream of the electric arc so as to react with the hot products leaving the arc region.

20 16) The method of any one of the preceding paragraphs whereby the electric arc is replaced by a microwave-generated plasma.

17) The method of any one of the preceding paragraphs wherein the cyanamide is reacted with water and oxygen in a fuel cell to produce carbon dioxide, water, and nitrogen, thereby generating energy.

18) The method of any one of the preceding paragraphs wherein the dicyandiamide is reacted with water and oxygen in a fuel cell to produce carbon dioxide, water, and nitrogen, thereby generating energy.

30 19) The method of any one of the preceding paragraphs wherein the source of carbon is natural gas.

20) The method of any one of the preceding paragraphs wherein the source of carbon is biochar.

21) The method of any one of the preceding paragraphs wherein the source of carbon is waste plastic.

40 22) The method of paragraph 21) wherein at least a portion of the waste plastic is tire-waste.

23) The method of any one of the preceding paragraphs wherein the source of carbon is a mixture of coal and hydrogen.
24) The method of any one of the preceding paragraphs wherein gaseous hydrogen is added to the source mixture.

25) The method of any one of the preceding paragraphs wherein product dicyandiamide is separated from the solid products.

26) The method of paragraph 25) wherein the separation of dicyandiamide from the solid is accomplished by heating above 209 °C and decanting the molten dicyandiamide.

27) The method of any one of the preceding paragraphs wherein the product water is separated by hydration of the alkaline-earth oxide to alkaline-earth hydroxide.

28) The method of any one of the preceding paragraphs wherein all calcium compounds are replaced by the corresponding magnesium compounds.

29) The method of any one of the preceding paragraphs wherein all calcium compounds are replaced by a mixture of the corresponding calcium and magnesium compounds.

30) A method to produce transportation fuel comprising: a) mixing a source of carbon and of hydrogen with calcium oxide and nitrogen gas with a practical minimum of free oxygen and, preferably, about 1 weight percent of CaF2 to act as a catalyst or flux; b) subjecting this combination to an electric arc to produce a mixture of gaseous and solid products; c) reacting the products with an amount of water sufficient to eliminate the amount of calcium carbide that has produced in step b), burning acetylene gas thereby produced, and retaining the heat and the remaining solids, which consist of calcium cyanamidé and other products that are passed to a reaction vessel; d) reacting the calcium cyanamidé according to the Frank-Caro Process, thereby obtaining cyanamidé and calcium carbonate; e) using heat to convert the calcium carbonate to calcium oxide for use in step a); f) separating the cyanamidé product from water and other products; g) converting by known art the cyanamidé to dicyandiamidé, which is also known as cyanoguanidine; and h) marketing of this dicyandiamidé as a safe transportation fuel with a melting point of about 209°C.

31) The method of paragraph 30) wherein a mixture of dicyandiamidé and calcium hydroxide is reacted with water or steam, preferably with a catalyst that may be a mixture of metallic zinc and vanadium pentoxide, or a catalyst where a vanadium compound is in the oxidation state lower than +5 to form ammonia and calcium carbonate, the substantially pure ammonia being used as a fuel.

32) The method of paragraph 31) wherein the ammonia is separated into nitrogen and hydrogen by either electrolysis or thermal cracking and the hydrogen is used as fuel.
33) The method of any one of paragraphs 31) to 32) wherein the dicyandiamide is combined with oxygen and burned to produce heat.

34) The method of any one of paragraphs 31) to 33) wherein a mixture of dicyandiamide and a combustion enhancer is mixed with oxygen and burned to produce heat.

35) The method of paragraph 34) wherein the combustion enhancer is hydrogen, an alcohol, a petroleum-based fuel, or a mixture of these.

36) The method of any one of paragraphs 31) to 35) wherein the electric arc is a rotating-arc.

37) The method of any one of paragraphs 31) to 36) wherein the electric arc is a DC arc.

38) The method of any one of paragraphs 31) to 37) whereby the nitrogen is injected at a point where the products leaving the electric arc have cooled to a temperature in the range of 800-1200 C.

39) The method of any one of paragraphs 31) to 38) whereby the electric arc is replaced by a microwave-generated plasma.

40) The method of any one of paragraphs 31) to 39) wherein the dicyandiamide is reacted with water and oxygen in a fuel cell to produce carbon dioxide, water, and nitrogen, thereby generating energy.

41) The method of any one of paragraphs 31) to 40) wherein the source of carbon and of hydrogen is natural gas.

42) The method of any one of paragraphs 31) to 41) wherein the source of carbon is biochar.

43) The method of any one of paragraphs 31) to 42) wherein the source of carbon and of hydrogen is waste plastic.

44) The method of paragraph 43) wherein at least a portion of the waste plastic is tire-waste.

45) The method of any one of paragraphs 31) to 44) wherein the source of carbon and of hydrogen is a mixture of coal and hydrogen.

46) The method of any one of paragraphs 31) to 45) wherein gaseous hydrogen is added to the source mixture.
47) The method of any one of paragraphs 31) to 46) wherein product dicyandiamide is separated from the solid products.

48) The method of paragraph 47) wherein the separation of dicyandiamide from the solid is accomplished by heating above 209°C and decanting the molten dicyandiamide.

49) The method of any one of paragraphs 31) to 48) wherein the product water is separated by hydration of the alkaline-earth oxide to alkaline-earth hydroxide.

50) The method any one of paragraphs 31) to 49) wherein all calcium compounds are replaced by the corresponding magnesium compounds.

51) The method of any one of paragraphs 31) to 50) wherein all calcium compounds are replaced by a mixture of the corresponding calcium and magnesium compounds.

52) The method any one of paragraphs 31) to 51) wherein molten dicyandiamide is injected into the cylinder of a Diesel engine when the piston is near top-dead-center.

53) The method of any one of paragraphs 31) to 52) wherein molten dicyandiamide is aspirated into the intake manifold of an Otto Cycle engine.

54) The method of any one of paragraphs 31) to 53) wherein molten dicyandiamide is aspirated into the fuel-air intake stream of a gas turbine engine.

55) The method of any one of paragraphs 31) to 54) wherein solid dicyandiamide is feed into the fuel intake stream of a steam turbine generator.

56) The method of any one of paragraphs 31) to 55) wherein molten dicyandiamide is feed into the fuel intake stream of a steam turbine generator.

57) The method of any one of paragraphs 31) to 56) wherein solid dicyandiamide is feed into the fuel intake stream of a reciprocating steam engine.

58) The method of any one of paragraphs 31) to 57) wherein molten dicyandiamide is feed into the fuel intake stream of a steam turbine generator.

59) The method of any one of paragraphs 31) to 58) wherein solid dicyandiamide is feed into the fuel intake stream of a reciprocating steam engine.

60) The method of any one of paragraphs 31) to 59) wherein at least some of the free hydrogen gas that is produced in step b) is reacted with carbon dioxide according to the known art Sabatier Reaction to produce methane and water, this methane being added to the supply of source carbon and hydrogen materials.
61) The method of paragraph 60) wherein free hydrogen gas obtained from carbon monoxide that is produced in step b) and that is reacted with water according to a known art "Water Gas Shift Reaction" to produce free hydrogen gas and carbon dioxide that are added to the supply of source materials for the Sabatier Reaction.

62) The method of any one of paragraphs 31) to 61) wherein at least some of the free hydrogen gas that is produced in step b) is reacted with carbon dioxide according to the known art Bosch Reaction to produce carbon and water, this carbon being added to the supply of source carbon and hydrogen materials.

63) The method of paragraph 62) wherein at least a portion of the carbon dioxide needed for the Sabatier Reaction is obtained from the atmosphere by spontaneous reaction of either calcium oxide or magnesium oxide to calcium carbonate or magnesium carbonate that is subsequently heated to obtain the concentrated carbon dioxide and to recover the calcium oxide or magnesium oxide.

64) The method of paragraph 63) wherein at least some of the acetylene produced is partially oxidized to produce carbon black that is added to the supply of carbon material.

65) The method of paragraph 64) wherein at least a portion of the carbon dioxide needed for the Sabatier Reaction is obtained from the atmosphere by spontaneous reaction of either calcium hydroxide or magnesium hydroxide to calcium carbonate or magnesium carbonate that is subsequently heated to obtain the concentrated carbon dioxide and to recover the calcium oxide or magnesium oxide.

66) The method of paragraph 65) wherein at least a portion of the carbon dioxide needed for the Bosch Reaction is obtained from the atmosphere by spontaneous reaction of either calcium oxide or magnesium oxide to calcium carbonate or magnesium carbonate that is subsequently heated to obtain the concentrated carbon dioxide and to recover the calcium oxide or magnesium oxide.

67) A method to produce transportation fuel comprising: a) by known art producing urea for available energy and sources of carbon, hydrogen, nitrogen, and oxygen; b) heating this urea with magnesium oxide or magnesium dioxide or magnesium carbonate or a mixture of these oxygen containing magnesium compounds at a molar ratio of urea to magnesium compound in the range of about 1:1 to about 4:1 to a temperature between about 133 C and about 160 C until it is thoroughly melted; c) transferring the molten material of step b) to a device where it is heated to between about 230 C to about 400 C with continuous mixing or tumbling or kneading action until a solid is formed; d) calcining this solid, which contains magnesium cyanamide, at temperatures between 600 C and 900 C; reacting this magnesium cyanamide with water and carbon dioxide to form cyanamide and magnesium carbonate; e) separating the cyanamide from the magnesium carbonate; f) heating the
magnesium carbonate above 500 °C to recover the MgO if MgO or Mg(OH)₂ are used for
step b) or powdering the MgCO₃ to a grain size between 1 µm to 200 µm if the carbonate is
used in step b); g) converting by known art the cyanamide to dicyandiamide, which is also
known as cyanothritol; and h) marketing of this dicyandiamide as a safe transportation
fuel with a melting point of about 209°C.

68) The method of paragraph 67) wherein ammonia that is produced as a by-product of the
reaction of urea is retained and reused to make urea.

69) The method of any one of paragraphs 67) to 68) wherein a mixture of dicyandiamide and
calcium hydroxide is reacted with water or steam, preferably with a catalyst that may be a
mixture of metallic zinc and vanadium pentoxide, to form ammonia and calcium carbonate,
the substantially pure ammonia being used as a fuel.

70) The method of paragraph 69) wherein the ammonia is separated into nitrogen and
hydrogen by either electrolysis or thermal cracking and the hydrogen is used as fuel.

71) The method of any one of paragraphs 67) to 70) wherein the dicyandiamide is combined
with oxygen and burned to produce heat.

72) The method of any one of paragraphs 67) to 72) wherein a mixture of dicyandiamide and
a combustion enhancer is combined with oxygen and burned to produce heat.

73) The method of paragraph 72) whereby the combustion enhancer is hydrogen, an
alcohol, a fossil fuel, or a mixture of these.

74) The method of any one of paragraphs 67) to 73) wherein the dicyandiamide is reacted
with water and oxygen in a fuel cell to produce carbon dioxide, water, and nitrogen, thereby
generating energy.

75) The method of any one of paragraphs 67) to 74) wherein molten dicyandiamide is
injected into the cylinder of a Diesel engine when the piston is near top-dead-center.

76) The method of any one of paragraphs 67) to 75) wherein molten dicyandiamide is
aspirated into the intake manifold of an Otto Cycle engine.

77) The method of any one of paragraphs 67) to 76) wherein molten dicyandiamide is
aspirated into the fuel-air intake stream of a gas turbine engine.

78) The method of any one of paragraphs 67) to 77) wherein solid dicyandiamide is feed into
the fuel intake stream of a steam turbine generator.
79) The method of any one of paragraphs 67) to 78) wherein molten dicyandiamide is feed into the fuel intake stream of a steam turbine generator.

80) The method of any one of paragraphs 67) to 79) wherein solid dicyandiamide is feed into the fuel intake stream of a reciprocating steam engine.

81) The method of any one of paragraphs 67) to 80) wherein molten dicyandiamide is feed into the fuel intake stream of a steam turbine generator.

82) The method of any one of paragraphs 67) to 81) wherein solid dicyandiamide is feed into the fuel intake stream of a reciprocating steam engine.

83) The method of any one of paragraphs 31) to 82) wherein the calcium cyanamide is separated from the unreacted calcium carbide by heating the mixture in the range of 1000 - 1200 C, whereby the calcium cyanamide sublimes from the mixture and can be collected for further processing.

84) The method of any one of paragraphs 31) to 83) wherein following the removal of calcium cyanamide described in claim 54) the mixture containing calcium carbide and other products resulting from the reaction is recycled back to the step involving the addition of nitrogen to the calcium carbide resulting in the formation of additional calcium cyanamide.

85) The method of any one of paragraphs 31) to 84) whereby the dicyandiamide is combined with water at temperatures greater than 150C yielding ammonia and carbon dioxide.

86) The method of paragraph 85) whereby the ammonia is used to fuel an internal combustion engine.

87) The method of paragraph 85) or 86) whereby the ammonia is used to fuel a solid oxide fuel cell.

88) The method of any one of paragraphs 85) to 87) whereby a combustion enhancer is added to the ammonia before entering the engine.

89) The method of paragraph 88) whereby the combustion enhancer is selected from the group consisting of hydrogen, an alcohol, a ketone, a low-molecular weight hydrocarbon, a fossil fuel, a combination of the above.

90) The method of paragraph 89) where the hydrogen is produced by partially decomposing the ammonia into hydrogen and nitrogen.
91) The method of any one of paragraphs 85) to 90) whereby a catalyst is present to enhance the decomposition of the dicyandiamide.

92) The method of paragraph 91) where the catalyst is a vanadium-containing compound.

93) The method of paragraph 92) where the vanadium is in an oxidation state selected from the group consisting of the +1 state, +2 state, +3 state, a combination of the above.

94) The method of any one of paragraphs 31) to 93) wherein a mixture of dicyandiamide is reacted with water or steam, preferably with a catalyst that may be a mixture of metallic zinc and vanadium pentoxide, to form a mixture of ammonia and carbon dioxide being used as a fuel.

95) The method of paragraph 94) wherein the mixture of ammonia and carbon dioxide may be scrubbed essentially free of carbon dioxide so that a substantially pure ammonia being used as a fuel.

96) A method to produce transportation fuel comprising: a) mixing a source of carbon and of hydrogen with calcium oxide and nitrogen gas with a practical minimum of free oxygen and, preferably, about 1 weight percent of CaF$_2$ to act as a catalyst or flux; b) subjecting this combination to an electric arc to produce a mixture of gaseous and solid products; c) reacting the products with an amount of water sufficient to eliminate the amount of calcium carbide that has produced in step b), burning acetylene gas thereby produced, and retaining the heat and the remaining solids, which consist of calcium cyanamide and other products that are passed to a reaction vessel; d) reacting the calcium cyanamide according to the Frank-Caro Process, thereby obtaining cyanamide and calcium carbonate; e) using heat to convert the calcium carbonate to calcium oxide for use in step a); f) separating the cyanamide product from water and other products; and g) marketing the cyanamide as a fuel that has a melting temperature of about 46 C and is only mildly toxic.

97) The method of paragraph 96) wherein a mixture of cyanamide and calcium hydroxide is reacted with water or steam, preferably with a catalyst that may be a mixture of metallic zinc and vanadium pentoxide, or a catalyst where a vanadium compound is in the oxidation state lower than +5 to form ammonia and calcium carbonate, the substantially pure ammonia being used as a fuel.

98) The method of paragraph 96) or 97) wherein the ammonia is separated into nitrogen and hydrogen by either electrolysis or thermal cracking and the hydrogen is used as fuel.

99) The method of any one of paragraphs 96) to 98) wherein the cyanamide is combined with oxygen and burned to produce heat.
100) The method of any one of paragraphs 96) to 99) wherein a mixture of cyanamide and a combustion enhancer is combined with oxygen and burned to produce heat.

101) The method of paragraph 100) wherein the combustion enhancer is hydrogen, an alcohol, a fossil fuel, or a mixture of these.

102) The method of any one of paragraphs 96) to 101) wherein the electric arc is a rotating-arc.

103) The method of any one of paragraphs 96) to 102) wherein the electric arc is a DC arc.

104) The method of any one of paragraphs 96) to 103) whereby the nitrogen is injected at a point where the products leaving the electric arc have cooled to a temperature in the range of 800-1200 C.

105) The method of any one of paragraphs 96) to 104) whereby the electric arc is replaced by a microwave-generated plasma.

106) The method of any one of paragraphs 96) to 105) wherein the cyanamide is reacted with water and oxygen in a fuel cell to produce carbon dioxide, water, and nitrogen, thereby generating energy.

107) The method of any one of paragraphs 96) to 106) wherein the source of carbon and of hydrogen is natural gas.

108) The method of any one of paragraphs 96) to 107) wherein the source of carbon is biochar.

109) The method of any one of paragraphs 96) to 108) wherein the source of carbon and of hydrogen is waste plastic.

110) The method of paragraph 109) wherein at least a portion of the waste plastic is tire-waste.

111) The method of any one of paragraphs 96) to 110) wherein the source of carbon and of hydrogen is a mixture of coal and hydrogen.

112) The method of any one of paragraphs 96) to 111) wherein gaseous hydrogen is added to the source mixture.

113) The method of any one of paragraphs 96) to 112) wherein product cyanamide is separated from the solid products.
114) The method of paragraph 113) wherein the separation of cyanamide from the solid is accomplished by heating above 46 °C and decanting the molten cyanamide.

115) The method of any one of paragraphs 96) to 114) wherein the product water is separated by hydration of the alkaline-earth oxide to alkaline-earth hydroxide.

116) The method of any one of paragraphs 96) to 115) wherein all calcium compounds are replaced by the corresponding magnesium compounds.

117) The method of any one of paragraphs 96) to 116) wherein all calcium compounds are replaced by a mixture of the corresponding calcium and magnesium compounds.

118) The method of any one of paragraphs 96) to 117) wherein molten cyanamide is injected into the cylinder of a Diesel engine when the piston is near top-dead-center.

119) The method of any one of paragraphs 96) to 118) wherein molten cyanamide is aspirated into the intake manifold of an Otto Cycle engine.

120) The method of any one of paragraphs 96) to 119) wherein molten cyanamide is aspirated into the fuel-air intake stream of a gas turbine engine.

121) The method of any one of paragraphs 96) to 120) wherein solid cyanamide is feed into the fuel intake stream of a steam turbine generator.

122) The method of any one of paragraphs 96) to 121) wherein molten cyanamide is feed into the fuel intake stream of a steam turbine generator.

123) The method of any one of paragraphs 96) to 122) wherein solid cyanamide is feed into the fuel intake stream of a reciprocating steam engine.

124) The method of any one of paragraphs 96) to 123) wherein solid cyanamide is feed into the fuel intake stream of a gas turbine engine.

125) The method of any one of paragraphs 96) to 124) wherein molten cyanamide is feed into the fuel intake stream of a reciprocating steam engine.

126) The method of any one of paragraphs 96) to 125) wherein at least some of the free hydrogen gas that is produced in step b) is reacted with carbon dioxide according to the known art Sabatier Reaction to produce methane and water, this methane being added to the supply of source carbon and hydrogen materials.

127) The method of 126) wherein free hydrogen gas obtained from carbon monoxide that is produced in step b) and that is reacted with water according to a known art "Water Gas Shift
Reaction" to produce free hydrogen gas and carbon dioxide that are added to the supply of source materials for the Sabatier Reaction.

128) The method of any one of paragraphs 96) to 127) wherein at least some of the free hydrogen gas that is produced in step b) is reacted with carbon dioxide according to the known art Bosch Reaction to produce carbon and water, this carbon being added to the supply of source carbon and hydrogen materials.

129) The method of any one of paragraphs 96) to 128) wherein at least a portion of the carbon dioxide needed for the Sabatier Reaction is obtained from the atmosphere by spontaneous reaction of either calcium oxide or magnesium oxide to calcium carbonate or magnesium carbonate that is subsequently heated to obtain the concentrated carbon dioxide and to recover the calcium oxide or magnesium oxide.

130) The method of any one of paragraphs 96) to 129) wherein at least some of the acetylene produced is partially oxidized to produce carbon black that is added to the supply of carbon material.

131) The method of any one of paragraphs 96) to 130) wherein at least a portion of the carbon dioxide needed for the Sabatier Reaction is obtained from the atmosphere by spontaneous reaction of either calcium hydroxide or magnesium hydroxide to calcium carbonate or magnesium carbonate that is subsequently heated to obtain the concentrated carbon dioxide and to recover the calcium oxide or magnesium oxide.

132) The method of any one of paragraphs 96) to 131) wherein at least a portion of the carbon dioxide needed for the Bosch Reaction is obtained from the atmosphere by spontaneous reaction of either calcium oxide or magnesium oxide to calcium carbonate or magnesium carbonate that is subsequently heated to obtain the concentrated carbon dioxide and to recover the calcium oxide or magnesium oxide.

133) A method to produce transportation fuel comprising: a) by known art producing urea from available energy and sources of carbon, hydrogen, nitrogen, and oxygen; b) heating this urea with magnesium oxide or magnesium dioxide or magnesium carbonate or a mixture of these oxygen containing magnesium compounds at a molar ratio of urea to magnesium compound in the range of about 1:1 to about 4:1 to a temperature between about 133 C and about 160 C until it is thoroughly melted; c) transferring the molten material of step b) to a device where it is heated to between about 230 C to about 400 C with continuous mixing or tumbling or kneading action until a solid is formed; d) calcining this solid, which contains magnesium cyanamide, at temperatures between 600 C and 900 C; e) separating the cyanamide from the magnesium carbonate; f) heating the magnesium carbonate above 500 C to recover the MgO if MgO or Mg(OH)₂ are used for step b) or powdering the MgCO₃ to a grain size between 1 µη to 200 µη if the
carbonate is used in step b); and g) marketing the cyanamide as a fuel that has a melting
temperature of about 46°C, is stabilized by a fraction of a weight percent of magnesium ion
that is retained during this process, and is only mildly toxic.

5 134) The method of paragraph 133) wherein ammonia that is produced as a by-product of
the reaction of urea is retained and reused to make urea.

135) The method of paragraph 133) or 134) wherein a mixture of cyanamide and calcium
hydroxide is reacted with water or steam, preferably with a catalyst that may be a mixture of
metallic zinc and vanadium pentoxide, to form ammonia and calcium carbonate, the
substantially pure ammonia being used as a fuel.

136) The method of paragraph 135) wherein the ammonia is separated into nitrogen and
hydrogen by either electrolysis or thermal cracking and the hydrogen is used as fuel.

15 137) The method of any one of paragraphs 133) to 136) wherein the cyanamide is combined
with oxygen and burned to produce heat.

138) The method of any one of paragraphs 133) to 137) wherein a mixture of cyanamide
and a combustion enhancer is combined with oxygen and burned to produce heat.

139) The method of paragraph 138) whereby the combustion enhancer is hydrogen, an
alcohol, a fossil fuel, or a mixture of these.

25 140) The method of any one of paragraphs 133) to 139) wherein the cyanamide is reacted
with water and oxygen in a fuel cell to produce carbon dioxide, water, and nitrogen, thereby
generating energy.

141) The method of any one of paragraphs 133) to 140) wherein molten cyanamide is
injected into the cylinder of a Diesel engine when the piston is near top-dead-center.

142) The method of any one of paragraphs 133) to 141) wherein molten cyanamide is
aspirated into the intake manifold of an Otto Cycle engine.

35 143) The method of any one of paragraphs 133) to 142) wherein molten cyanamide is
aspirated into the fuel-air intake stream of a gas turbine engine.

144) The method of any one of paragraphs 133) to 143) wherein solid cyanamide is feed
into the fuel intake stream of a gas turbine engine.

40 145) The method of any one of paragraphs 133) to 144) wherein molten cyanamide is feed
into the fuel intake stream of a steam turbine engine.
146) The method of any one of paragraphs 133) to 145) wherein solid cyanamide is feed into the fuel intake stream of a steam turbine engine.

147) The method of any one of paragraphs 133) to 146) wherein molten cyanamide is feed into the fuel intake stream of a reciprocating steam engine.

148) The method of any one of paragraphs 133) to 147) wherein solid cyanamide is feed into the fuel intake stream of a reciprocating steam engine.

149) The method of any one of paragraphs 133) to 148) wherein the calcium cyanamide is separated from the unreacted calcium carbide by heating the mixture in the range of 1000 - 1200 °C, whereby the calcium cyanamide sublimes from the mixture and can be collected for further processing.

150) The method of any one of paragraphs 96) to 149) whereby following the removal of calcium cyanamide described in paragraph 149) the mixture containing calcium carbide and other products resulting from the reaction is recycled back to the step involving the addition of nitrogen to the calcium carbide resulting in the formation of additional calcium cyanamide.

151) The method of any one of paragraphs 96) to 150) whereby the cyanamide is combined with water at temperatures greater than 150°C yielding ammonia and carbon dioxide.

152) The method of paragraph 151) whereby the ammonia is used to fuel an internal combustion engine.

153) The method of paragraph 151) whereby the ammonia is used to fuel a solid oxide fuel cell.

154) The method of paragraph 152) whereby a combustion enhancer is added to the ammonia before entering the engine.

155) The method of paragraph 154) whereby the combustion enhancer is selected from the group consisting of hydrogen, an alcohol, a ketone, a low-molecular weight hydrocarbon, a fossil fuel, a combination of the above.

156) The method of paragraph 155) where the hydrogen is produced by partially decomposing the ammonia into hydrogen and nitrogen.

157) The method of any one of paragraphs 96) to 156) whereby a catalyst is present to enhance the decomposition of the dicyandiamide.

158) The method of paragraph 157) where the catalyst is a vanadium-containing compound.
159) The method of paragraph 158) where the vanadium is in an oxidation state selected from the group consisting of the +1 state, +2 state, +3 state, a combination of the above.

160) The method of any one of paragraphs 96) to 159) wherein a mixture of cyanamide is reacted with water or steam, preferably with a catalyst that may be a mixture of metallic zinc and vanadium pentoxide, to form a mixture of ammonia and carbon dioxide being used as a fuel.

161) The method of paragraph 160) wherein the mixture of ammonia and carbon dioxide may be scrubbed essentially free of carbon dioxide so that a substantially pure ammonia being used as a fuel.

162) A method for generating energy from a cyanamide composition, the method comprising: (a) reacting the composition with water to form ammonia and carbon dioxide; and (b) oxidizing the ammonia formed in step (a) to form water and nitrogen generating energy.

163) The method of paragraph 162), wherein the weight of cyanoguanidine in the composition is equal to about 10% to about 100% of the weight of the composition.

164) The method of paragraph 162) or 163), wherein a portion of the water formed in step (b) is reacted with the composition in step (a) to form ammonia.

165) The method of any one of paragraphs 162) to 164), wherein the composition reacts with water in step (a) at a temperature ranging between about 50° C and about 360° C and a pressure ranging between about 1 ambient atmosphere and 200 standard atmospheres.

166) The method of paragraph 165), wherein the method comprises mixing or contacting the composition with a catalyst capable of catalyzing the reaction of the composition with water in step (a).

167) The method of paragraph 166), wherein the catalyst is an oxide of a metal, wherein the metal is selected from the group consisting of iron, nickel, vanadium, and zinc.

168) The method of paragraph 166), wherein the vanadium catalyst is a composition of vanadium pentoxide with metallic zinc resulting in a composition wherein the oxidation states of vanadium are selected from the group consisting of +1, +2, +3, and a combination thereof.

169) The method of any one of paragraphs 162) to 168), wherein the composition further comprises a component selected from the group consisting of a combustible fuel, a combustion enhancer, ammonia, ammonium bicarbonate, ammonium carbonate, ammonium hydroxide, calcium cyanamide, magnesium cyanamide, zinc cyanamide, calcium
hydroxide, magnesium hydroxide, zinc hydroxide, hydrogen cyanamide, cyanoguanidine,
guanidine, ammonium carbamate, guanylurea, urea, calcium carbide, magnesium carbide,
zinc carbide, water, and a combination thereof.

170) The method of paragraph 169), wherein the component is a combustible fuel present in
an amount which can be combusted to generate a sufficient amount of heat to initiate a
reaction of cyanoguanidine with water.

171) The method of paragraph 169), wherein the composition is a suspension which
contains a surfactant to help maintain the suspension of the components in the liquid
components.

172) The method of any one of paragraphs 162) to 171), wherein the method comprises
mixing or contacting the composition with an enzyme capable of catalyzing the reaction of
the composition with water.

173) The method of paragraph 172), wherein the enzyme is capable of catalyzing the
reaction of the composition with water at a temperature ranging between room temperature
and a temperature at which the half-life of the enzyme is less than 1 minute.

174) The method of paragraph 172), wherein the enzyme is selected from the group
consisting of arginase, urease, and a combination thereof.

175) The method of any one of paragraphs 162) to 174), wherein step (b) comprises burning
the ammonia formed in step (a).

176) The method of paragraph 175), wherein nitrogen oxides are formed in step (b) and the
method further comprises reacting a portion of the unburned ammonia from the exhaust of
combustion step (b) with the nitrogen oxides to reduce the nitrogen oxides and the unburned
ammonia.

177) The method of paragraph 175), wherein the ammonia is combusted in an internal
combustion engine having a compression ratio selected from the group consisting of a
compression ratio between 9:1 and 30:1 and a compression ratio greater than 30:1.

178) The method of any one of paragraphs 162) to 177), wherein at least a fraction of the
carbon dioxide is stored under pressure to serve one or more purposes chosen from
prevention of release to the atmosphere, provision of a reactant in a chemical process,
provision of inert gas to extinguish fire, provision of feed stock for dry ice, preserving food,
provision of compressed gas to power a pneumatic device and a combination thereof.

179) The method of any one of paragraphs 162) to 178), wherein a portion of the water
produced in step (b) is retained to aid in the retention of the carbon dioxide under pressure.
A method for generating energy from a composition containing cyanoguanidine comprising: (a) reacting the composition with water to form ammonia and carbon dioxide; (b) converting the ammonia formed in step (a) to nitrogen and hydrogen; and (c) oxidizing the hydrogen formed in step (b) to form water generating energy.

The method of paragraph 180), wherein the weight of the weight of cyanoguanidine in the composition is equal to about 10% to about 100% of the weight of the composition.

The method of any one of paragraphs 180) to 181), wherein the composition reacts with water in step (a) at a temperature ranging between about 50° C and about 240° C and a pressure ranging between about 1 ambient atmosphere and 50 standard atmospheres.

The method of any one of paragraphs 180) to 182), wherein a portion of the water exhausted by a fuel cell or by an internal or external combustion engine is reacted with the composition to form ammonia in step (a).

The method of any one of paragraphs 180) to 183), wherein the method comprises mixing or contacting the composition with a catalyst capable of catalyzing the reaction of the composition with water in step (a).

The method of paragraph 184), wherein the catalyst is an oxide of a metal, wherein the metal is selected from the group consisting of iron, nickel, vanadium and zinc.

The method of paragraph 185), wherein the catalyst is a composition of vanadium pentoxide that has been treated with metallic zinc.

The method of any one of paragraphs 180) to 186), wherein the composition further comprises a component selected from the group consisting of a combustible fuel, a combustion enhancer, ammonia, ammonium bicarbonate, ammonium carbonate, ammonium hydroxide, calcium cyanamide, magnesium cyanamide, zinc cyanamide, calcium hydroxide, magnesium hydroxide, zinc hydroxide, hydrogen cyanamide, cyanoguanidine, guanidine, ammonium carbamate, guanyurea, urea, calcium carbide, magnesium carbide, zinc carbide, water, and a combination thereof.

The method of paragraph 187), wherein the component is a combustible fuel present in an amount which can be combusted to generate a sufficient amount of heat to initiate a reaction of cyanoguanidine with water.

The method of any one of paragraphs 180) to 188), wherein the composition is a suspension which contains a surfactant to help maintain the suspension of the components in the liquid components.
190) The method of any one of paragraphs 180) to 189), wherein the method comprises mixing or contacting the composition with an enzyme capable of catalyzing the reaction of the composition with water.

5 191) The method of paragraph 190), wherein the enzyme is capable of catalyzing the reaction of the composition with water at a temperature ranging between room temperature and a temperature at which the half-life of the enzyme is less than 1 minute.

192) The method of paragraph 190) or 191), wherein the enzyme is selected from the group consisting of arginase, urease, and a combination thereof.

193) The method of any one of paragraphs 180) to 192), wherein the hydrogen is separated by passing through a semi-permeable membrane that passes hydrogen but not other matter.

194) The method of paragraph 193) wherein the semi-permeable membrane is a thin film of Pd metal, Pt metal, or a dense random packing of hard spheres type amorphous metal composed of mischmetal and at least one transition metal.

195) A method for providing a cyanoguanidine containing composition, the method comprising: (a) using a source of energy to separate hydrogen from water; (b) reacting the hydrogen formed in step (a) with carbon dioxide to form carbon and water; (c) reacting a portion of the carbon formed in step (b) with calcium oxide to form calcium carbide; (d) reacting the calcium carbide formed in step (c) with a nitrogen to form a composition containing calcium cyanamide; (e) further processing the composition containing calcium cyanamide to form a composition containing cyanoguanidine.

196) The method of paragraph 195) wherein the source of energy in step (a) is selected from the group consisting of electricity generated from wind, electricity generated from ocean waves, electricity generated from hydroelectric facilities, electricity generated from solar energy, electricity generated from nuclear energy, electricity from a power grid provided as part of a load-leveling process, electricity generated from fossil fuel combustion, electricity generated from agricultural waste combustion, electricity generated from forestry waste combustion, electricity generated from municipal waste combustion, electricity generated from the tidal flow of ocean water, solar energy as used in a chemical process for the splitting of water into hydrogen and oxygen, and a combination thereof.

197) The method of any one of paragraphs 195) to 196) wherein method used to provide the nitrogen in step (d) is selected from the group consisting of fractional distillation of liquefied air, a pressure swing absorption process, collection of the partially oxygen-depleted exhaust from a combustion process, and a combination thereof.

198) The method of any one of paragraphs 195) to 197) wherein the source of carbon dioxide in step (b) is selected from the group consisting of carbon dioxide extracted from the
air, carbon dioxide extracted from products created by the combustion of fossil fuels, carbon
dioxide extracted from products created by the combustion of agricultural waste, carbon
dioxide extracted from products created by the combustion of forestry waste, carbon dioxide
extracted from products created by the combustion of municipal waste, and a combination
thereof.

199) The method of any one of paragraphs 195) to 198) wherein the weight of
cyanoguanidine in the composition formed in step (d) is equal to about 10% to about 100%
of the weight of the composition.

200) The method of any one of paragraphs 195) to 199) wherein the composition further
comprises a component selected from the group consisting of a combustible fuel, a
combustion enhancer, ammonia, ammonium bicarbonate, ammonium carbonate, ammonium
hydroxide, calcium cyanamide, magnesium cyanamide, zinc cyanamide, calcium
hydroxide, magnesium hydroxide, zinc hydroxide, hydrogen cyanamide, cyanoguanidine,
guanidine, ammonium carbamate, guanylurea, urea, calcium carbide, magnesium carbide,
zinc carbide, water, and a combination thereof.

201) The method of any one of paragraphs 195) to 200) wherein the energy is used to
separate hydrogen from a solution containing sodium chloride, thereby producing sodium
and chlorine-containing substances.

202) An apparatus for producing cyanamide-based compositions comprising: (a) a reactor
with a first section containing an electric arc and provisions for introducing CaO and a
carbon source to form compositions containing calcium carbide in a finely divided state; (b) a
second section where the hot product from step (a) is contacted with nitrogen to form a
composition containing calcium cyanamide; (c) a third section for collecting and cooling the
calcium cyanamide composition.

203) The apparatus of paragraph 202), wherein a reflector is incorporated into the first
section to partially reflect heat back into the region of the arc.

204) The apparatus of paragraph 203), wherein the reflector is constructed of molybdenum.

205) The apparatus of paragraph 203) or 204) wherein the reflector is constructed of quartz,
and contains metallic silver to partially reflect heat back into the region of the arc.

206) The apparatus of any one of paragraphs 203) to 205), wherein the reflector is cooled
by a fluid to prevent damage to the reflector.

207) The apparatus of any one of paragraphs 202) to 206) wherein the first section of the
reactor is separated from the second section of the reactor by a device that inhibits the
movement of gases between the sections and allows the transport of the calcium carbide composition from the first section to the second section.

208) The apparatus of any one of paragraphs 202) to 207) wherein heat emitted by the apparatus is used to preheat the reactants prior to entering the first section of the reactor.

209) The apparatus of any one of paragraphs 202) to 208) wherein heat emitted by the apparatus is used to partially decompose calcium carbonate into calcium oxide.

210) The apparatus of any one of paragraphs 202) to 209) wherein heat emitted by the apparatus is used to partially decompose a hydrocarbon compound into carbon and hydrogen.

211) The apparatus of any one of paragraphs 202) to 210) wherein heat emitted by the apparatus is used to partially decompose calcium carbonate into calcium oxide, to preheat the reactants prior to entering the first section of the reactor, and to partially decompose a hydrocarbon compound into carbon and hydrogen.

212) The apparatus of any one of paragraphs 202) to 211) wherein the reaction product carbon monoxide (CO) is removed from the first section of the reactor and used as a fuel.

213) The apparatus of any one of paragraphs 202) to 212) wherein the carbon source is selected from the group consisting of selected from the list containing elemental carbon, charcoal, methane, a hydrocarbon fuel, an organic hazardous waste, and a combination thereof.

214) The apparatus of paragraph 213), wherein the carbon source is produced from carbon dioxide and hydrogen.

215) The apparatus of paragraph 213) or 214), wherein the carbon dioxide is extracted from the air.

216) The apparatus of paragraph 214), wherein the hydrogen is produced using multi-chamber electrodialysis process to produce hydrogen gas, oxygen gas, NaOH solution, and hydrochloric acid from brine.

217) The apparatus of any one of paragraphs 202) to 217) wherein the second section of the reactor comprises a fluidized bed.

40 216) The method of any one of paragraphs 162) to 201) whereby the cyanamide-based material is stored in close proximity to one or more fuel cell that are capable of generating electrical energy from ammonia, which may be of the solid oxide type, and that are
maintained under conditions, such as temperature, ready to begin generating electrical energy when ammonia is supplied.

217) A system for providing power to one or more rotary arcs or plasma arcs, comprising: a continuous or intermittent power source; a transformer coupled to the intermittent power source, the transformer being configured to transform power from the intermittent power source to power with appropriate operating parameters for the rotary or plasma arcs; and a tap controller coupled to the transformer, the tap controller being configured to monitor and control the transformer such that a constant voltage is provided to the rotary or plasma arcs from the transformer regardless of the load of the rotary or plasma arcs and the power output provided by the intermittent power source.

218) The system of paragraph 217), further comprising a control system coupled to the tap controller, the control system being configured to operate the tap controller.

219) The system of paragraph 217) or 218), further comprising a control system coupled to the tap controller, the control system being configured to operate the tap controller using at least one predictive algorithm.

220) The system of any one of paragraphs 217) to 219), further comprising one or more sensors coupled to the system, the sensors being configured to monitor one or more operating parameters of the rotary or plasma arcs, the intermittent power source, and/or the transformer.

221) The system of any one of paragraphs 217) to 220), further comprising: a control system coupled to the tap controller; and one or more sensors coupled to the system configured to monitor one or more operating parameters of the rotary or plasma arcs, the intermittent power source, and/or the transformer; wherein the control system is configured to operate the tap controller based on operating parameter data collected from the sensors.

222) The system of any one of paragraphs 217) to 221), wherein the tap controller is configured to store, for future use, load provided by the transformer that is in excess of the load required by the rotary or plasma arcs.

223) The system of any one of paragraphs 217) to 222), wherein the intermittent power source comprises a windmill.

224) The system of any one of paragraphs 217) to 223), wherein the intermittent power source comprises a gas turbine.

225) The system of any one of paragraphs 217) to 224), wherein the tap controller is configured to control power output in a range between about 1 megavolt amps (MVA) and about 500 MVA.
226) The system of any one of paragraphs 217) to 225), wherein the tap controller is
classified to automatically control the power provided to the rotary or plasma arcs.

5 227) The system of any one of paragraphs 217) to 226), wherein the tap controller is
classified to automatically control the power provided to the rotary or plasma arcs to within
about 20% of the power required by the rotary or plasma arcs.

228) A method for controlling power provided to one or more rotary or plasma arcs from a
continuous or intermittent power source, comprising: monitoring one or more operating
parameters of the rotary or plasma arcs, the intermittent power source, and a transformer
coupled to the intermittent power source that transforms power from the intermittent power
source to power with appropriate operating parameters for the rotary or plasma arcs;
controlling the power output of the transformer using a tap controller coupled to the
transformer and the rotary or plasma arcs such that a constant voltage is provided to the
rotary or plasma arcs regardless of the load of the rotary or plasma arcs and the power
output provided by the intermittent power source.

229) The method of paragraph 228), further comprising controlling the power output of the
transformer using at least one predictive algorithm.

230) The method of paragraph 228) or 229), further comprising controlling the power output
of the transformer using at least one predictive algorithm that assesses the monitored
operating parameters of the rotary or plasma arcs, the intermittent power source, and the
transformer.

231) The method of any one of paragraphs 228) to 230), further comprising monitoring the
operating parameters of the rotary or plasma arcs, the intermittent power source, and the
transformer using one or more sensors coupled to the rotary or plasma arcs, the intermittent
power source, and the transformer.

232) The method of any one of paragraphs 228) to 231), further comprising storing, for
future use, load provided by the transformer that is in excess of the load required by the
rotary or plasma arcs.

233) The method of any one of paragraphs 228) to 232), wherein the intermittent power
source comprises a windmill.

234) The method of any one of paragraphs 228) to 233), wherein the intermittent power
source comprises a gas turbine.

235) The method of any one of paragraphs 228) to 234), further comprising controlling the
power output of the transformer in a range between about 1 megavolt amps (MVA) and
about 500 MVA.

236) The method of any one of paragraphs 228) to 235), further comprising automatically controlling the power provided to the rotary or plasma arcs.

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237) The method of any one of paragraphs 228) to 236), further comprising automatically controlling the power provided to the rotary or plasma arcs to within about 20% of the power required by the rotary or plasma arcs.

10 238) A method of removing hydrogen sulfide or other sulfur-containing compounds from a contaminated methane gas mixture comprising hydrogen sulfide, carbon dioxide, and a gas selected from the group consisting of hydrogen, methane, and a mixture of hydrogen and carbon monoxide and various hydrocarbons, oxygenated hydrocarbons, sulfur-containing hydrocarbons, aromatic hydrocarbons, aliphatic hydrocarbons, which method comprises:

15    (a) mixing said contaminated methane gas mixture with calcium oxide particles while feeding said contaminated methane gas mixture and calcium oxide into a rotary or plasma arc to form calcium carbide, calcium sulfide, carbon monoxide, hydrogen, and mixtures thereof,

(b) maintaining a temperature of about 2000 degrees Centigrade of said contaminated methane gas stream when passing through a rotary or plasma arc during which calcium carbide, carbon monoxide, hydrogen, and calcium sulfide are created or pass through said arc,

(c) separating carbon monoxide and hydrogen from the created solid calcium sulfide and calcium carbide,

25    (d) cooling the created solid calcium sulfide and calcium carbide to about 1000 degrees Centigrade,

(d) adding nitrogen gas to the cooled mixture of calcium carbide and calcium sulfide to form a new mixture of calcium cyanamide and calcium sulfide,

(e) adding water and carbon dioxide to the mixture of calcium sulfide and calcium cyanamide and non-reacted calcium carbide

(f) stripping the gases hydrogen sulfide and acetylene and removing from hydrogen cyanamide, water, and calcium carbonate,

(g) filtering solids

(g) adjusting water filtrate to pH 8.0 or greater,

35    (h) filtering cyanoguanidine from water and drying cyanoguanidine.

239) The method of paragraph 238) further comprising the addition of calcium chloride to the mixture of (a).

40 240) The method of paragraph 238) or 239) further comprising the addition of calcium fluoride to the mixture of (a).
241) A method of removing mercury and hydrogen sulfide or other sulfur-containing compounds from a contaminated methane gas mixture comprising hydrogen sulfide, carbon dioxide, and a gas selected from the group consisting of hydrogen, methane, and a mixture of hydrogen and carbon monoxide and various hydrocarbons, oxygenated hydrocarbons, sulfur-containing hydrocarbons, aromatic hydrocarbons, aliphatic hydrocarbons, which method comprises:

(a) mixing said contaminated methane gas mixture with calcium oxide particles while feeding said contaminated methane gas mixture and calcium oxide into a rotary or plasma arc to form calcium carbide, calcium sulfide, mercury vapors, mercury sulfide vapors, carbon monoxide, hydrogen, and mixtures thereof,

(b) maintaining a temperature of about 2000 degrees Centigrade of said contaminated methane gas stream during passage through a rotary or plasma arc in which calcium carbide, carbon monoxide, hydrogen, calcium sulfide, aromatic mercury compounds and mercury sulfide are created or pass through said arc,

(c) separating carbon monoxide, hydrogen, mercury vapors, and mercury sulfide vapors from the created solid calcium sulfide and calcium carbide,

(d) cooling the created solid calcium sulfide and calcium carbide to about 1000 degrees Centigrade,

(e) adding nitrogen gas to the cooled mixture of calcium carbide and calcium sulfide to form a new mixture of calcium cyanamide and calcium sulfide,

(f) adding water and carbon dioxide to the mixture of calcium sulfide and calcium cyanamide and non-reacted calcium carbide,

(g) stripping and removing hydrogen sulfide and acetylene from the solution of hydrogen cyanamide, water, and precipitated calcium carbonate,

(h) adjusting water filtrate to pH 8.0 or greater,

(i) filtering cyanoguanidine from water and drying cyanoguanidine.

242) The method of paragraph 241) further comprising the addition of calcium chloride to the mixture of (a).

243) The method of paragraph 241) or 242), further comprising the addition of calcium fluoride to the mixture of (a).

244) A method of removing mercury, metal sulfides or other sulfur-containing compounds, zinc-containing compounds, copper-containing compounds, gallium-containing compounds, germanium-containing compounds contained within and from margins of coal seams, which are often collected as "boney piles", which method comprises:

(a) flotation of high-sulfur coal or "boney piles" for the removal of iron pyrite

(b) drying of remaining coal particles

(c) mixing said coal particles from (b) with calcium oxide particles prior to or when feeding coal particles and calcium oxide particles, as a uniform mixture, and carried into into a rotary arc with an inert gas, such as nitrogen, to form solid calcium carbide particles,
mercury compound vapors, mercury sulfide vapors, zinc compound vapors, copper compound vapors, gallium compound vapors, germanium compound vapors, carbon monoxide, hydrogen, and mixtures thereof,

(d) maintaining a temperature of about 2000 degrees Centigrade and a strong electric field of said coal particles, calcium oxide particles, and heated metal compound vapors during passage through a rotary arc in which calcium carbide, mercury compound vapors, mercury sulfide vapors, zinc compound vapors, copper compound vapors, gallium compound vapors, germanium compound vapors, carbon monoxide and hydrogen are created or pass through said arc,

(e) separating mercury compound vapors, mercury sulfide vapors, zinc compound vapors, copper compound vapors, gallium compound vapors, germanium compound vapors, carbon monoxide and hydrogen from the created solid calcium carbide and any solid-non-vapor compounds,

(d) cooling the created solid calcium carbide and solid-non-vapor compounds to about 1000 degrees Centigrade,

(d) adding nitrogen gas to the cooled mixture of calcium carbide and solid-non-vapor compounds to form a new mixture of calcium cyanamide and solid-non-vapor compounds,

(e) adding water and carbon dioxide to the mixture of calcium cyanamide and solid-non-vapor compounds and non-reacted calcium carbide,

(f) stripping and removing remaining volatiles, such as hydrogen sulfide and acetylene from the solution of hydrogen cyanamide, water, and precipitated calcium carbonate and solid-non-vapor compounds,

(g) filtering solids

(h) adjusting water filtrate to pH 8.0 or greater

(i) filtering cyanoguanidine from water and drying cyanoguanidine.

245) The method of any one of paragraphs 238) to 244), further comprising the addition of calcium chloride to the mixture of (c).

246) The method of any one of paragraphs 238) to 245), further comprising the addition of calcium fluoride to the mixture of (c).

247) A method of producing urea from cyanoguanidine, the method comprising production of cyanoguanidine as previously disclosed, hydrolysis of the cyanoguanidine to produce ammonia and carbon dioxide, and combination of the ammonia and carbon dioxide to produce ammonium carbamate, and reaction of the ammonium carbamate to produce urea.

248) A method of producing a urea-containing fertilizer from cyanoguanidine, the method comprising production of cyanoguanidine as previously disclosed, partial hydrolysis of the cyanoguanidine to produce a composition containing one or more of the following materials: cyanoguanidine, guanylurea, guanidine, urea, ammonia and carbon dioxide, separating the gaseous components from the above composition and providing the composition for use as a fertilizer.
249) The method of paragraph 247) or 248) wherein the gaseous components ammonia and carbon dioxide are separated from the composition and are combined to form ammonium carbamate which is subsequently reacted to form urea.

5

250) The method of any one of paragraphs 247) to 249) whereby a catalyst containing vanadium is used to facilitate the decomposition of the cyanoguanidine.

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251) The method of paragraph 250) wherein the catalyst containing vanadium comprises a composition containing vanadium pentoxide ($V_2O_5$) and metallic zinc, the zinc reacting with the vanadium pentoxide during hydrolysis to produce a composition containing lower oxidation states of vanadium.

252) The method of any one of paragraphs 238) to 245), further comprising the addition of a composition containing calcium chloride and calcium fluoride to the mixture of (a).

BRIEF DESCRIPTION OF DRAWINGS

Embodiments of the invention and/or principles and practice relevant to the invention will now be described by way of example only with reference to the accompanying figures in which:

Fig. 1 shows a schematic flowchart illustrating the formation of cyanamide, indicating two options for the delivery of $N_2$ to the reaction.

Fig. 2 shows a schematic flowchart illustrating the formation of cyanamide from urea.

Fig. 3 shows a schematic description of the rotary arc synthesis of a cyanamide-based composition using the reagents calcium oxide and carbon.

Fig. 4 shows a schematic description of the rotary arc synthesis of a cyanamide-based composition using the reagents calcium oxide and methane.

Fig. 5 shows a schematic description of the rotary arc synthesis of a cyanamide-based composition using the reagents calcium oxide and carbon with a reflector to reflect rotary arc light.

Fig. 6 shows a schematic description of the rotary arc synthesis of a cyanamide-based composition using the reagents calcium oxide and methane with a reflector to reflect rotary arc light.

Fig. 7 shows a schematic description of a rotary arc component of this apparatus by means of valves; wherein a) the reagents calcium oxide and carbon are introduced to the rotary arc and reflector assembly so that a constant pressure is maintained within the rotating arc and reflector components of this apparatus and b) as the solid (calcium carbide) product of this pressurized compartment is separated and passed through valves to a fluidized bed
maintained as a temperature controlled gradient for synthesis of the cyanamide-based composition.

Fig. 8 shows a schematic description of a rotary arc component of this apparatus by means of valves; wherein a) the reagents calcium oxide and methane are introduced to the rotary arc and reflector assembly so that a constant pressure is maintained within the rotating arc and reflector components of this apparatus and b) as the solid (calcium carbide) product of this pressurized compartment is separated and passed through valves to a fluidized bed maintained as a temperature controlled gradient for synthesis of the cyanamide-based composition.

Fig. 9 shows a schematic flowchart as a means to safely store electrical energy in the form of chemical energy by using the reagents nitrogen and carbon and where off-site electrical power can be automatically switched from power grid or source to rotary arc and synthesis of cyanoguanidine.

Fig. 10 shows a schematic flowchart as a means to safely store electrical energy in the form of chemical energy by using the reagents nitrogen and methane and where on-site or stranded electrical power can be automatically switched from power grid or source to rotary arc and synthesis of cyanoguanidine.

Fig. 11 shows a schematic flowchart as a means to safely store electrical energy in the form of chemical energy by using the reagents nitrogen and carbon and where off-site electrical power can be used to synthesize cyanoguanidine.

Fig. 12 shows a schematic flowchart as a means to safely store electrical energy in the form of chemical energy by using the reagents nitrogen and methane and where off-site electrical power can be used to synthesize cyanoguanidine.

Fig. 13 shows a schematic flowchart as a means to safely store electrical energy in the form of chemical energy by using the reagents nitrogen and carbon and where on-site or stranded electrical power can be automatically switched from power grid or source to rotary arc and synthesis of calcium cyanamide.

Fig. 14 shows a schematic flowchart as a means to safely store electrical energy in the form of chemical energy by using the reagents nitrogen and methane and where on-site or stranded electrical power can be automatically switched from power grid or source to rotary arc and synthesis of calcium cyanamide.

Fig. 15 shows a schematic flowchart as a means to safely store electrical energy in the form of chemical energy by using the reagents nitrogen and carbon and where off-site electrical power can be used to synthesize calcium cyanamide.
Fig. 16 shows a schematic flowchart as a means to safely store electrical energy in the form of chemical energy by using the reagents nitrogen and methane and where off-site electrical power can be used to synthesize calcium cyanamide.

5 Fig. 17 shows a schematic flowchart where synthesized cyanamide-based compositions made from a metal oxide, a carbon source and electrical energy can be stored and transported in the form of chemical energy that in turn may be used for multiple fuel and multiple nitrogen-based commodity applications.

10 Fig. 18 shows a schematic flowchart illustrating the production of cyanoguanidine using a rotary arc.

15 Fig. 19 shows a schematic flowchart illustrating the production of cyanoguanidine using a rotary arc.

15 FURTHER DESCRIPTION OF THE INVENTION

Cyanoguanidine produced for use as a fuel is not 100% pure cyanoguanidine. Accordingly, the term "cyanoguanidine" as used herein is intended to denote cyanoguanidine including any one of the components of cyanoguanidine resulting from commercial production such as 1-cyanoguanidine, 2-cyanoguanidine, guanylurea, guanidine, urea, ammonium carbonate, ammonium carbamate, biuret, ammeline, melamine, or a mixture of two or more of these components.

The reaction of cyanoguanidine with water can be described by the following stoichiometric equation:

\[
\text{Equation (A)} \quad (\text{NH}_2)\text{C}=\text{NCN} + 4\text{H}_2\text{O} = 2\text{CO}_2 + 4\text{NH}_3
\]

30 This reaction is accomplished in several steps. In the first step a molecule of cyanoguanidine reacts with water to form guanylurea. Guanylurea reacts with water to form guanidine, carbon dioxide, and ammonia. Guanidine reacts with water to form urea and ammonia. The urea molecule immediately reacts with water to form two molecules of ammonia and one molecule of carbon dioxide. The reaction with water is preferably carried out at a temperature ranging between about 50° C and about 240° C and a pressure ranging between about 1 ambient atmosphere and about 50 standard atmospheres. The heat required for the decomposition, which is endothermic, may be obtained from waste heat generated by an engine or fuel cell in which ammonia, or hydrogen is combusted or oxidized. This heat source may be supplemented with an additional energy source, particularly to initiate the reaction. A preferred additional energy source is a battery that may be part of the apparatus of the invention and that serves as a source of electricity.
The weight of cyanoguanidine in the composition may range between about 10% and about 100% of the composition. In one embodiment, the composition can be stored as a solid and transferred to the reaction chamber by melting at temperatures below 210°C. Pure cyanoguanidine melts at 209-212°C. Forming a mixture with other components such as urea will lower the melting point. The heat required to melt the composition may be obtained by the heat generated by an engine or fuel cell. This heat source may be supplemented by electrical resistance heating where the heating elements are inside or surrounding the container holding the composition. In another embodiment, the cyanoguanidine is dissolved in a solvent, such as water, anhydrous ammonia, ethanol, or a petroleum-based solvent and transferred to the reaction chamber as a solution. When ethanol or petroleum-based liquids are used as the solvent, the solvent vapor exits the reaction chamber along with the ammonia and serves to enhance the combustion qualities of the resulting mixture. Use of water captured from the exhaust of an engine or fuel cell reduces the need to carry water and improves the specific energy of the fuel.

The composition may contain a component selected from the group consisting of a combustible fuel, a combustion enhancer, and a combination thereof. In the first and second embodiment of the method of the invention, the combustible fuel can be present in an amount which can be combusted to generate a sufficient amount of heat to initiate the reaction of the composition with water to form ammonia. Alternatively, the engine can begin operation on stored ammonia, and the fuel cell can begin operation on stored hydrogen until the heat produced by the engine or fuel cell is adequate to increase the reaction rate of the composition with water. A compression-ignition engine can operate initially using injection of the cyanoguanidine composition when the ethanol or methanol concentration of the composition exceeds about 30%. In the third embodiment of the method of the invention, the heat needed to start the reaction can be supplied electrically using a connection to the local electric utility lines.

The oxidation of hydrogen to form water may be performed by combusting the hydrogen in an engine. Similarly, the oxidation of ammonia to form nitrogen and water may be performed by combusting the ammonia in an engine. Alternatively, the ammonia and hydrogen may be oxidized in an ammonia fuel cell and a hydrogen fuel cell, respectively. Examples of fuel cells include high temperature fuel cells such as solid oxide fuels cell and molten carbonate fuel cells, and relatively lower temperature fuel cells such as alkaline-fuel cells, PEM fuel cells and phosphoric acid fuel cells.

The combustion of ammonia to form water and nitrogen may also lead to the formation of nitrogen oxides which have the general formula \( N_xO_y \), such as, for example, NO or \( NO_2 \). Elevated levels of the nitrogen oxides are obtained depending upon reaction conditions. The nitrogen oxides are pollutants and their emission is regulated. An advantage of using ammonia as the fuel in the present invention is that pollution caused by the nitrogen oxides may be abated or eliminated by reaction of unburned ammonia exiting the combustion.
chamber with the nitrogen oxides in a post combustion reactor. The unburned ammonia acts as a reducing agent to convert nitrogen oxides into molecular nitrogen.

The use of ammonia and the method of reducing nitrogen oxides has been described in several patents as a way to reduce $\text{NO}_x$ in both mobile and stationary combustion sources. Representative patents include U.S. Pat. Nos. 5,399,325, 6,403,046, 6,354,079, 6,312,650, 6,182,443, 6,146,605, 5,832,720, 5,746,144, 5,399,326, 5,281,403 and 5,240,689.

While ammonia has been used as a stationary source pollutant remover, it has not been used for mobile applications, possibly because most consumers would not notice any change in the performance of the vehicle in the absence of the pollutant remover and would therefore forget to refill the tank containing the pollutant remover. Accordingly, manufacturers are looking for a solution that does not require a second fill-up in addition to the one required for the fuel. Currently, the solutions to this problem are to include three way catalysts as additives to the fuel or to feed small amounts of gasoline into an exhaust reactor.

The use of compositions containing cyanoguanidine provides a simple and efficient solution to the problem of pollution caused by nitrogen oxides. Because cyanoguanidine produces ammonia which acts as both the fuel and the NOx reducing agent, an apparatus that uses cyanoguanidine as the fuel also provides for its own pollution abatement. As long as there is fuel to run a vehicle there will be some unburned ammonia present in the exhaust to remove the NOx produced by the combustion. The air/ammonia ratio of the fuel mixture can be adjusted to supply the minimum amount of unburned ammonia in the exhaust needed to completely decompose the nitrogen oxides. Accordingly, consumers would only require one fill-up, since the same substance would serve both purposes.

The composition may also include a combustion enhancer. Preferred combustion enhancers include ammonium nitrate, cyanoguanidine nitrate, nitrocyano guanidine, ammonia, hydrazine, and certain water soluble compounds which can be made from renewable sources or waste, such as isopropanol, ethanol and methanol.

Several embodiments can be used to generate energy from the composition containing cyanoguanidine when reacted with water according to the method of the invention. In a first embodiment, the cyanoguanidine reacts with water to form ammonia, according to equation (A). The ammonia formed from the reaction of cyanoguanidine with water is then oxidized to form water and nitrogen generating energy. The oxidation of ammonia may be performed by combusting the ammonia in an engine. The engine may be an engine having a compression ratio at least similar to compression ratios ordinarily used in the art, such as a compression ratio of 9:1, or a compression ratio higher than compression ratios ordinarily used in the art, such as a compression ratio of 30:1 or greater, or a compression ratio ranging between 9:1 and 30:1. Alternatively, the ammonia may be heated in an ammonia fuel cell. The first embodiment of the method of the invention may further include the step of reacting a
sufficient amount of the unburned ammonia in the combustion exhaust with nitrogen oxides formed from the combustion of ammonia to reduce the nitrogen oxides.

In a second embodiment of the method of the invention, the cyanoguanidine in the composition reacts with water to form ammonia, according to equation (A). The ammonia formed from the reaction of cyanoguanidine with water is then `reformed` or converted into nitrogen and hydrogen. The hydrogen formed from the conversion of ammonia is then oxidized to form water, generating energy. The oxidation of hydrogen may be performed by combusting the hydrogen in an engine. Alternatively, the hydrogen may be oxidized in a hydrogen fuel cell. The amount of energy required to bring the fuel cell to operating temperature for this reaction can be provided by an electric heater or by the oxidation of a small amount of hydrogen in situ.

In a third embodiment of the method of the invention, the cyanoguanidine in the composition reacts with water to form ammonia, according to equation (A). The ammonia formed from the reaction of cyanoguanidine with water is then `reformed` or converted into nitrogen and hydrogen. The hydrogen is then stored in a container until being dispensed into the fuel tank of a vehicle using hydrogen as a fuel. The safety of using the solid, relatively non-flammable, cyanoguanidine composition as the means for effectively storing hydrogen and producing hydrogen on-demand with only a small amount of hydrogen in the apparatus at any time, will allow this apparatus to provide a safe source of hydrogen at numerous locations within cities and along highways as refueling stations for hydrogen-powered vehicles.

In the second and third embodiments of the method of the invention, the hydrogen formed from "reforming" ammonia can contain carbon monoxide, if the carbon dioxide product from equation (A) is not removed prior to the "reforming". Even if the carbon dioxide is removed, the "reformed" mixture will contain traces of ammonia. Both carbon monoxide and ammonia are detrimental to the performance of many hydrogen fuel cells. These deleterious contaminants can be removed from the hydrogen by passing the "reformed" gas through a semi-permeable membrane that passes hydrogen but not other matter. This semi-permeable membrane can be a thin film of Pd metal, Pt metal, or a dense random packing of hard spheres type amorphous metal composed of mischmetal and at least one transition metal as described by Van Vechten in the U.S. Patent Application "DRPHS-Type Amorphous Metal Proton Transfer Membrane for Fuel Cells" filed 11 March 2003 by James A. Van Vechten claiming priority to Provisional Patent Application 60/363,520 of 28 March 2002.

The decomposition of cyanoguanidine according to equation (A) can be accomplished in the presence of a catalyst which increases the rate of decomposition. The catalyst may be a metal oxide. In an exemplary embodiment, the catalyst is vanadium pentoxide that has been partially reduced with metallic zinc to a lower oxidation state than that of the pentoxide. Catalysts can decrease in effectiveness due to contamination or structural changes during use. Accordingly, the catalyst in the reaction chamber can be contained in a replaceable
cartridge which can be removed from the reaction chamber and replaced with a cartridge containing fresh catalyst. The removed cartridge can be reactivated or recycled.

The use of an enzyme allows the reaction of cyanoguanidine with water in equation (A) to proceed at lower temperatures than the reaction in the absence of the enzyme. The temperature of the enzyme-catalyzed reaction may range between room temperature and a temperature at which the half-life of the enzyme is less than 1 minute. The enzyme may be provided in a tank equipped with a filter which prevents the enzyme from leaving but which is permeable to the gases formed. Alternatively, the enzyme may be immobilized on a substrate. Suitable substrates include ion exchange resins, ceramics, and polymeric materials. The substrate may be in the form of a sheet or beads.

In an exemplary embodiment, the enzymes capable of catalyzing the reaction of cyanoguanidine with water to form ammonia are arginase and urease. These enzymes catalyze the reaction at a temperature which is preferably between about 0°C and about 60°C, more preferably about 60°C. The heat required to maintain the process at this temperature is available from proton exchange membrane (PEM) fuel cell stacks which may be easily integrated into the apparatus of the invention to provide a low temperature energy sink.

Enzymes can decrease in effectiveness due to contamination, structural changes, or denaturing of the enzyme during use. Accordingly, the enzyme in the reaction chamber can be contained in a replaceable cartridge which can be removed from the reaction chamber and replaced with a cartridge containing fresh enzyme. The removed cartridge can be reactivated or recycled.

Concern over the effects of rising carbon dioxide concentrations in the atmosphere have led to proposals to limit the emissions of carbon dioxide from vehicles and stationary energy sources. Even though the reaction of cyanoguanidine compositions with water only releases an amount of carbon dioxide equal to the amount used during the production of the cyanoguanidine composition, it may be advantageous to store the carbon dioxide produced according to equation (A), so that use of cyanoguanidine fuel together with storage of carbon dioxide will result in a net decrease of the amount of carbon dioxide released to the atmosphere. The carbon dioxide can be stored under pressure in a container or can be stored under pressure as a solution in a container holding water. The carbon dioxide gas or solution could then be transferred at fueling stations for other uses or sequestered in geologic formations. The ability to store carbon dioxide produced from cyanoguanidine compositions is feasible because the carbon to hydrogen ratio of 1:9 for cyanoguanidine is higher than for many other non-hydrogen alternative fuel.

A new alternative fuel will be successful only if it can be produced in an efficient and environmentally acceptable manner without the consumption of expensive or scarce raw materials. Accordingly, it is another object of the invention to provide a method for providing
a cyanoguanidine containing composition. The method in one embodiment comprising: (a) using a source of energy to separate hydrogen from water; (b) reacting the hydrogen formed in step (a) with carbon dioxide to form water and either methane via the Sabatier reaction or elemental carbon via the Bosch reaction. (c) reacting a portion of the elemental carbon, methane, or a combination of these to form sequentially calcium carbide, calcium cyanamide, hydrogen cyanamide, and cyanoguanidine to form a composition containing cyanoguanidine. In one exemplary embodiment, the source of the energy in step (a) is renewable energy from wind power. The potential for wind power is extremely high in some remote regions such as the Aleutian Islands or Patagonia. The potential for harnessing the renewable energy in such remote locations has not been realized because of the lack of efficient means for storing or distributing that energy. Production of cyanoguanidine via the method of this invention provides a means to harness and store the electricity produced from renewable energy sources such as electricity generated from wind, electricity generated from ocean waves, electricity generated from hydroelectric facilities, electricity generated from solar energy, electricity generated from agricultural waste combustion, electricity generated from forestry waste combustion, electricity generated from municipal waste combustion, and electricity generated from the tidal flow of ocean water. In addition to renewable energy sources, cyanoguanidine containing compositions can also be effectively produced using electricity produced by conventional means for which the level of generating capacity exceeds the current demand. This is a form of load-levelling whereby generating plants can operate at a constant level with excess electrical energy being converted into cyanoguanidine containing compositions.

The carbon dioxide needed for the production of compositions containing cyanoguanidine can be supplied from several sources including carbon dioxide extracted from the air, carbon dioxide extracted from products created by the combustion of fossil fuels, carbon dioxide extracted from products created by the combustion of agricultural waste, carbon dioxide extracted from products created by the combustion of forestry waste, carbon dioxide extracted from products created by the combustion of municipal waste, and a combination thereof. In one exemplary embodiment, the carbon dioxide is extracted from the exhaust from a combustion process. As a result of the combustion, the exhaust is depleted of oxygen. Following the extraction of carbon dioxide, the remaining gas is primarily nitrogen which can be used as the source of nitrogen needed for production of ammonia. The nitrogen can also be supplied from conventional sources using fractional distillation of liquefied air or pressure swing absorption of air.

In addition to producing hydrogen by electrolysis for production of cyanoguanidine, use of brine or other salts in the electrolysis process can produce sodium and chlorine-containing compounds which are in high demand. The production of the chlorine-containing compounds will provide an additional source of profit and encourage the establishment of cyanoguanidine producing facilities. In one exemplary embodiment a 4-chamber or multi-chamber electrodialysis process produces NaOH, hydrogen gas, oxygen gas, and hydrochloric acid. The NaOH is used to absorb carbon dioxide directly from the atmosphere
to form sodium carbonate and/or sodium bicarbonate. The hydrochloric acid can regenerate the carbon dioxide from the sodium salts to produce the carbon dioxide for the Sabatier or Bosch reaction as needed.

5 When reacted in the presence of water, cyanoguanidine generates ammonia and carbon dioxide. Ammonia is a known fuel which can run internal and external combustion engines. The ammonia can also be decomposed to give its constituent elements nitrogen and hydrogen. The hydrogen may then be used in an engine or in a hydrogen fuel cell. However, upon hydrolysis with water, one molecule of cyanoguanidine produces four molecules of ammonia, with eight of the hydrogen atoms coming from the water molecule. Accordingly, the cyanoguanidine-water system can theoretically yield up to 7.7% of hydrogen where the weight of all the water needed is considered in the calculation. In the case that all the water needed is captured from the exhaust and is not included in the weight calculation, cyanoguanidine can theoretically yield up to \( (12/84) = 14.3\% \) hydrogen by weight. The density of cyanoguanidine is approximately 1.4 kg/liter. When using water captured from the exhaust, one liter of cyanoguanidine can supply 200 grams of hydrogen. This figure of 200 grams of hydrogen per liter is extremely favorable when considering all the positive safety features of a solid cyanoguanidine-based fuel compared to cryogenic liquid hydrogen, as well as the fact that the bulk of a cryogenic tank has an unfavorable effect on the energy density value of cryogenic liquid hydrogen. The density of liquid hydrogen is 79 grams of hydrogen per liter so pure cyanoguanidine, using water captured from the exhaust, stores effectively 2.5 times more hydrogen per liter than liquid hydrogen, without any consideration of the bulk of the cryogenic tank which would reduce the amount of liquid hydrogen that could be stored in a given volume.

25 The present invention also has significant advantages over fossil fuels and many alternative fuels in terms of safety. The present invention gives ammonia on demand, so that at any given time the amount of ammonia present is very low and does not pose any safety concern. The cyanoguanidine composition has a low toxicity, about the same as vitamin C and a lower toxicity than table salt. It can be stored in paper, cardboard or plastic containers or in open air.

In embodiments of the invention, as discussed above, ammonia generated from the reaction of cyanoguanidine with water is oxidized or combusted to produce energy. While pure ammonia has also been proposed as a fuel, the use of pure ammonia has several drawbacks. Ammonia is a gas at room temperature and requires high pressure to liquefy. It is a corrosive substance which in large quantities may cause respiratory problems and even death. While it is possible to dissolve ammonia in water to produce a fuel, the resulting fuel has a pH of over 11 and a strong ammonia odor. Finally, ammonia has a relatively low energy density compared to gasoline and other alternative fuels. The use of cyanoguanidine as a source of ammonia in the present invention maintains only small quantities of ammonia in the device at any time. This removes most of the problems associated with storing large quantities of ammonia in a device.
The present invention is also environmentally advantageous. Although carbon dioxide is one of the products of the hydrolysis of cyanoguanidine in reaction (A), an equal amount of carbon dioxide is removed from the atmosphere to make cyanoguanidine when it is produced using the Sabatier or Bosch processes. Accordingly, the production of ammonia according to the invention may not entail any net contribution to greenhouse gas emissions. The other reactants required for the preparation of cyanoguanidine are nitrogen, water, carbon dioxide, and calcium oxide, which is recycled in the production process.

The present invention is attractive for use in load-levelling electric power grids because it can add supply very quickly by providing ammonia to a fuel cell, which can start generating electric energy in a few seconds, and can add load in a few seconds by powering up the electric arc reactor, which does not waste the excess energy, as do the resistive loads commonly used in the prior art to shave peaks. Gas turbine generators, other thermal generators, and hydroelectric generators require much longer times to turn on to add supply and may waste energy when turning off. The "Hydrogen Hub" concept to provide load-levelling proposes to generate and to store ammonia at sites distributed around urban areas. This alternative suffers from the danger that ammonia might escape into the urban environment causing great disruption or even death. The present invention reduces that danger.

The preferred practice of this invention will depend upon the nature of the source of carbon and of hydrogen and of the market for by-products that will be produced. The by-products that are produced will depend upon the elements other than carbon and hydrogen that are in the source materials. If no elements other than carbon and hydrogen are present in the source material, then no by-products other than carbon, hydrogen, hydrocarbons, and possibly some compounds containing nitrogen, can be formed and all of the calcium oxide or magnesium oxide that is used can be recovered. Then the relative cost of CaO and of MgO will not matter, but cost of the process may depend upon the choice. At present the processes using CaO are better developed than the corresponding processes for MgO because CaO from limestone has long been more abundant in the market. Note the reaction energies required for the recovery of the alkaline-earth oxides are less for Mg than for Ca; Reaction (16) for Ca requires heating above 840 °C and 178 kJ/mole whereas

\[ \text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2 \]  

requires heating above 500 °C and 118 kJ/mole. For the hydrates,

\[ \text{Ca(OH)}_2 \rightarrow \text{CaO} + \text{H}_2\text{O} \]  

requires heating to 512 °C and 63.9 kJ/mole, while

\[ \text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O} \]  

(23)
requires heating to 332 °C and 29 kJ/mole. Thus, when properly developed the process for MgO will likely be less expensive than the corresponding processes for CaO.

5 If, for example, a significant amount of chlorine is present in the source material (perhaps as polyvinylchloride plastic waste), then some of the alkaline-earth oxide will be consumed and either calcium chloride (CaCl₂) or magnesium chloride (MgCl₂) will be produced. Both of these are used for environmentally benign road deicing and as desiccants but may command different prices at the time.

10 Consider now the first preferred practice for the production of the dicyandiamide or cyanamide fuel, which is illustrated in Fig. 1 as "option #1", using natural gas as the main source of hydrogen and as at least a portion of the source of carbon. Because, as noted above, the use of pure methane would result in a large excess of hydrogen gas and because components of the gas with more carbon atoms per molecule might be separated and put to more economic uses, one may add a second source of carbon, such as finely divided biochar, which is discussed in Li et al. (op. cit.) or finely divided coal, which is discussed in Kim et al. (op. cit.), or other sources of carbon, such as finely divided plastic waste, which might include tire waste. The amount of added carbon source material added to the mix should be adjusted, according to the type of such material, to optimize the mix of products. For this writing it will here be assumed that the alkaline-earth that is selected is calcium and be understood that it might instead be magnesium, as discussed above. One loads the finely divided solid CaO, the source or sources of carbon and of hydrogen and nitrogen gas and, preferably, about 1 weight percent of CaF₂ to act as a catalyst or flux into an electric-arc furnace, which may be of the DC arc type but preferably is of the rotating-arc type and is preferable provided with known art to employ a fluidized bed using the nitrogen gas or to include a fluidized bed for allowing different temperature gradients, thereby allowing a greater concentration of the most desirable compounds or reactants. As one runs the electric arc, products that will include the desired CaCN₂ and H₂N CN, but also some inadvertently produced CaC₂, as well as residual CaO and some CaCO₂, C, and other solids depending upon the source materials together with the gaseous products including residual nitrogen gas, CO, CO₂, and steam. These are separated as practicable with known art. Water is added to the mixture of solid CaF₂, CaCN₂ and CaC₂ (plus some residual CaO) causing the CaC₂ to react to acetylene and calcium hydroxide. Any residual CaO will also react to calcium hydroxide. The calcium hydroxide is treated with heat to recover CaO and provide steam. The CaCN₂ reacts slowly with the water and will be passed to a second reaction vessel where it is reacted with water and carbon dioxide, which is stored from other reactions, especially the conversion of calcium carbonate to recovered CaO and carbon dioxide, to form cyanamide and calcium carbonate.

35 The second preferred practice for the production of the dicyandiamide or cyanamide fuel is illustrated in Fig. 1 as "option #2". In this case the nitrogen gas is not introduced until after the electric arc has driven Reaction 1 to make CaC₂ at temperatures of about 2000 °C (see
Li et al., op. cit.). This allows the reaction with nitrogen to proceed at the optimum temperature for formation of calcium cyanamide and avoids the energy needed to heat the nitrogen gas (in the presence of carbon) to such a temperature and the precautions needed to deal properly with the possible formation of HCN gas. After the reaction volume has cooled to about 1000 °C the nitrogen gas is introduced optionally additional heating supplied to maintain the reactants at the desired temperature for a longer time to drive reaction (8) to form CaCN$_2$. From thereon the practice is as described above for "option #1".

The third preferred practice for the production of the dicyandiamide or cyanamide fuel employs a variant on the first two preferred embodiments. Here the motivation is the economic utilization of free hydrogen gas, which is uneconomic to store or to transport, that is produced abundantly in cases like that of stranded natural gas when another source of carbon is not available and when the local production of ammonia or urea is not desired (see reactions (2) and (4) above). Note that any amount of carbon dioxide that may be desired can be spontaneously captured from the atmosphere by exposing CaO, or Ca(OH)$_2$, or MgO, or Mg(OH)$_2$ to the atmosphere,

$$\text{CaO} + \text{Air} \rightarrow (\text{Air-} \text{CO}_2) + \text{CaCO}_3$$  \hspace{1cm} (26)

or

$$\text{Ca(OH)}_2 + \text{Air} \rightarrow (\text{Air-} \text{CO}_2) + \text{CaCO}_3 + \text{H}_2\text{O}$$  \hspace{1cm} (27)

or

$$\text{MgO} + \text{Air} \rightarrow (\text{Air-} \text{CO}_2) + \text{MgO}_3$$  \hspace{1cm} (28)

or

$$\text{Mg(OH)}_2 + \text{Air} \rightarrow (\text{Air-} \text{CO}_2) + \text{MgCO}_3 + \text{H}_2\text{O}$$  \hspace{1cm} (29)

then separating the calcium carbonate or magnesium carbonate from any water, then heating this carbonate to drive Reaction (16) or (21) to obtain essentially pure carbon dioxide and to recover calcium oxide or magnesium oxide. At least some of this carbon dioxide is reacted with at least some of the free gas hydrogen according to the known art Sabatier Reaction,

$$\text{CO}_2 + 4 \text{H}_2 \rightarrow \text{CH}_4 + 2 \text{H}_2\text{O}$$  \hspace{1cm} (30)

This methane is added to the natural gas being supplied used to make cyanamide as described above.

The fourth preferred practice for the production of the dicyandiamide or cyanamide fuel employs a variant on the first two preferred embodiments is that is illustrated in Fig. 2. Here the motivation is the economic utilization of carbon monoxide, such as that produced from stranded natural gas in reactions such as Reactions (2) or (4). Thus, what is well known in art as a "Water Shift Reaction",

$$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$$  \hspace{1cm} (31)
is used to provide more free hydrogen gas for the Sabatier Reaction to obtain more methane.

5 The fifth preferred practice employs a variant on the first two preferred embodiments. Here the carbon that is needed to make cyanamide is obtained from carbon dioxide obtained from the atmosphere, as by one of the Reactions (26) to (29) followed by the heating of the calcium carbonate or magnesium carbonate as described above, or from any other source is reacted with free hydrogen gas, which may be obtained by electrolysis of fresh water or of seawater, according to the known art Bosch Reaction,

\[ \text{CO}_2 + 2 \text{H}_2 \rightarrow \text{C} + 2 \text{H}_2\text{O} \]  \hspace{1cm} (32)

to form solid graphitic carbon and water. Note that if carbon-free energy (from a renewable and sustainable source such as a solar, wave, or wind energy converter) is used to power the process and to obtain all the carbon and nitrogen from the atmosphere and to obtain all the hydrogen from electrolysis of fresh water, then this preferred practice is carbon neutral. If the hydrogen is obtained by electrolysis of seawater and if the co-produced NaOH is used to sequester carbon dioxide from the atmosphere or in the sea, then preferred practice is carbon-negative. If the fuel of the present invention is to be converted to ammonia before it is oxidized, rather than oxidized directly as dicyandiamide as described at Reaction (14), then water must be added to it as

\[ (\text{H}_2\text{CN})_2 + 4 \text{H}_2\text{O} \rightarrow 4 \text{NH}_3 + 2 \text{CO}_2 \]  \hspace{1cm} (33)

If the fuel of the present invention is to be converted to ammonia before it is oxidized, rather than oxidized directly as cyanamide as described at Reaction (14), then water must be added to it as

\[ \text{H}_2\text{NCN} + 2 \text{H}_2\text{O} \rightarrow 2 \text{NH}_3 + \text{CO}_2 \]  \hspace{1cm} (33)

One then oxidizes the ammonia according to

\[ 4 \text{NH}_3 + 3 \text{O}_2 \rightarrow 2 \text{N}_2 + 6 \text{H}_2\text{O} \]  \hspace{1cm} (34)

or converts the ammonia to hydrogen and nitrogen, either by electrolysis or by thermal cracking, and oxidizes the hydrogen.

The sixth preferred practice for the production of the dicyandiamide or cyanamide fuel is illustrated in the accompanying Figures. One begins with urea (CONH₂H₄). The production of urea from natural gas is a very well developed and widely practiced art. Weber et al. taught in U.S. Patent 5,753,199 the production of calcium cyanamide (CaNCN) from urea
and CaO or Ca(OH)$_2$ or CaCO$_3$. We instead produce dicyandiamide \((H_2NCN)_2\) or cyanamide from urea and MgO, Mg(OH)$_2$ or MgCO$_3$. The net reaction is

\[
2 \text{CON}_2\text{H}_4 \rightarrow (H_2\text{NCN})_2 + 2 \text{H}_2\text{O}, \tag{35a}
\]

or

\[
\text{CON}_2\text{H}_4 \rightarrow \text{H}_2\text{NCN} + \text{H}_2\text{O}, \tag{35b}
\]

so that ideally none of the magnesium compound would be lost, but in practice a small amount is lost. In the case of cyanamide, this can in fact serve to stabilize the cyanamide.

10 The Reaction (35) occurs in stages according to the magnesium compound used.

For MgO:

\[
2 \text{CON}_2\text{H}_4 + 2 \text{MgO} \rightarrow 2 \text{MgNCN} + 4 \text{H}_2\text{O}; \tag{36a}
\]

or

\[
\text{CON}_2\text{H}_4 + \text{MgO} \rightarrow \text{MgNCN} + 2 \text{H}_2\text{O};
\]

\[
\text{MgNCN} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{MgC}_3 + \text{H}_2\text{NCN};
\]

\[
\text{MgC}_3 \rightarrow \text{MgO} + \text{CO}_2. \tag{36b}
\]

For Mg(OH)$_2$:

\[
2 \text{CON}_2\text{H}_4 + 2 \text{Mg(OH)}_2 \rightarrow 2 \text{MgNCN} + 6 \text{H}_2\text{O};
\]

\[
2 \text{MgNCN} + 2 \text{CO}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{MgC}_3 + 2 \text{H}_2\text{NCN},
\]

\[
2 \text{MgC}_3 \rightarrow 2 \text{MgO} + 2 \text{CO}_2, \tag{37a}
\]

or

\[
2 \text{H}_2\text{NCN} \rightarrow (H_2\text{NCN})_2.
\]

For MgCO$_3$:

\[
2 \text{CON}_2\text{H}_4 + 2 \text{MgCO}_3 \rightarrow 2 \text{MgNCN} + 2 \text{CO}_2 + 4 \text{H}_2\text{O};
\]

\[
2 \text{MgNCN} + 2 \text{CO}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{MgC}_3 + 2 \text{H}_2\text{NCN},
\]

\[
\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2, \tag{37b}
\]

\[
\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2.
\]
2 H₂NCN → (H₂NCN)₂ . (38a)

or

\[ \text{CON}_2\text{H}_4 + \text{MgCO}_3 \rightarrow \text{MgNCN} + \text{C}_2\text{O}_2 + 2 \text{H}_2\text{O} ; \]

\[ \text{MgNCN} + \text{C}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{MgC}_3\text{O}_3 + \text{H}_2\text{NCN} . \] (38b)

The source of magnesium and fixed oxygen and urea is mixed at a molar ratio that may vary
between the stoichiometric ratio of 1:1 and a ratio of as much as 4 moles of urea for each
mole of the magnesium compound, which has been found to produce a greater amount of
cyanamide but which reacts excess urea to ammonia and carbon dioxide, which can be
recycled to make more urea. This mixture is first heated to between 130 °C and about 200
°C until it is substantially melted (the melting point of pure urea being 133 °C), preferably in a
tube with a screw system for extruding the molten material. This typically takes 5 to 30
minutes depending on the magnitude of the charge. The melted material is then transferred
to a second furnace where it is heated to between about 250 °C and 400 °C and stirred,
kneaded, or tumbled until a solid forms. This reactor preferably contains ceramic or steel
balls of order 1 cm diameter to comminute the solid. This solid is then calcined at a
temperature between about 600 °C and 900 °C. The resulting solid powder is mostly
MgNCN. It is reacted with water and carbon dioxide as,

\[ \text{MgNCN} + \text{H}_2\text{O} + \text{C}_2\text{O}_2 \rightarrow \text{MgC}_3\text{O}_3 + \text{H}_2\text{NCN} . \] (39)

The cyanamide is then separated from the magnesium carbonate. This may be done by
decanting it in its molten state (its melting point being 46 °C). Alternatively it may be
dissolved in water and decanted. Alternatively it may be separated by shaking the two dry
powders of different density. The cyanamide is then dimerized by known art, e.g., as
described by Barrett or by Cameron.

The hydrolysis of dicyandiamide, of cyanamide, and of relevant related compounds is
described by Brill et al. (1997) and (1998). Such hydrolysis is needed to convert the fuel
from the relatively inert state in which it is distributed, stored, and transported to a state in
which it is readily oxidized. In the first preferred practice for the use of dicyandiamide or
cyanamide fuel within the combustion chamber of the engine, the water is there produced
from the combustion of the dicyandiamide and of such other fuel that has been mixed with it.

The second preferred practice for the use of the dry dicyandiamide or cyanamide fuel being
extracted from its fuel tank and mixed with hot water obtained from the exhaust of engine
being fueled in a proportion equal to or in some excess of the stoichiometric ratio of 4 moles
of water for each mole dicyandiamide. This mixture is conveyed into a pressure vessel
containing a catalyst, preferably zinc reduced vanadium pentoxide, and heated to a
temperature between 150 C and 400 C. Reaction (12) occurs therein. The resulting mixture
of ammonia, carbon dioxide, and any excess water is then conveyed as a supercritical fluid
and injected into the cylinder of a Diesel engine. (The critical temperature and critical
pressure for ammonia are 132.4 °C and 11.29 MPa, for carbon dioxide are 31 °C and 7.38 MPa, and for water are 374 °C and 22.1 MPa.) This supercritical fluid may be mixed with a combustion enhancer. Alternatively a liquid combustion enhancer may be added to the dicyandiamide fuel before it is conveyed to the pressure vessel for hydrolysis. Alternatively, in the case of cyanamide, the cyanamide fuel may be dissolved in or mixed as a slurry with a liquid combustion enhancer before it is conveyed to the pressure vessel for hydrolysis. The Diesel engine may incorporate a spark plug to improve the combustion.

The third preferred practice for the use of the dry dicyandiamide or cyanamide fuel being extracted from its fuel tank and mixed with hot water obtained from the exhaust of engine being fueled in a proportion equal to or in some excess of the stoichiometric ratio of 4 moles of water for each mole dicyandiamide or cyanamide. This mixture is conveyed into a pressure vessel containing a catalyst, preferably zinc reduced vanadium pentoxide, and heated to a temperature between 150 °C and 400 °C. Reaction (12) occurs therein. The resulting mixture of ammonia, carbon dioxide, and any excess water is then conveyed, either as a supercritical fluid or as a mixture of supercritical ammonia and supercritical carbon dioxide and any steam, to the intake manifold of an Otto cycle engine and aspirated therein. A combustion enhancer may be added. Alternatively a liquid combustion enhancer may be added to the dicyandiamide fuel before it is conveyed to the pressure vessel for hydrolysis. Alternatively, in the case of cyanamide, the cyanamide fuel may be dissolved in or mixed as a slurry with a liquid combustion enhancer before it is conveyed to the pressure vessel for hydrolysis.

The fourth preferred practice for the use of the dry dicyandiamide or cyanamide fuel being extracted from its fuel tank and mixed with hot water obtained from the exhaust of engine being fueled in a proportion equal to or in some excess of the stoichiometric ratio of 4 moles of water for each mole dicyandiamide or cyanamide. This mixture is conveyed into a high temperature pressure vessel containing a catalyst, preferably zinc reduced vanadium pentoxide, and heated to a temperature between 150 °C and 400 °C. Reaction (12) occurs therein. The resulting mixture of ammonia, carbon dioxide, and any excess water is conveyed, either as a supercritical fluid or as a mixture of supercritical ammonia and supercritical carbon dioxide and any steam, to a low temperature pressure chamber containing water and some ammonia at a temperature below 50 °C and as cool as practicable. The supercritical fluid is sparged therein. Liquid is withdrawn from this low temperature pressure vessel while the concentration of ammonia is below the solubility limit of ammonia at the temperature of this liquid and ambient pressure (about 0.1 MPa). Metering and measurement apparatus of the known art are provided to maintain this condition. (The solubility limit of ammonia in water is known to be, in g of ammonia per kg of water, 180 at 60 °C, 250 at 50 °C, 310 at 40 °C, 400 g at 30 °C, and 520 g at 20 °C.) Then carbon dioxide, which has much lower solubility in water, is vented from this liquid to the atmosphere. (The solubility of carbon dioxide in water is known to be, in g of carbon dioxide per kg of water, 0.55 at 60 °C, 0.8 at 50 °C, 1.0 at 40 °C, 1.3 at 30 °C, and 1.7 at 20 °C.) The with reduced carbon dioxide is then heated to a temperature such that the ammonia
concentration exceeds the solubility limit, but below the boiling point for water, and gaseous ammonia is vented and retained as fuel. The ammonia depleted liquid is the returned to the low temperature pressure vessel. This heating may be done in a heat exchange system with the initial fluid from the high temperature pressure vessel. The carbon dioxide separation part of this is practice has some resemblance to the regenerable aqua ammonia process for CO$_2$ sequestration system for power plant flue gasses that was presented by Yeh, Resnik, and Pennline. Alternatively a liquid combustion enhancer may be added to the dicyandiamide fuel before it is conveyed to the high temperature pressure vessel for hydrolysis or to ammonia gas. Alternatively, in the case of cyanamide, the cyanamide fuel may be dissolved in or mixed as a slurry with a liquid combustion enhancer before it is conveyed to the pressure vessel for hydrolysis.

Note that when uses the fuel of the present invention in this way, the amount of water that is needed for the conversion to ammonia is 2/3 of the amount of water produced by the final oxidation. It is clearly advantageous to obtain the water needed for the conversion to ammonia from the water produced by oxidation. For some of the devices to be fuelled with the present invention, such as fuel cells, the capture of the water produced by oxidation will be obvious to those skilled in the art. For other cases, such as Otto Cycle or Diesel Cycle internal combustion engines, the method to capture such a large fraction of the water produced by oxidation may not be entirely obvious, so it is here described.

It is noted that steam turbines and steam reciprocating engines used on land where there is abundant clean freshwater often allow their steam exhaust to escape, but steam turbines and steam reciprocating engines used on ships at sea, where make-up water is made from seawater at substantial expense, generally have, in addition to the high pressure equipment, low pressure turbines or low pressure cylinders, often exhausting into a partial vacuum where the steam is condensed against a heat sink cooled by seawater. In this way ships capture almost all the water used for steam. (They generally do not capture the water produced by oxidizing hydrocarbon fossil fuels because that exhaust is too polluted due to impurities in such fuel.) Therefore, steam turbines and steam reciprocating engines using the fuel of the present invention in the ammonia or hydrogen oxidation mode may obtain the water needed for the conversion to ammonia by adopting the art that is well known for such engines running on ships.

Gas turbines running on fossil fuel on land or in the air generally do not capture water from their exhaust because of the pollution and because of a lack of economic motivation. However, a low pressure turbine can be attached to the exhaust of the high pressure turbine that is designed to run on ammonia or hydrogen so that the final exhaust is cool enough to capture at least 2/3 of water produced.

Some prior art Otto Cycle and Diesel Cycle internal combustion engines (ICEs) that are turbocharged obtain the power to compress the incoming air from a gas turbine running off the exhaust from the cylinders. Thus, whereas the water generally comes out of the cylinder
of an ICE as steam, it cools as it passes through the exhaust pipe and any muffler, catalytic converter, and turbine that is in its path to the environment. Present vehicles regularly discharge some liquid water, which might easily be captured if it were wanted, as well as some water vapor. Therefore, an ICE fueled in the ammonia mode or the hydrogen mode with the present invention may obtain the water needed for the conversion by using a low pressure turbine on the exhaust manifold sufficient to condense and capture at least 2/3 of the water produced by oxidation of the fuel.

Of course, the addition of a low pressure turbine to the exhaust will increase the energy efficiency of the engine. It will also have other benefits. First, it will reduce the noise emitted by the engine, particularly if it is an ICE or reciprocating engine. Depending on economic and legal requirements, it may do this to the extent that no other muffler is required. Second, it will reduce the temperature of the exhaust gasses over the time that they pass through the turbine, rather than abruptly as in the prior art. This will allow the oxides of nitrogen, NO\textsubscript{x}, which are all undesired compounds with positive heats of formation, either to burn with the excess air that is in the exhaust,

\[ 2 \text{NO}_x + 0_2 \rightarrow \text{N}_2 + (x + 1) 0_2 + \text{heat} \] \hspace{1cm} (40)

or to rearrange among themselves,

\[ 2 \text{NO}_x \rightarrow \text{N}_2 + x 0_2 + \text{heat} \] \hspace{1cm} (41)

Also, although the heat of formation of hydrogen cyanide gas, HCN, is positive and very large, 135 kJ/mole, so that very little of it will be formed at the oxidation temperatures that devices fuel by the present invention will produce, it is very undesirable and tightly regulated, it can also burn in the excess air of the exhaust,

\[ 4 \text{HCN} + 3 0_2 \rightarrow 2 \text{N}_2 + 2 \text{H}_20 + 2 \text{C}_0 2 + \text{heat} \] \hspace{1cm} (42)

or dissociate,

\[ 2 \text{HCN} \rightarrow \text{N}_2 + \text{H}_2 + 2 \text{C} + \text{heat} \] \hspace{1cm} (43)

These reactions will also improve the energy efficiency of the device, but this benefit will be small because the concentrations of these pollutants will be small.

If the legal restrictions on these pollutants are so strict that Reactions (40) to (43) are not sufficient in a practicable low pressure turbine are not sufficient to meet them without a catalytic converter of the prior art, then the reaction may be enhanced by adding sparking systems, which may be powered by the low pressure turbine itself. Alternatively, a small fraction of the ammonia that can be obtained by adding water to the fuel of the present
invention can be added to exhaust to reduce the pollutants according to the prior art known as Selective Catalytic Reduction, SCR,

\[ \text{NH}_3 + \text{NO}_x \rightarrow \text{N}_2 + \text{H}_2\text{O} \quad (44) \]

In this way the need of a catalytic converter of the prior art, with its expensive metals, may be avoided.

Further examples are set out below to illustrate the novel method of producing cyanoguanidine and the use of a vanadium-zinc catalyst in the hydrolysis of cyanoguanidine.

Production of Cyanoguanidine From Methane and Calcium Oxide - Rotating Arc Reactor

A mixture of methane (CH\textsubscript{4}) gas and entrained calcium oxide (CaO) particles, in the molar ratio 3:1 (i.e. three moles of CH\textsubscript{4} per mole of CaO) is fed continuously to a tubular reaction chamber, maintained at a temperature of about 2000° C by the presence of a rotating electric arc. Magnetic coils surround the reaction chamber and maintain a magnetic field of about 120 gauss within the reaction chamber to rapidly rotate the arc. The cathode is a 0.25" graphite rod held in the center of a cylindrical graphite anode with a 0.5" inside diameter. The arc is powered by a power supply of the type used for arc-welding with a maximum output voltage of 160 volts. The arc is started in argon gas and once established the gas flow is switched to methane and the vibratory feeder supplying the CaO started. The arc power level is 25 kW. The CaO particles are in the size range of 44-75 μm. About 1% of calcium fluoride is added to the CaO to facilitate the subsequent reaction of the calcium carbide with nitrogen gas. The methane flow rate is 16 liter/minute. The reaction chamber of 1.0" inside diameter is fabricated from a suitable high temperature refractory material able to withstand high temperature reducing environments. Under these conditions 70-90% of the CaO is converted to calcium carbide with a particle size of about 0.3 μm.

The particulate calcium carbide is allowed to cool to about 1000° C before entering through a valve the region of the reaction chamber containing the nitrogen gas. The nitrogen gas purity is higher than 99.9%. The flow rate of the nitrogen is adjusted in the range of 0.5-2.5 liter/minute to maintain the calcium carbide in a fluidized state. The nitrogen gas enters through a fritted quartz plate at the bottom of the reaction chamber. After a period of 8 minutes the flow of nitrogen is stopped and the product calcium cyanamide together with some unreacted calcium carbide is removed from the reactor. After cooling, 10 g of the product is stirred with 40 g of water to form a slurry. After the release of acetylene gas stops, the solution is cooled to 20° C and 10 g of carbon dioxide is bubbled into the slurry with stirring over a period of 8 hours. The insoluble material is removed by filtering and the solution evaporated to dryness at 80° C to yield 6-8 g of cyanoguanidine.
Production of Cvanoguanidine From Methane and Calcium Oxide - Non-Rotating Arc Reactor

A mixture of methane (CH4) gas and entrained calcium oxide (CaO) particles, in the molar ratio 3:1 (i.e. three moles of CH4 per mole of CaO) is fed continuously to a reaction chamber, maintained at a temperature of about 2000° C by the presence of an electric arc. The electrodes are 0.25° graphite rods held approximately perpendicular to the flow direction of the reactants and separated by 0.25°. The arc is powered by a power supply of the type used for arc-welding with a maximum output voltage of 160 volts. The arc is started in argon gas and once established the gas flow is switched to methane and the vibratory feeder supplying the CaO started. The arc power level is 25 kW. The CaO particles are in the size range of 44-75 μm. About 1% of calcium fluoride is added to the CaO to facilitate the subsequent reaction of the calcium carbide with nitrogen gas. The methane flow rate is 16 liter/minute. The reaction chamber of 1.0” inside diameter is fabricated from a suitable high temperature refractory material able to withstand high temperature reducing environments. Under these conditions 70-90% of the CaO is converted to calcium carbide with a particle size of about 0.3 μm.

The particulate calcium carbide is allowed to cool to about 1000° C before entering through a valve the region of the reaction chamber containing the nitrogen gas. The nitrogen gas purity is higher than 99.9%. The flow rate of the nitrogen is adjusted in the range of 0.5-2.5 liter/minute to maintain the calcium carbide in a fluidized state. The nitrogen gas enters through a fritted quartz plate at the bottom of the reaction chamber. After a period of 8 minutes the flow of nitrogen is stopped and the product calcium cyanamide together with some unreacted calcium carbide is removed from the reactor. After cooling, 10 g of the product is stirred with 40 g of water to form a slurry. After the release of acetylene gas stops, the solution is cooled to 20° C and 10 g of carbon dioxide is bubbled into the slurry with stirring over a period of 8 hours. The insoluble material is removed by filtering and the solution evaporated to dryness at 80° C to yield 6-8 g of cyanoguanidine.

Hydrolysis of Cvanoguanidine

A mixture of 1.5708 gms of vanadium pentoxide, 50.1454 gms of water (stoichiometric excess), 5.01 11 gms cyanoguanidine, 1.6707 gm zinc (chip size ~ 3-4 mm square) were placed within a steel pressure reaction vessel of approximately 330 cubic centimeters with ¼ inch brass needle valve and ¼ inch copper tubing being attached for venting. This mixture and pressure reaction vessel was heated to 193-195°C and vented at 10 minute intervals. Ammonia was tested for and confirmed with each venting. Each vented exhaust was pH 10.5.

By observation the largest volume of ammonia was noted during the first and second venting. Following the 5th venting no further steam or ammonia or carbon dioxide was noted. With no further production of any pressurized gas being perceived the steel pressure
reaction vessel was opened and a trace of ammonia was noted. All remaining reaction products were dry.

Calculations of remaining reactants:

5 Vanadium residue with zinc chips - 3.2026 gms

Vanadium residue minus zinc chip weight - 3.2026 - 1.6707 = 1.5319 gms

10 Vanadium pentoxide original weight minus vanadium residue weight: 1.5708 - 1.5319 = 0.0389 gm non-hydrolyzed cyanoguanidine

Non-hydrolyzed cyanoguanidine divided by starting amount of cyanoguanidine: 0.0389 / 5.0111 = 0.00776 or ~1% cyanoguanidine non-hydrolyzed or 99+% hydrolyzed.

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Patent Documents

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WO/2005/108289 Guanidine Based Composition and System for Same; Graupner

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US5,753,199 Process for the Production of Calcium Cyanamide for Urea, Weber; Guenther, Klima; Hubertus, and Wolferstetter; Johann

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US4,013,757 High Pressure Thermal Hydrolysis Process to Decompose Triazines in Acid Waste Streams, Sidney Berkowitz and Charles V. Juelke

US3,403,053 Enzyme Activated Biochemical Battery Michael, G. Del Duca

US7,060,233 Process for the simultaneous removal of sulfur and mercury

US7,912,358 Alternative energy source usage for in situ heat treatment processes

Other Documents


Ullmann’s Encyclopedia of Industrial Chemistry (John Wley, New York) Vol. A8, p. 151 Table 2.


CLAIMS

1. A method of generating energy from water and a composition comprising cyanoguanidine, the method comprising

   (a) reacting the composition with water to form ammonia;

   and

   (b) oxidizing the ammonia formed in step (a) to form water and nitrogen thereby generating energy

   or

   (b') converting the ammonia formed in step (a) into nitrogen and hydrogen; and oxidising the said hydrogen to form water thereby generating energy.

2. A method according to claim 1, wherein the reaction of step (a) occurs in the presence of a catalyst comprising vanadium and zinc.

3. A method according to claim 2, wherein the vanadium is vanadium pentoxide and the zinc is metallic zinc.

4. A method according to any one of the preceding claims, wherein the weight of cyanoguanidine in the composition is equal to about 10% to about 100% of the weight of the composition.

5. A method according to any one of the preceding claims, wherein the method comprises step (b) and the water formed in step (b) is reacted with the composition in step (a) to form ammonia.

6. A method according to any one of the preceding claims, wherein the method comprises step (b) and wherein step (b) comprises burning the ammonia formed in step (a).

7. A method according to claim 6, wherein the ammonia is combusted in an internal combustion engine or an external combustion engine.
8. A method according to claim 6 or claim 7, wherein nitrogen oxides are formed in step (b) and the method further comprises reacting a portion of the unburned ammonia from the exhaust of combustion step (b) with the nitrogen oxides to reduce the nitrogen oxides and the unburned ammonia.

9. A method according to any one of the preceding claims, wherein the composition reacts with water in step (a) at a temperature between about 50°C and about 240°C and a pressure between about 1 atmosphere and 50 atmospheres.

10. A method according to any one of claims 1 to 5, wherein the method comprises step (b') and wherein the ammonia is oxidised in an ammonia fuel cell.

11. A method according to any one of the preceding claims, wherein water exhausted by a fuel cell or by an internal or external combustion engine is reacted with the composition to form ammonia in step (a).

12. A method of temporarily storing electrical energy in the form of chemical energy using a composition comprising cyanoguanidine, the method comprising:

(a) use of electrical energy, nitrogen, a metal oxide and a carbon source to produce a composition comprising cyanoguanidine;

(b) storing the composition or transporting the composition to remote locations where electrical energy is required;

(c) combining the composition with water to generate ammonia;

(d) using the ammonia to generate electrical energy when needed; and

(e) supplying that electrical energy to a transmission line.

13. A method (suitably a SCR method) of reducing the NOx content of engine exhaust, the method comprising the step of introducing (e.g. injecting) cyanoguanidine into the exhaust gases.

14. A method (suitably a SNCR method) of reducing the NOx content of flue gases, the method comprising the step of introducing (e.g. injecting) cyanoguanidine into the flue gases.
Fig. 1
Making Cyanamide from Urea

Melt Urea at greater than 131°C and mix with Mg²⁺ Compound at less than 162°C

Mix, Tumble, Knead at a temperature range of 225 - 405°C

Calcine Solid at a temperature range of 600 - 900°C

MgCO₃ & MgNCN

MgCO₃ + MgNCN + H₂O + CO₂ → MgCO₃ & H₂NCN

Recover Mg²⁺ Compound and recycle

H₂NCN → Output Product

Fig. 2
Fig. 3
Fig. 4

LEGEND

CaCN₂ – calcium cyanamide –
CaO – quicklime, calcium oxide
CO – carbon monoxide
CaC₂ – calcium carbide –
C – Carbon
H₂ – hydrogen
N₂ – nitrogen
CaCN₂ - calcium cyanamide
CaO - quicklime, calcium oxide
CO - carbon monoxide
CaC₂ - calcium carbide
C - Carbon
H₂ - hydrogen
N₂ - nitrogen

LEGEND

Fig. 5
Fig. 7
Fig. 9

Electrical Generation and Energy Storage
On-Site Cyanoguanidine Synthesis

Control Electronics

\[ \text{Control Electronics} \]

\[ \rightarrow \text{Cyanoguanidine Synthesis} \]

\[ \rightarrow \text{Cyanoguanidine Storage} \]

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

Calcium carbonate (CaCO}_3\] recycled to CaO using waste heat, the combustion of CO + H\_2, a kiln and/or resistive heating

Fuel or Fertilizer

Electrical generation

Peak Power

Fig. 10

Electrical Generation and Energy Storage
On-Site Cyanoguanidine Synthesis

Control Electronics

\[ \text{Control Electronics} \]

\[ \rightarrow \text{Cyanoguanidine Synthesis} \]

\[ \rightarrow \text{Cyanoguanidine Storage} \]

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

Calcium carbonate (CaCO}_3\] recycled to CaO using waste heat, the combustion of CO + H\_2, a kiln and/or resistive heating

Fuel or Fertilizer

Electrical generation

Peak Power
Electrical Generation and Energy Storage

Off-Site Cyanoguanidine Synthesis

\[ \text{Cyanoguanidine Synthesis} \rightarrow \text{Cyanoguanidine Storage} \rightarrow \text{Water, heat and catalyst(s)} \rightarrow \text{NH}_3 + \text{CO}_2 \]

Calcium carbonate (CaCO_3) recycled to CaO using waste heat, the combustion of CO + H_2, a kiln and/or resistive heating

Fuel or Fertilizer

Electrical generation

Fig. 11

Electrical Generation and Energy Storage

Off-Site Cyanoguanidine Synthesis

\[ \text{N}_2 \rightarrow \text{Cyanoguanidine Synthesis} \rightarrow \text{Cyanoguanidine Storage} \rightarrow \text{Water, heat and catalyst(s)} \rightarrow \text{NH}_3 + \text{CO}_2 \]

Calcium carbonate (CaCO_3) recycled to CaO using waste heat or heat from the combustion of CO + H_2, a kiln and/or resistive heating

Fuel or Fertilizer

Electrical generation

Fig. 12
Fig. 13

Electrical Generation and Energy Storage
On-Site Calcium Cyanamide Synthesis

Control Electronics

N₂

Calcium Cyanamide

Carbon (charcoal)

Electrical Power

Calcium carbonate (CaCO₃) recycled to CaO using waste heat, the combustion of CO + H₂, a kiln and/or resistive heating

Calcium Cyanamide Storage

Hot water or Steam

NH₃ + CO₂

Fuel or Fertilizer

Electrical generation

Peak Power

Fig. 14

Electrical Generation and Energy Storage
On-Site Calcium Cyanamide Synthesis

Control Electronics

N₂

Methane CH₄

Electrical Power

Calcium carbonate (CaCO₃) recycled to CaO using waste heat, the combustion of CO + H₂, a kiln and/or resistive heating

Calcium Cyanamide

Calcium Cyanamide Storage

Hot water or Steam

NH₃ + CO₂

Fuel or Fertilizer

Electrical generation

Peak Power
Electrical Generation and Energy Storage
Off-Site Calcium Cyanamide Synthesis

Fig. 15

Electrical Generation and Energy Storage
Off-Site Calcium Cyanamide Synthesis

Fig. 16
Central Synthesis of Calcium Cyanamide and/or Cyanoguanidine – Satellite Hubs

A method of storing and transporting electrical energy in the form of chemical energy

- Rail Road - Locomotive
  Generator or Engine

- Ammonia Transportation

- Shipping
  Generator or Engine

- Non-Commercial Shipping
  Generator or Engine

- Off-Road
  Generator or Engine

- Load-Leveling
  Generator or Engine

- Non-Fuel Uses

- On-Road
  Generator or Engine

- Industry

- NH₃

- Fertilizer

- Industry

- Fertilizer

- Guanidine compositions

Fig. 17
Coal Dust and Carbon → Rotary Arc → CaO

2nd Step Bosch Reaction

C + H₂O ↔ H₂ + CO
Electrolysis product

CaC₂ + CO
Calcium carbide

CaC₂ + N₂
Exothermic

C + Ca N=C=N + Heat
(Calcium cyanamide)

C + Ca N=C=N + H₂O + CO₂

H-N=C=N-H + CaCO₃
(Cyanamide solution)

Filter → CaCO₃ + Heat → CO₂ + CaO

H-N=C=N-H + Alkaline solution
(Cyanamide) (pH 8.0 or higher)

Filter and dry with waste heat

Cyanoguanidine

(waste heat is used to dry cyanoguanidine)

(OR) CO + ½ O₂ → CO₂ + Heat
Electrolysis product

Fig. 18
Reaction #1: CaO + Coal dust → CaC₂ + CO
(Rotary Arc)

Waste heat reclaimed

Reaction #2: Electrolysis of water → H₂ + ½ O₂
a) H₂ + CO → C + H₂O
   AND/OR
b) ½ O₂ + CO → CO₂ + heat

Toxic Element "Vapor" Scrubbing Step #1
(~2000°C)

Reaction #3: CaC₂ + N₂ → Ca N≡C≡N + C + heat
(Strongly Exothermic)

Reaction #4: Ca N≡C≡N + H₂O + CO₂ → H-N≡C≡N-H + CaCO₃

Filter CaCO₃
Toxic Element "Precipitate" Scrubbing Step #2
(Low temperature)

Reaction #5: H-N≡C≡N-H + Alkaline bath → Cyanoguanidine

Filter & dry cyanoguanidine
with reclaimed waste heat

Cyanoguanidine

Reaction #6: Filtered CaCO₃ + waste heat → CO₂ + CaO

Carbon to Rotary Arc

Bosch Reaction if CO₂
is not reused for
CaCO₃ formation

CaO to Rotary Arc

Fig. 19