US 20090202413A1

(19) **United States**

(12) **Patent Application Publication**

Saxena

(10) **Pub. No.: US 2009/0202413 A1**

(43) **Pub. Date: Aug. 13, 2009**

(54) **CARBON SEQUESTRATION AND PRODUCTION OF HYDROGEN AND HYDRIDE**

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(21) Appl. No.: **12/258,886**

(22) Filed: **Oct. 27, 2008**

Related U.S. Application Data

(60) Provisional application No. 60/982,473, filed on Oct. 25, 2007.

Publication Classification

(51) **Int. Cl.**

C01B 35/10	(2006.01)
C01B 3/02	(2006.01)
C01B 6/04	(2006.01)

(52) **U.S. Cl.** **423/277**; 423/648.1; 423/647

(57) **ABSTRACT**

This invention describes a complete sequestration of carbon (CO_2 and CO) from coal burning plants. In this process, hydrogen can be generated which in turn permits the reduction in the cost of hydride synthesis. The hydrides store hydrogen for on-board application for automobiles and fuel cells. Hydrogen generation and synthesis of hydrides is accomplished by using an integrated approach in which coal is used as a fuel and carbon is sequestered in the process. The CO and or CO_2 produced in coal burning power plants and the heat is used when available for producing hydrogen and hydrides. Carbon is used both as a reactant and as a fuel. Economically hydrogen production cost is comparable to or less than the current price of hydrogen produced from fossil-fuel with the added benefit of carbon sequestration and reducing global warming. Specific processes for synthesizing important hydrogen storage materials, hydrides are described. A hydrogen based automobile becomes viable as the cost of the hydrogen production and hydride synthesis is reduced. Although coal-burning power plant is specified here, any power plant, coal- or natural gas-burning, can be subjected to similar treatment.

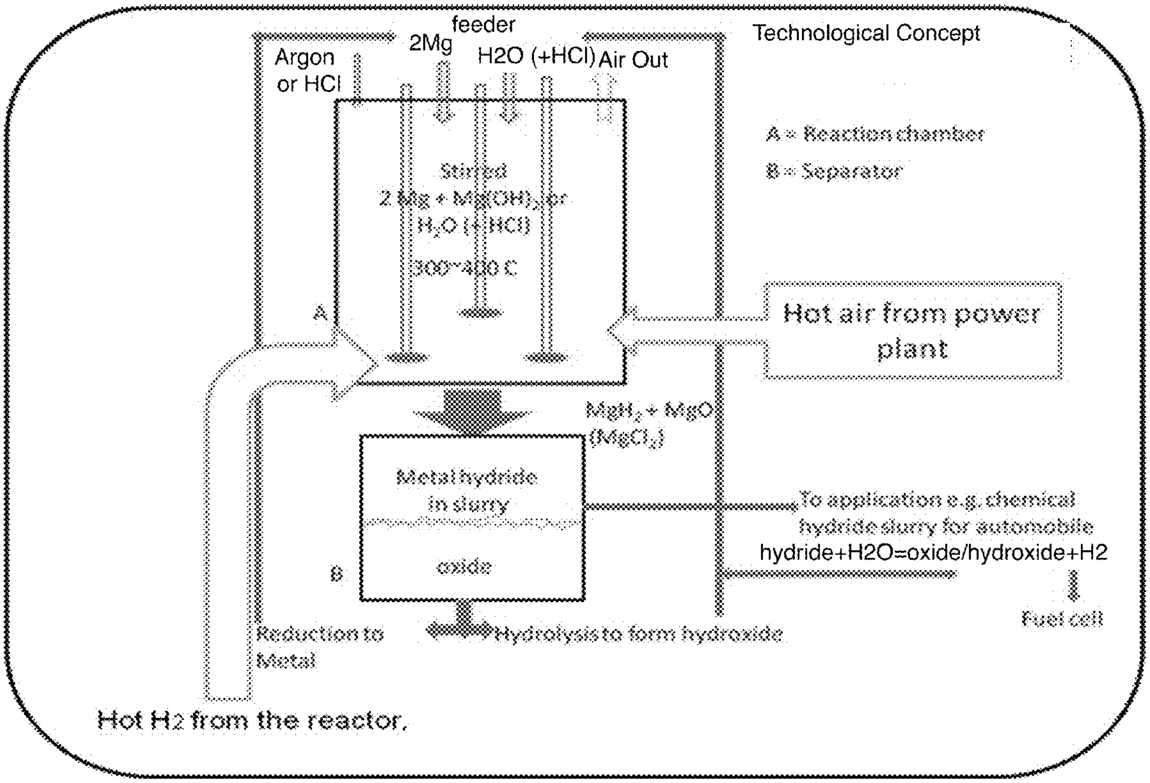
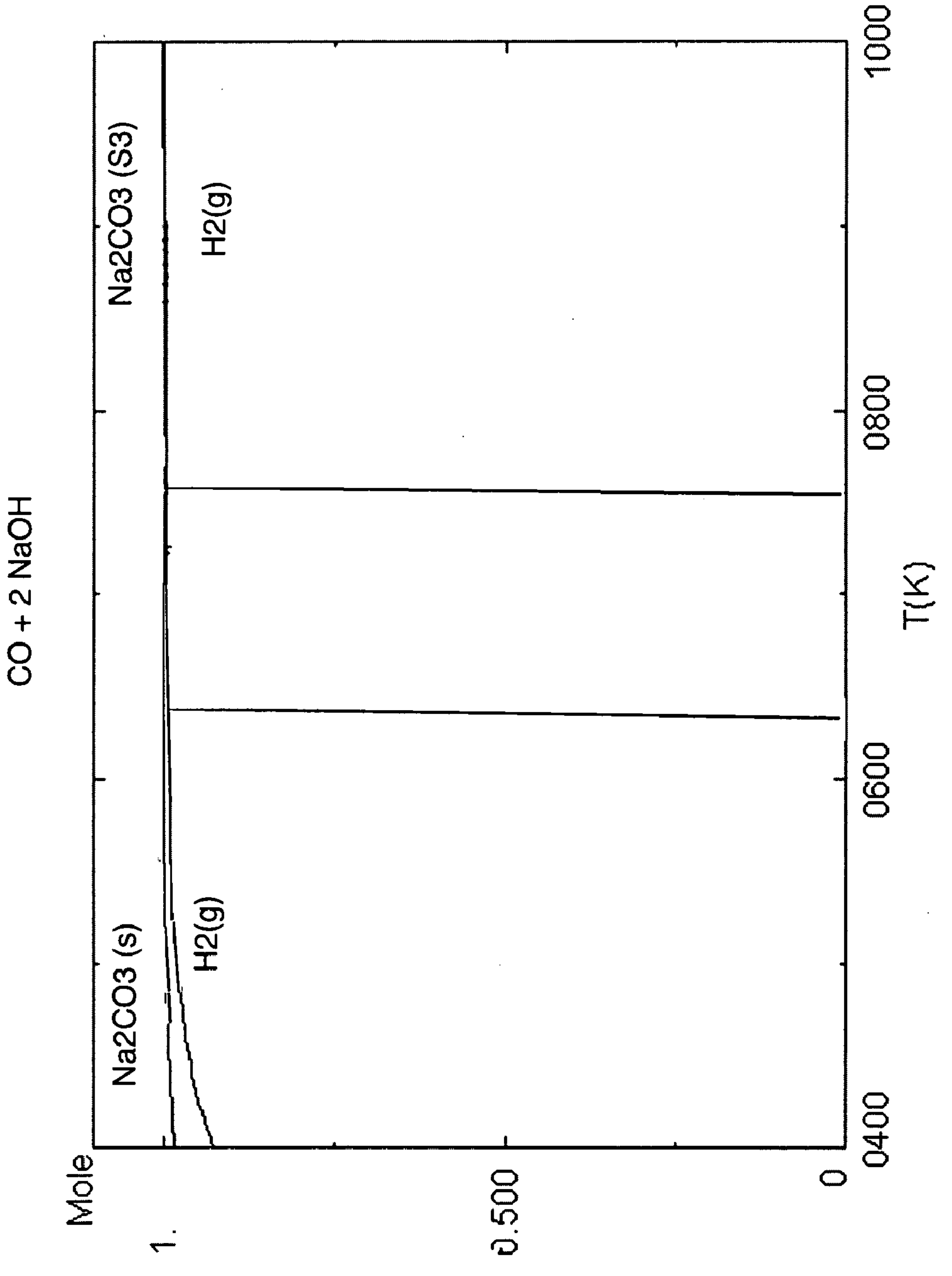


FIG. 1


CO + 2 NaOH
Mole
1.
0.500
0
0400
0600
0800
1000
T(K)
Na2CO3 (s)
H2(g)
Na2CO3 (S3)
H2(g)

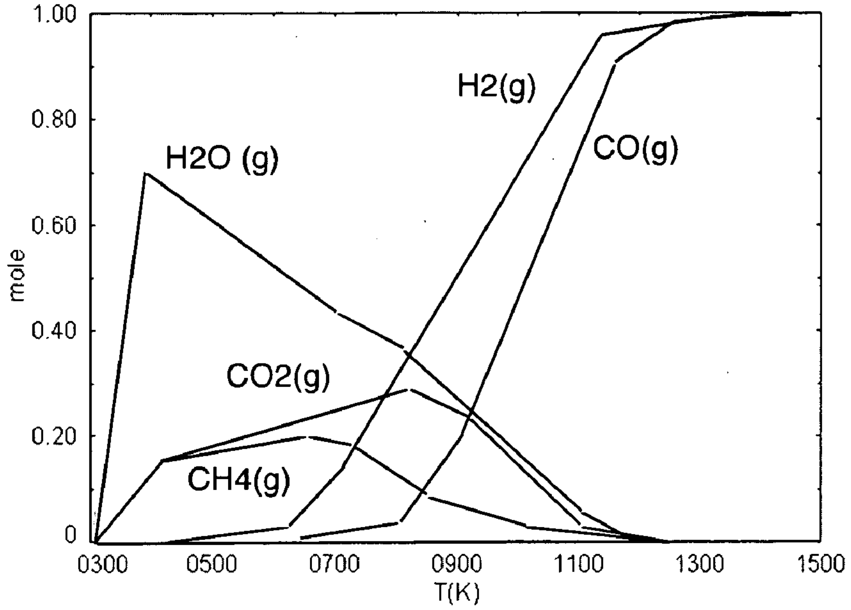


Fig. 2A: Equilibrium composition of C + H_2O.

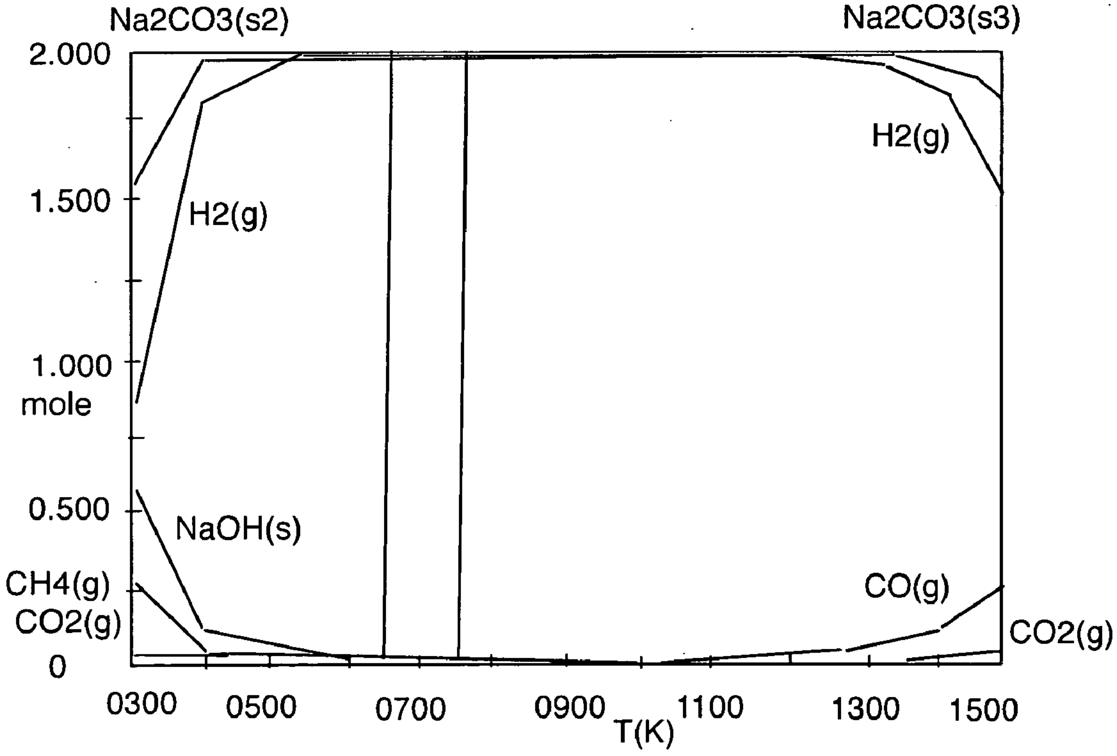


Fig.2B. Equilbrium composition in the mixture 4 NaOH+CO_2+C.

FIG. 3A

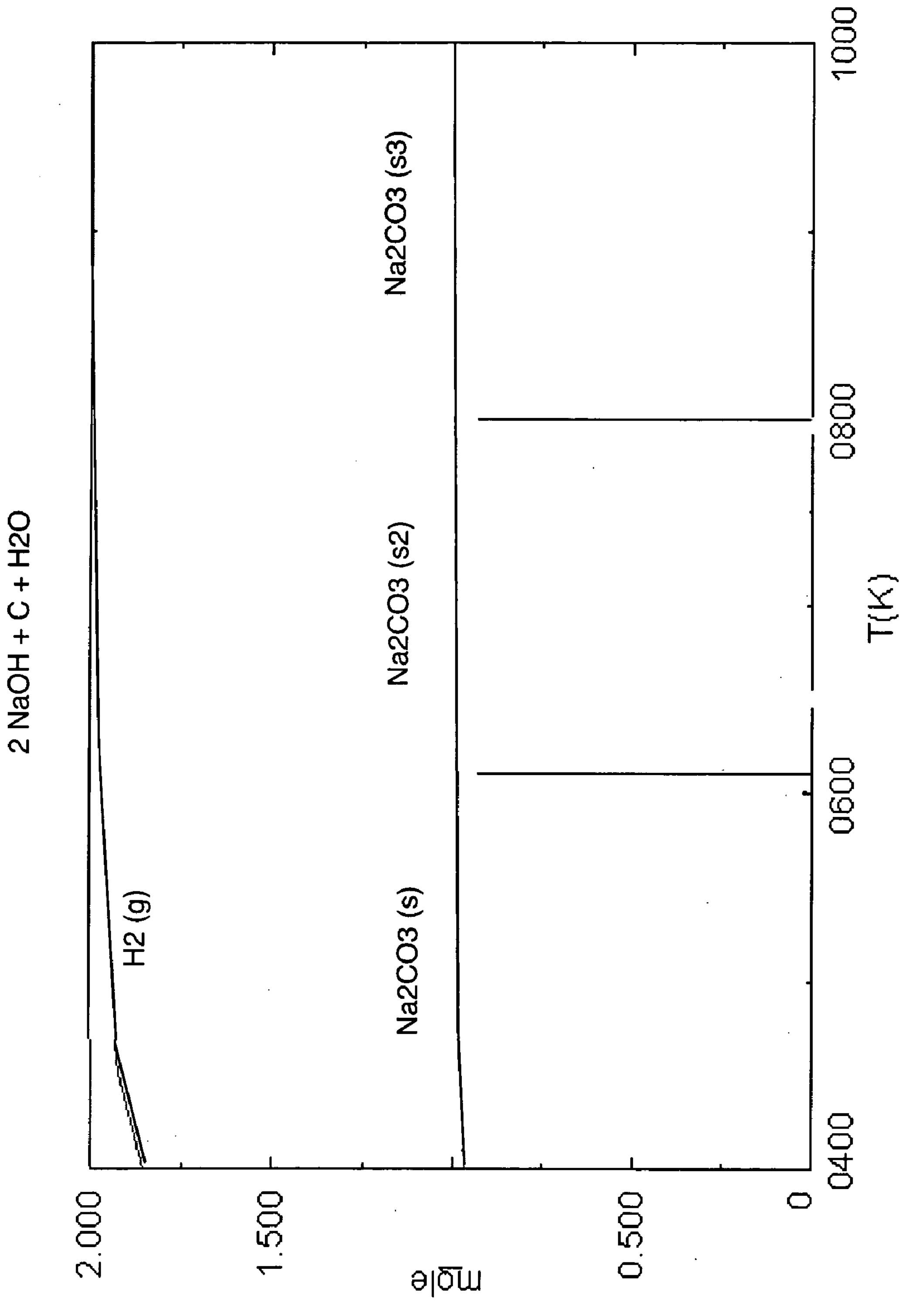

2 NaOH + C + H2O
H2 (g)
Na2CO3 (s)
Na2CO3 (s2)
Na2CO3 (s3)
mole
2.000
1.500
0.500
0
T(K)
0400
0600
0800
1000

FIG. 3B

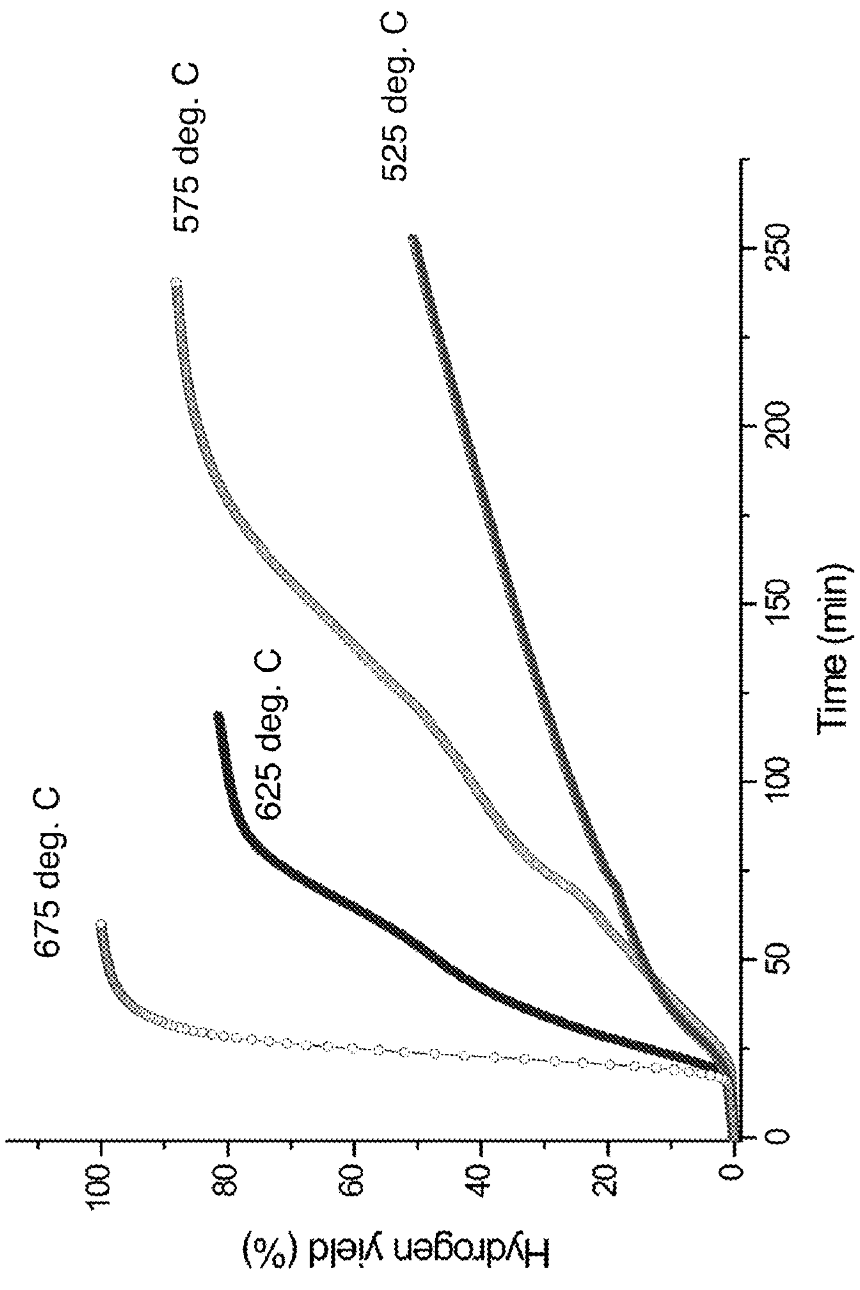

675 deg. C
625 deg. C
575 deg. C
525 deg. C
Hydrogen yield (%)
0
20
40
60
80
100
Time (min)
0
50
100
150
200
250

FIG. 3C

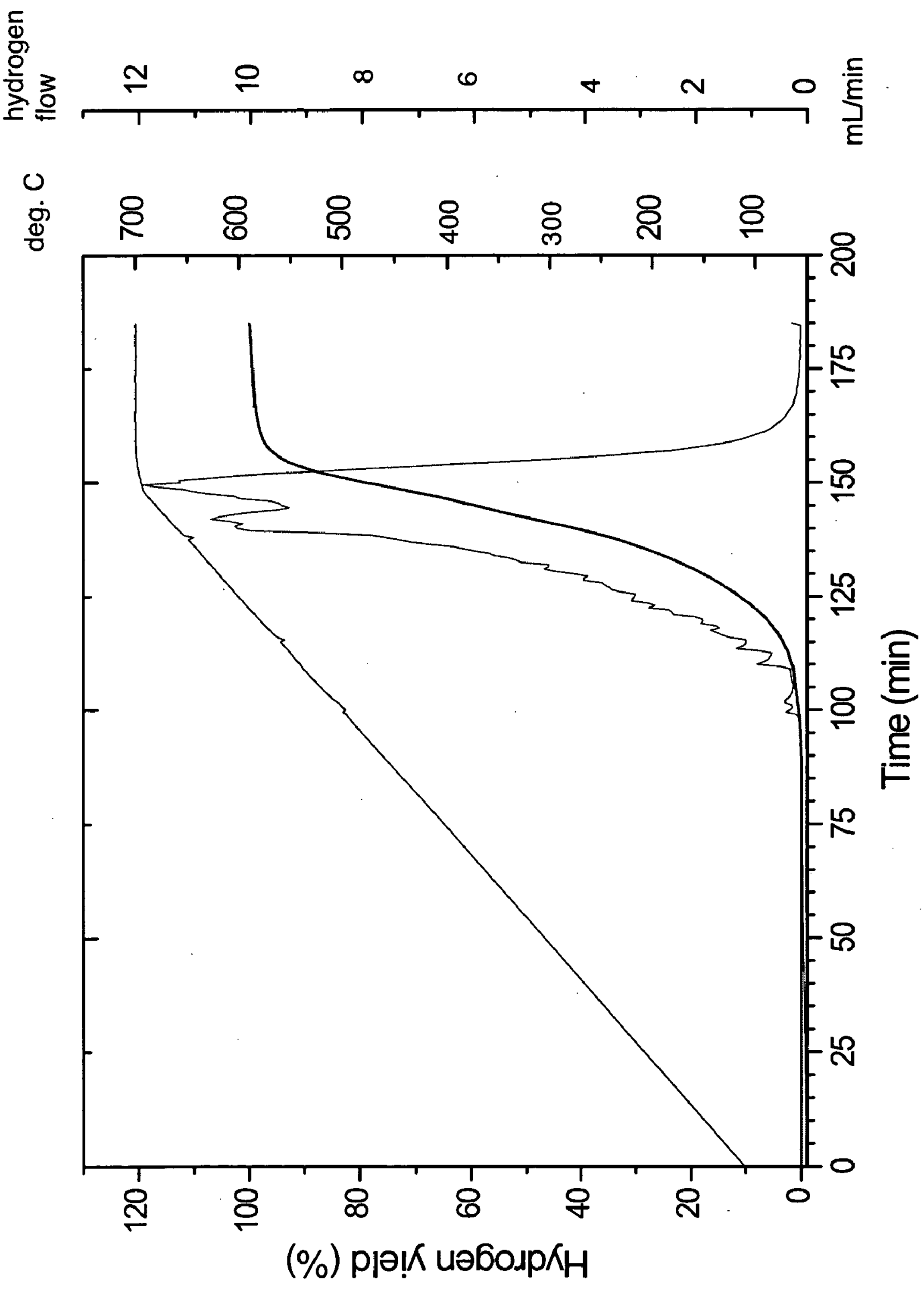

Hydrogen yield (%)
0
20
40
60
80
100
120
Time (min)
0
25
50
75
100
125
150
175
200
deg. C
100
200
300
400
500
600
700
hydrogen flow
mL/min
0
2
4
6
8
10
12

FIG. 4

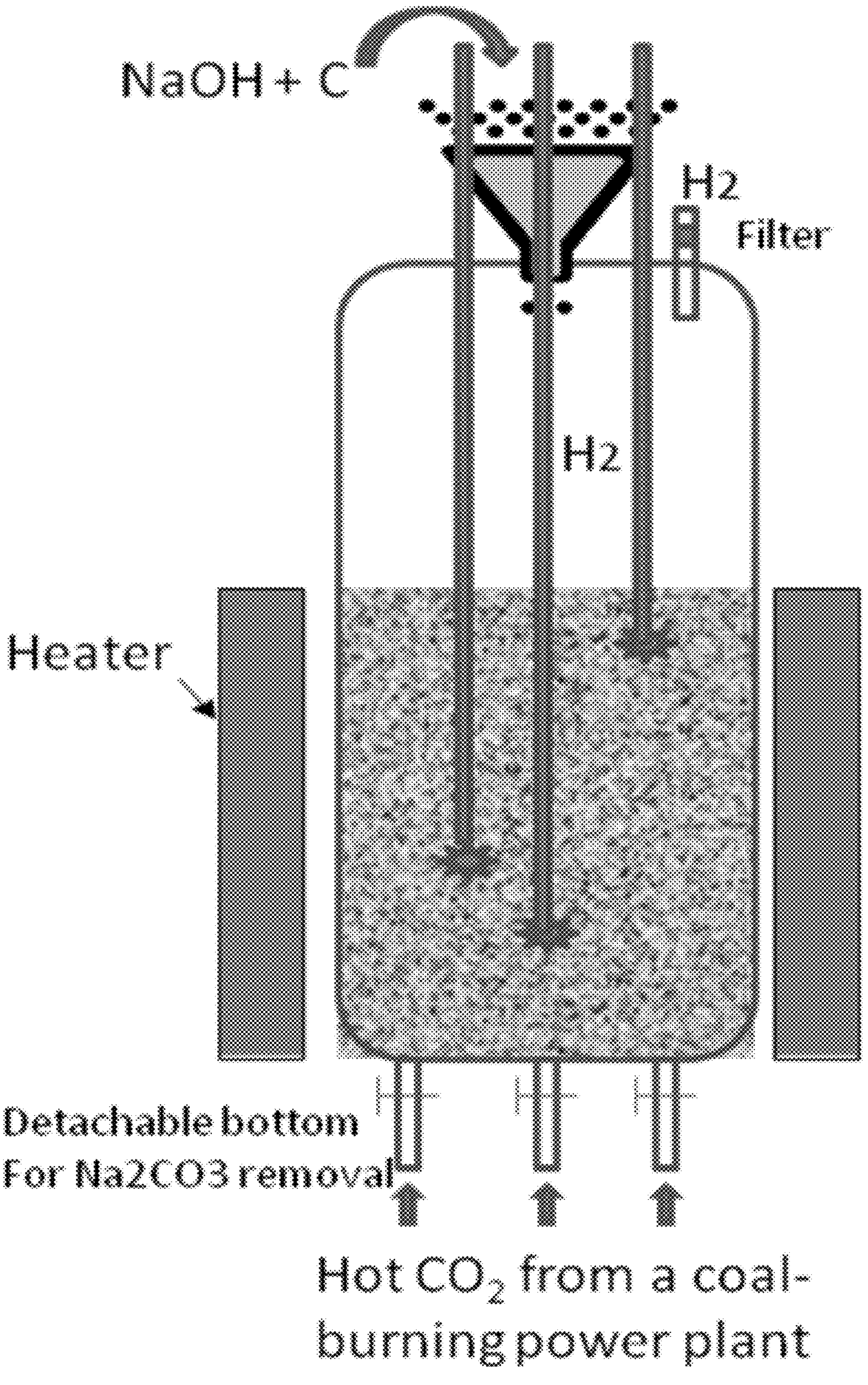
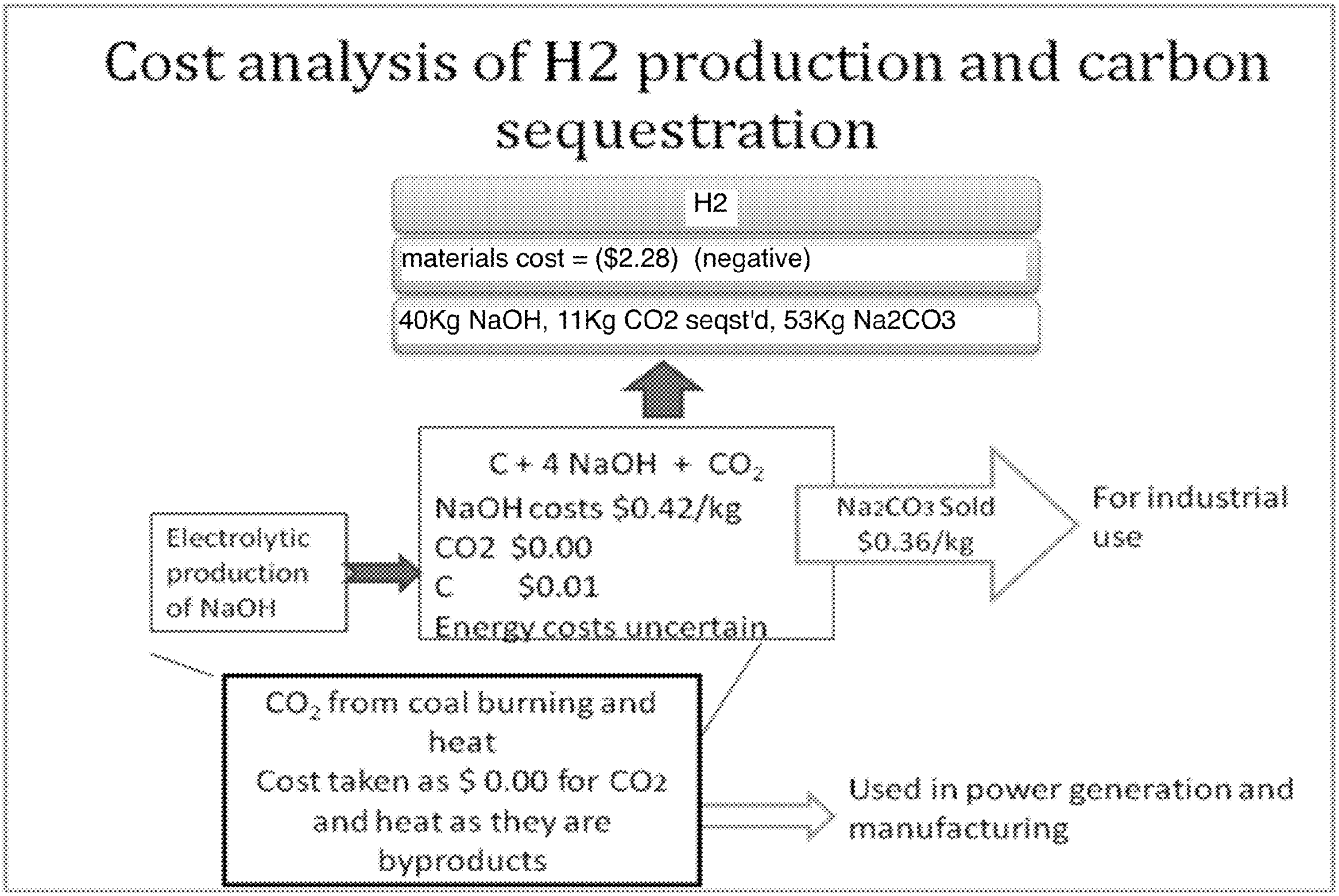

NaOH + C
H2
Filter
H2
Heater
Detachable bottom
For Na2CO3 removal
Hot CO_2 from a coal-burning power plant

FIG. 5



Cost analysis of H2 production and carbon sequestration

H2

materials cost = ($2.28) (negative)

40Kg NaOH, 11Kg CO2 seqst'd, 53Kg Na2CO3

$C + 4\,NaOH + CO_2$

NaOH costs $0.42/kg

CO2 $0.00

C $0.01

Energy costs uncertain

Electrolytic production of NaOH

Na2CO3 Sold $0.36/kg

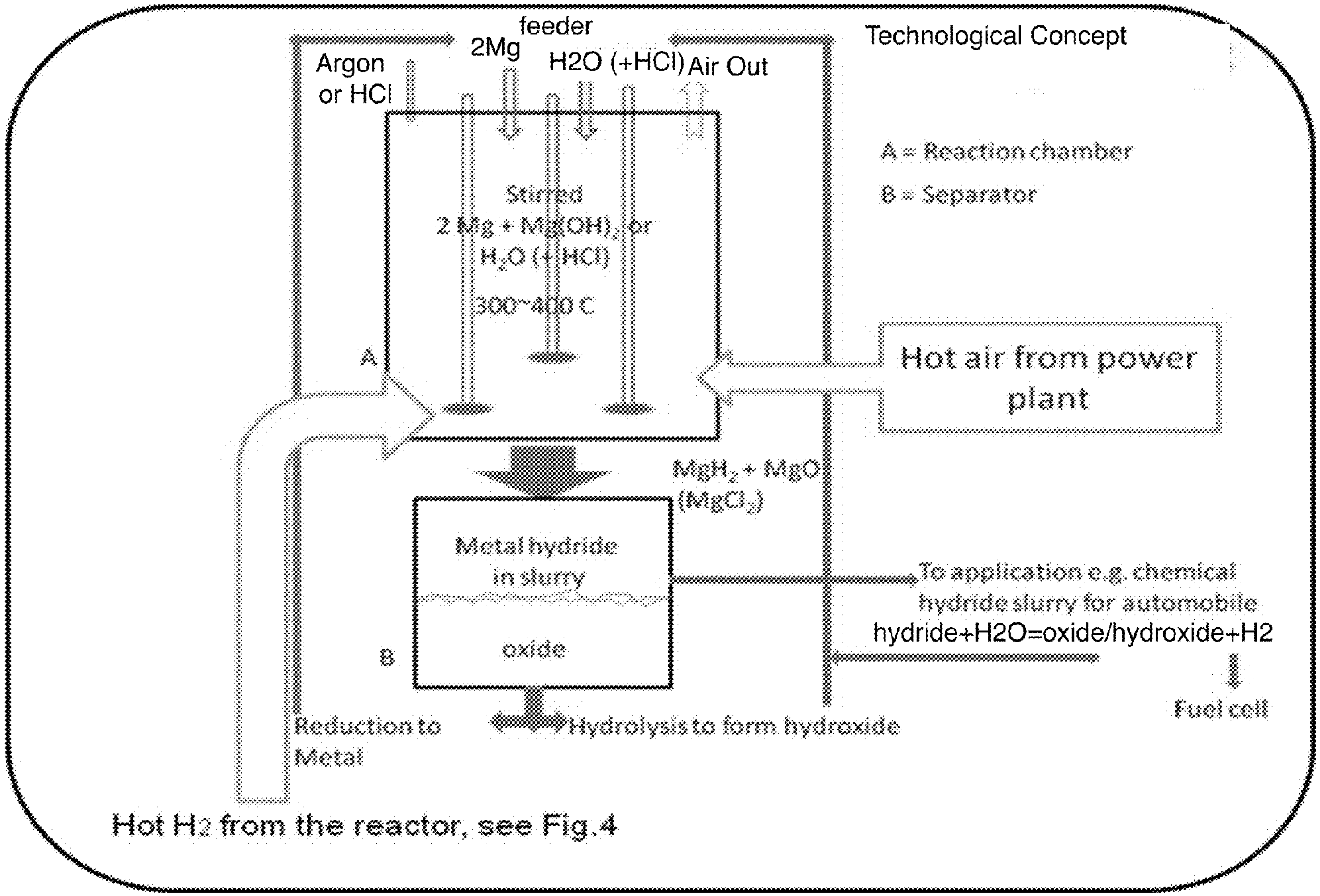
For industrial use

CO_2 from coal burning and heat

Cost taken as $ 0.00 for CO2 and heat as they are byproducts

Used in power generation and manufacturing

FIG. 6


Technological Concept
Argon
or HCl
2Mg
feeder
H2O (+HCl)
Air Out
A = Reaction chamber
B = Separator
Stirred
2 Mg + Mg(OH)$_2$ or
H$_2$O (+HCl)
300~400 C
A
Hot air from power
plant
MgH$_2$ + MgO
(MgCl$_2$)
Metal hydride
in slurry
oxide
B
To application e.g. chemical
hydride slurry for automobile
hydride+H2O=oxide/hydroxide+H2
Fuel cell
Reduction to
Metal
Hydrolysis to form hydroxide
Hot H2 from the reactor, see Fig.4

CARBON SEQUESTRATION AND PRODUCTION OF HYDROGEN AND HYDRIDE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority under 119(e) to U.S. Ser. No. 60/982,473 filed 25 Oct. 2008, the contents of which are incorporated herein in their entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] No federal government funds were used in researching or developing this invention.

NAMES OF PARTIES TO A JOINT RESEARCH AGREEMENT

[0003] Not applicable.

REFERENCE TO A SEQUENCE LISTING

[0004] A table or a computer list appendix on a compact disc

[0005] [ ] is

[0006] [X] is not

included herein and the material on the disc, if any, is incorporated-by-reference herein.

FIELD OF THE INVENTION

[0007] The present invention relates to a system of processes for producing hydrogen gas that take advantage of emission of CO and CO_2 and heat from the coal-burning power plants. The hydrogen thus produced is used to synthesize hydrides at much reduced costs. The use of this invention will lead to carbon sequestration and reduce global warming. The invention is presented in two parts; part 1 deals with hydrogen production with carbon sequestration and part 2 with synthesis of hydrides for on-board hydrogen generation in automobiles.

BACKGROUND OF THE INVENTION

[0008] Steam methane reforming is the most common and the least expensive method to produce hydrogen at present. Coal can also be reformed to produce hydrogen, through gasification. Hydrogen production by CO_2-emitting-free methods are either more expensive compared to those ones using fossil fuel or are in the very early stages of development. Taking into account that United States has more proven coal reserves than any other country coal based technology of hydrogen production is the most attractive. However, effective and low cost carbon sequestration technology has to be developed.

[0009] Hydrogen is regarded as the energy for future but to produce and use hydrogen either by direct combustion or in a fuel cell, we need to use other sources of energy. Thus hydrogen or use of any material in producing energy cannot be an environmentally clean and economically viable solution unless we sequester carbon in economically viable way. The use of hydrogen is being promoted on a federal level with massive support from DOE and there is little doubt that we will soon have the hydrogen solution for our transportation and other energy uses. However, it is a sad fact that such energy will continue to be dependent on the use of fossil fuel for long time and may not be economic. To turn things around, we have to use alternate methods of using coal, producing hydrogen and hydrides. Many hydrides are currently under consideration for use in on-board generation of hydrogen and the cost of producing the hydride is an important consideration. This invention is unique because although we use carbon in producing hydrogen, the carbon is sequestered simultaneously as hydrogen is produced and hydrogen is reacted with suitable metals to produce hydrides.

[0010] Coal is used extensively in producing synthetic fuels. Use of coal in gasifiers is well established and hydrogen may be produced by the reaction: $C+2H_2O=CO_2+2H_2$. Gasifiers are operated between 800 and 1500 K, depending on the conditions involving steam, oxygen and/or air a mixture of CO_2, CO, H_2, CH_4 and water. The CO produced can be further processed by the shift-gas reaction to produce H_2 with production of CO_2: $CO+H_2O=CO_2+H_2$.

[0011] The following is an extract from "The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs (2004), National Academy of Engineering (NAE), Board on Energy and Environmental Systems (BEES)" and shows the importance of the present project:

"Carbon Emissions Associated with Current Hydrogen Production

[0012] At the present time, global crude hydrogen production relies almost exclusively on processes that extract hydrogen from fossil fuel feedstock. It is not current practice to capture and store the by-product CO_2 that results from the production of hydrogen from these feedstocks. Consequently, more than 100 Mt C/yr are vented to the atmosphere as part of the global production of roughly 38 Mt of hydrogen per year."

[0013] It would then appear that when coal is used in gasifiers or in direct burning in power- and other manufacturing-plants, CO_2 and CO are prominent among other gases. Their emission in the atmosphere is not only harming the environment but as considered here is also a waste of resources. For industry this has been an economic issue and someone else's problem. This invention will provide a clear economic incentive to sequester carbon (CO_2 and CO) without significantly affecting our current modes of operations. We consider several such processes below.

Related Patents

Carbon Sequestration

[0014] U.S. Pat. No. 7,132,090, D. Dziedzic, K. B. Gross, R. A. Gorski, J. T. Johnson,

[0015] Sequestration of carbon dioxide

[0016] U.S. patent application 20030017088, W. Downs and H. Sarv

[0017] Method for simultaneous removal and sequestration of CO_2 in a highly efficient manner

[0018] U.S. patent application 20010022952, G. H. Rau and K. G. Caldeira

[0019] Method and apparatus for extracting and sequestration carbon dioxide

[0020] U.S. Pat. No. 5,261,490, T. Ebinuma

[0021] Method for dumping and disposing of carbon dioxide gas and apparatus therefore

[0022] U.S. Pat. No. 6,667,171, D. J. Bayless, M. L. Vis-Morgan and G. G. Kremer

[0023] Enhanced practical photosynthetic CO2 mitigation

[0024] U.S. Pat. No. 6,598,407, O. R. West, C. Tsouris and L. Liang

[0025] Method and apparatus for efficient injection of CO2 in ocean

[0026] U.S. Pat. No. 5,562,891, D. F. Spencer and W. J. North

[0027] Method for the production of carbon dioxide hydrates

[0028] U.S. Pat. No. 5,293,751, A. Koetsu

[0029] Method and system for throwing carbon dioxide into the deep sea

[0030] U.S. Pat. No. 6,270,731, S. Kato, H. Oshima and M. Oota

[0031] Carbon dioxide fixation system

[0032] U.S. Pat. No. 5,767,165, M. Steinberg and Y. Dong

[0033] Method for converting natural gas and carbon monoxide to methanol and reducing CO2 emission

[0034] U.S. Pat. No. 6,987,134, R. Gagnon

[0035] How to convert carbon dioxide into synthetic hydrocarbon through a process of catalytic hydrogenation called CO2hydrocarbonation

Hydride

[0036] U.S. Pat. No. 5,958,098: Method and composition in which metal hydride particles are embedded in a silica network.

[0037] U.S. Pat. No. 5,308,553: Metal hydride compositions and methods.

[0038] U.S. Pat. Nos. 5,514,353 and 5,833,934: Demand responsive hydrogen generator based on hydride water reaction.

[0039] U.S. Pat. No. 20040258613: Process for the production and purification of sodium hydride.

[0040] U.S. Pat. No. 20050053547: Method for activating metal hydride material.

[0041] U.S. Pat. No. 20020100682:Hydrogen recharging system for fuel cell hydride storage reservoir.

[0042] U.S. Pat. No. 20030014917: Chemical hydride hydrogen generation system and an energy system incorporating the same.

[0043] U.S. Pat. No. 20040166057: Powder metal hydride hydrogen generator.

[0044] U.S. Pat. No. 20050058595 : Reactor and method for generating hydrogen from a metal hydride.

[0045] U.S. Pat. No. 6,143,270: anhydrous magnesium chloride

[0046] U.S. Pat. No. 5,665,220: Electrolytic magnesium production

[0047] U.S. Pat. No. 6,372,017: Method for producing magnesium

[0048] U.S. Pat. No. 5,782,952: Method for producing magnesium

[0049] U.S. Pat. No. 4,720,375: Process for producing magnesium oxide

[0050] U.S. Pat. No. 5,162,108: Method for preparing active magnesium hydride

[0051] U.S. Pat. No. 6,433,129, Amendola, S. C.; Kelly, M. T. "Compositions and Processes for Synthesizing Borohydride Compounds 2002.

[0052] U.S. Pat. No. 6,670,444, Amendola, S. C.; Kelly, M. T.; Ortega, J. V.; Wu, Y. "Process for Synthesizing Borohydride Compounds", 2003.

[0053] U.S. Pat. No. 6,524,542, Amendola, S. C.; Kelly, M. T.; Wu, Y "Process for Synthesizing Borohydride Compounds", 2003.

[0054] Ortega, J. V.; Wu, Y; Amendola, S. C.; Kelly, M. T. "Processes for Synthesizing Alkali Metal Borohydride Compounds" U.S. Pat. No. 6,586,563, 2003.

[0055] U.S. Pat. No. 2,469,879, Hurd, D. T. "Preparation of Boron Compounds", 1949.

[0056] U.S. Pat. No. 2,596,690, Hurd, D. T. "Preparation of Boron Compounds", 1952.

[0057] DE Patent 1095797, Jenkner, H. "Process for the Production of Boron Hydrides", 1960.

[0058] GB Patent 907462, Jenkner, H. "Improvements in or relating to the Manufacture of Boron Hydrides and Boron Hydrides containing Organic Substituent Radicals", 1960.

[0059] JP Patent 2002-193604, Kojima, Y; Haga, T.; Suzuki, K.; Hayashi, H.; Matsumoto, S.;

[0060] Nakanishi, H. "Method for Manufacturing Metal Borohydride", 2002

[0061] U.S. Pat. No. 3,734,842, Cooper, H. B. H. "Electrolytic Process for the Production of Alkali Borohydrides", 1973.

[0062] CN Patent Appl. 1396307A, Sun, Y; Liang, Z. "Electrochemical Process for Preparing Borohydride", 2003.

[0063] JP Patent 2002-173306, Suda, S. "Method of Manufacturing Metal Hydrogen Complex Compound", 2002.

[0064] DE Patent 1108670, Broja, G.; Schlabacher, W. "Process for the Production of Alkali Metal Borohydrides", 1959.

[0065] DE Patent 1067005, Schubert, F.; Lang, K.; Schlabacher, W. "Process for the Production of Borohydrides", 1959.

[0066] JP Patent, Haga, T.; Kojima, Y. "Method for Manufacturing Metal Borohydride" 2002-241109, 2002.

SUMMARY OF THE INVENTION

[0067] The present invention provides a system of reactions to produce hydrogen from sodium hydroxide and CO or CO_2 and carbon. The carbon gases are produced in industrial plants burning coal and thus available at no cost. These gases also can be obtained at relatively high temperature; the reaction of CO or CO_2 with sodium hydroxide is exothermic and hence no additional heating would be required. The CO or CO_2 would react to from sodium carbonate and thus carbon will be sequestered.

[0068] Another embodiment of the present invention provides the production of hydrogen if the industrial CO or CO_2 is not available. In such a case, sodium hydroxide reacts with water and carbon producing hydrogen and no carbon is released in the environment.

[0069] In yet another embodiment of the invention, the hydrogen produced cheaply with no carbon release in the atmosphere is used to synthesize hydrides at low cost. Magnesium hydride is produced by direct reaction with powdered magnesium and the hydrogen produced in previous embodiments. It may also be produced by a reaction among powdered magnesium, water and hydrogen (produced as described above or from other sources).

[0070] In the final embodiment of this invention, a method is provided to convert sodium- or lithium-borate ($NaBO_2$ or $LiBO_2$) to sodium- or lithium-borohydride and also their production using borates, magnesium, water and hydrogen.

[0071] In the last two embodiments of this invention, advantage is taken of the integration of the hydride synthesis process with currently operating or future coal-burning plants; thus saving costs and providing carbon sequestration.

However, the process described in each embodiment can be carried out independently of the power plants.

BRIEF DESCRIPTION OF THE DRAWINGS

[0072] The purpose of this invention and the tremendous advantages it entails for reduction in global warming gases needs to be fully understood from the study of the description along with the drawings wherein:

[0073] FIG. **1** shows the moles of hydrogen and sodium carbonate produced when sodium hydroxide and carbon monoxide are allowed to react. The carbon monoxide is presumably generated in a coal-burning process providing heat to another manufacturing process, e.g. synthesis of cement;

[0074] FIG. **2** shows in two parts a comparison of the calculated equilibrium compositions, which are easily verified in experiments. FIG. **2**A is a well known phase diagram showing the carbon-water system in a gasifier where hydrogen and CO mixture is produced up to very high temperatures. This diagram is included here to show a comparison with the reaction adopted in the present invention shown in FIG. **2**B. The temperature of hydrogen production is much lowered and the gas is pure hydrogen.

[0075] FIG. **3** shows that in absence of an industrial source of carbon-oxygen gases, this invention provides for the production of hydrogen from water, carbon and sodium hydroxide reaction with no emission of C—O gases. FIG. **3**A. Calculated results. FIG. **3**B. The mixture of NaOH and C was heated from 25° C. to 700° C. and the polythermal results of hydrogen production are shown. FIG. **3**C. The same mixture heated isothermally at 525, 575, 625 and 675° C.

[0076] FIG. **4** shows a possible method of hydrogen production. The stirred mixture of sodium hydroxide is reacted with CO_2 from coal-burning and C and heated to 800 K with heat contributions from hot hydrogen, hot CO_2 and hot air from the power plant. The reaction kinetics may be improved by use of a catalyst such SiO_2 and/or continuous stirring as shown in the figure.

[0077] FIG. **5** shows the cost of hydrogen production with carbon sequestration. The analysis depends on the current price structure of sodium products. Any reaction hydrogen producing reaction discussed in the text can be used with this arrangement.

[0078] FIG. **6** shows that the synthesis of a hydride using metal+water+heated H_2 is accomplished in this reactor which may be heated using hot air exhausted from a power plant according to this invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0079] The present invention provides a novel method of producing hydrogen with carbon sequestration; the novelty lies in the fact that gases produced in a coal-burning plant are used both for the energy and for the substance to react with sodium hydroxide reducing the cost simultaneously with eliminating the emission. If we further couple the metal hydride producing reaction with the above reactor system, we can also reduce the cost of metal hydrides for automobile use.

[0080] Hydrogen Production

[0081] We may use the following reactions:

[0082] $2NaOH\ (c)+CO(g)=Na_2CO_3\ (c)+H_2(g)$ ΔH=−1.19E5 J (600 K)

[0083] $4\ NaOH\ (c)+C\ (c)+CO_2(g)=2Na_2CO_3(c)+2\ H_2(g)$ ΔH=−6.62 E4 (600 K)

[0084] $2\ NaOH\ (c)+C(c)+H_2O(1)=Na_2CO_3(c)+2\ H_2(g)$ ΔH=6.458 E4 (600 K)

[0085] $3\ NaOH\ (c)+C(c)=Na_2CO_3(C)+Na+1.5\ H_2$ ΔH=−2.52E5 J (1100 K)

[0086] Reactions (1) and (2) are exothermic. Reaction (2) can be considered as a combination of the Boudouard reaction:

[0087] $C+CO_2=2\ CO$ and reaction (1). Reaction (2) may also be considered as a combination of

[0088] $2\ NaOH+CO_2=Na_2CO_3+H_2O$ and

[0089] $2\ NaOH+C+H_2O=Na_2CO_3+2\ H_2$

[0090] Process 1: Use of CO From Coal Burning

[0091] CO is not produced in coal burning because high ratio of air to coal is used. However if the heating requirement for the plant is fully met with a lower ratio such that CO is actually produced in some quantity, we could use the CO for producing hydrogen according to the following reaction

[0092] (1) $2NaOH+CO=Na_2CO_3+H_2$

[0093] If NaOH costs 42 cents per kg and Na_2CO_3 sells for 36 cents per kg, the hydrogen cost will be only the cost of the energy for this exothermic reaction, which would be an excellent value.

[0094] An equilibrium calculation in FIG. **1** shows that Na_2CO_3 also known as soda ash and hydrogen are produced over a wide temperature range starting from 400 to 1100 K. The reaction kinetics may be improved by use of a catalyst such SiO_2 and/or continuous stirring as described later.

[0095] However, if we switch to coal-burning plant design that produces significant CO, we will have to burn more coal for the same thermal effect as can be seen by calculating at 1000 K

[0096] C+Air (N_2 4,$O_2$1 mole)=CO2, ΔH=−2.746E5 J

[0097] C+Air (N_2 2,$O_2$0.5 mole)=0.763 CO+0.118 CO_2+0.12 C, ΔH=−6.628E4 J

[0098] A comparison of ΔH shows that 4 times heat is produced when CO_2 is maximized. Thus in order to maximize CO, we will have to burn 4 times carbon; since in doing so, we will produce as much more hydrogen and Na_2CO_3, the economics would not change.

[0099] Process 2: Use of CO_2 From Coal-Burning Plant

[0100] For existing power stations, where CO_2 is produced, we may choose another alternative and use CO_2 to react with water and Sodium hydroxide according to the reaction:

[0101] (2) $4NaOH+C+CO_2=Na_2CO_3+2H_2$

[0102] One may compare this reaction with the combination of the gasifier reaction $C+2H_2O=CO_2+2H_2$ and the CO_2 absorbing reaction $2NaOH+CO_2=Na_2CO_3+H_2O$ to accomplish similar result. It is shown in FIG. **2** (A and B) that the reaction (3) has definite advantage being the carbon-sequester and hydrogen producing reaction. The reaction kinetics may be improved by use of a catalyst such SiO_2 and/or continuous stirring as described later.

[0103] A comparison of the two figures shows that much higher temperature is required to obtain a significant amount of hydrogen mixed with CO in FIG. **2**A than is required when using reaction (2) (FIG. **2**B).

[0104] Process 3: Hydrogen Generation Without Input of CO or CO_2

[0105] We may consider reaction (3), if CO or CO_2 are not available from an industrial plant:

[0106] (3) $2\ NaOH+C+H_2O=Na_2CO_3+2\ H_2$

[0107] While this is an endothermic reaction, less amount of solids are required to produce the same amount of hydrogen. This may be helpful if the cost structure of the sodium compound alters in time. In this process 20 kg of NaOH will yield 26.5 kg of Na_2CO_3 for each 1 kg of hydrogen. Reaction (3) was considered by Saxena et al. (25) followed by Ishida et al. (26). However, this is the first demonstration that the process is cost effective (see below). FIG. **3**A shows the equilibrium calculated results while FIG. **3**B and C show the experimental results.

[0108] Hydrogen Production Details

[0109] FIG. **4** shows one possible construction of a plant comprising of a ceramic-lined steel cylinder. Engineering designs of various types may be possible. In this container, a mixture of NaOH: pulverized coal in 43:12 ratio by weight is introduced. Hot CO_2 from the power plant is entered from one end. The solid mixture is continually stirred with heating partly provided by the hot air from the coal-burning plant and partly by other heaters until all NaOH is converted to Na_2CO_3 and H_2. The exit gases are monitored for the CO_2 and the flow rate is adjusted accordingly. Reaction (1) may be similarly carried out and no carbon will be needed. Catalysis of the reactions, where coal is involved may be needed and has been discussed in detail in literature (17) (e.g. Probstein and Hicks, 2006). A high production rate would result if the hydrogen is formed by continuous flow processes. As envisaged here, the reactor is a closed system with a complete conversion of fixed ratio of reactants and production of the carbonate and hydrogen. Catalysis and partial conversion of the reactants will affect the costs.

[0110] The Cost Analysis

[0111] FIG. **5** and Table 1 show the cost analysis. Through reaction (2), we will sequester 11 kg of CO2 for every 43 kg of sodium hydroxide producing 1 kg of hydrogen and 53 kg of sodium carbonate. If we accept the following per kg prices:

[0112] If we accept the per kg prices in Table 1, there is an advantage in offsetting the energy costs. The new hydrogen DOE cost goal of $2.00-3.00/gge (delivered, untaxed, 2005$, by 2015) is independent of the pathway used to produce and deliver hydrogen. Better cost calculations are needed to insure the economic viability of the project. Note that less energy is required to electrolyze sodium chloride to produce sodium hydroxide than to produce sodium. It will be necessary to integrate the production of NaOH at the power plants instead of purchasing it from an outside manufacturer. In-house sodium hydroxide manufacturing will provide significant shipping cost savings, efficient process integration, and safety. There are many uses of Na_2CO_3 and as long as the use does not release the CO_2 to the atmosphere, the carbon sequestration remains effective. The analysis depends on the current price structure of sodium products.

TABLE 1

Materials cost calculated assuming equilibrium compositions

Solid	$Cost/Kg	Source	CO_2 sequestered/ Kg of H_2 produced	Solid Reactant Per Kg H_2	Solid Product Per Kg H_2
NaOH	0.18	The innovation-Group			
Na_2CO_3	0.187	USGS			
Na	3.50				
Coal	0.06	Titan-America			
H_2 from coal	1.04		0.0		
H_2 from natural gas	3.52		0.0		
H_2 (Reaction 3)	−(1.36)*		Zero emission	NaOH, 20	Na_2CO_3, 26.5
H2 (Reaction 4)	−(26)		Zero emission	NaOH, 40	Na_2CO_3, 35 + Na, 7.7
H_2 (Reaction 1)	−(2.72)*		14 Kg CO	NaOH, 40	Na_2CO_3, 53
H_2 (Reaction 2)	−(2.72)*		11 Kg CO_2	NaOH, 40	Na_2CO_3, 53

*Materials cost only; Cost of energy and other production cost not included.

[0113] We may also consider the following reaction to use sodium carbonate gainfully:

[0114] $Na_2CO_3(cr)+2\ C\ (graphite)=2\ Na\ (g)+3\ CO\ (g)$ (5)

[0115] This reaction is endothermic with H of 1. 16E6 J/mol and is largely complete around 1400 K. Since we rely on coal to provide the heat, the energy cost is not an issue. If we use this reaction to reduce the amount of sodium carbonate produced in reactions (1)-(4), we will further decrease the dependence on the selling price of Na_2CO_3.

[0116] Part 2: Reduction in CO_2 Emission

[0117] United States tops in CO_2-emissions per capita; in 2003, 121.3 metric tons of CO_2 were released in the atmosphere. In 2004 the total carbon release in North America was 1.82 billion tons. World-wide industrial nations were responsible for 3790 million metric tons of CO_2 (Kyoto-Related Fossil-fuel totals). It is clearly not practical to consider that we can sequester all this carbon with reaction (2) which would require production of NaOH on a massive scale which would cause further emission of CO_2 if fossil fuel is used in the production. However in all situations where industry is producing carbon gases and heat anyway, the production of hydrogen according to the reactions presented here, would lead to reduction of carbon in the atmosphere. Most benefit will be obtained if non-fossil sources of energy (hydroelectricity, nuclear-energy, solar and wind) are used for NaOH production.

[0118] More than 100 Mt C/yr are vented to the atmosphere as part of the global production of roughly 38 Mt of hydrogen per year. Through reaction (2), we will sequester 3 Mt carbon (11 Mt of CO_2) for every 40 Mt of sodium hydroxide producing 1 Mt of hydrogen and 53 Mt of sodium carbonate. The US production of NaOH is currently 16 Mt per year. 1300 Mt of NaOH will be needed to sequester all the carbon which is currently emitted in hydrogen production. In this process 33 Mt of H_2 will result. Sodium hydroxide is produced (along with chlorine and hydrogen) via the chloralkali process. This involves the electrolysis of an aqueous solution of sodium chloride. The sodium hydroxide builds up at the cathode, where water is reduced to hydrogen gas and hydroxide ion. The total H_2 produced in these reactions (reactions 1, 2 and electrolysis) if used in automobiles and other energy devices will have a very large effect on CO_2-emission.

[0119] We should also consider the possibility of simply removing the CO_2 emission by the reaction:

[0120] $2NaOH+CO_2=Na_2CO_3+H_2O$

[0121] In this process, 1 kg of CO_2 will be removed as 2.41 kg of sodium carbonate consuming 1.818 kg of NaOH. We will gain 11 cents per kg of CO_2 removal in material costs. The energy cost is separate. This is all based on the prices remaining at this level.

[0122] What is proposed here depends critically on maintaining the cost difference between Na_2CO_3 and NaOH at the current level.

[0123] Part 3: Hydride Production

[0124] With the availability of hydrogen already at a high temperature (hydrogen has the same heat capacity as air), we may use the hot gas in any innovative use in producing a hydride.

[0125] Synthesis of MgH_2

[0126] A direct reaction such as:

[0127] $Mg+H_2=MgH_2(\Delta H=-7.22E4, 400\ K)$ may be used; methods of activating a metal for reaction with hydrogen has been described amply in literature (1-7) e.g. for Mg by McClane et al.(1). With the hot H_2 provided in the present set up, there will be a further reduction in the cost of MgH_2 as is used in the Safe Hydrogen Method (1).

[0128] Two other methods are proposed here which take the advantage of the available hot hydrogen. In the first method, MgH_2 is synthesized as follows:

[0129] $3\ Mg+H_2O+H_2=2\ MgH_2+MgO\ (\Delta H=-4.56E5,400\ K)$

[0130] The addition of water promotes the above reaction to proceed forward vigorously.

[0131] Recycling of sodium- or lithium-borohydride from $NaBO_2$ or $LiBO_2$

[0132] A method to produce hydrogen on board using a borohydride and methods to synthesize it have been discussed in literature (8-15). Millenium Cell Inc (16) has demonstrated the use of $NaBH_4$ in fuel-cells which may be usable for running small devices as well as automobiles. For sodium borohydride to be widely utilized as an energy storage medium for hydrogen, the cost must be reduced by at least an order of magnitude from its present price. We propose the following set of reactions to solve this problem:

[0133] $NaBO_2+4Mg+2H_2O=NaBH_4+4MgO$

[0134] $(\Delta H, 300\ K=-1.04E6\ \text{to}\ \Delta H, 800\ K=-8.95\ Kj)$

[0135] $LiBO_2+4\ Mg+2\ H_2O=LiBH_4+4\ MgO$

[0136] $(\Delta H, 300\ K=-9.92E5\ \text{to}\ \Delta H, 600\ K=-9.11Kj)$

[0137] The sodium compound can be synthesized over 300 to 800 K, while the lithium compound over 300 to 600 K. Both of these reactions can be modified considering that H_2 is produced cheaply as discussed in this document as follows:

[0138] $NaBO_2+3\ Mg+1\ H_2O+1\ H_2=NaBH_4+3\ MgO\ (\Delta H=-6.9\ Kj, 600\ K)$,

[0139] $LiBO_2+3\ Mg+1\ H_2O+1\ H_2=LiBH_4+3\ MgO\ (\Delta H=-6.5\ Kj, 600\ K)$, thereby reducing the amount of MgO to be processed.

[0140] Since $NaBO_2$ or LiBO2 is the product in the hydrolysis reaction:

[0141] $Na/LiBH_4+2\ H_2O=Na/LiBO_2\ (aq)+4\ H_2$ the major cost is for the reduction of MgO to Mg, which is discussed by Saxena et al. (18). They studied the reaction $2Mg+H_2O$ producing MgH_2 and MgO or $Mg(OH)_2$. With the possible recycling of MgO using the SOM process [19], the cost of producing the hydride will be substantially reduced. The energy costs (which in this case since the reaction is exothermic and we may be able to use hot H_2 (FIG. **4**) as well as hot air from coal-burning power plants as used for electric generation or for manufacturing industrial products such as cement (FIG. **4-5**)), the energy cost can be minimized.

[0142] Hydride Production Details

[0143] FIG. **6** shows that the synthesis of a hydride using metal+water+heated H_2 is accomplished in this reactor which may be heated using hot air exhausted from a power plant according to this invention. Freshly powdered metal is used with water and the newly produced hydrogen from the reactor is used for the production.

[0144] Related References

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[0171] The references recited here are incorporated herein in their entirety, particularly as they relate to teaching the level of ordinary skill in this art and for any disclosure necessary for the commoner understanding of the subject matter of the claimed invention. It will be clear to a person of ordinary skill in the art that the above embodiments may be altered or that insubstantial changes may be made without departing from the scope of the invention. Accordingly, the scope of the invention is determined by the scope of the following claims and their equitable Equivalents.

What is claimed is:

1. A process to produce hydrogen through the reaction of sodium hydroxide with carbon monoxide and catalysts such as a metal or an oxide.

2. A process to produce hydrogen by reacting sodium hydroxide with carbon dioxide and carbon to produce sodium carbonate and hydrogen and catalysts such a metal or an oxide.

3. A process to produce hydrogen by reacting sodium hydroxide with carbon and water to produce sodium carbonate and hydrogen.

4. A process to produce magnesium hydride by reacting the hydrogen generated in claims **1-3** with magnesium metal powder.

5. A process to produce magnesium hydride by reacting the hydrogen produced in claims **1-3** with magnesium powder and water.

6. A process to produce sodium borohydride by reacting the hydrogen produced in claims **1-3** with sodium borate, magnesium and water

7. A process to produce lithium borohydride by reacting the hydrogen produced in claims **1-3** with lithium borate, magnesium and water.

8. The processes according to claims **1** and **2**, wherein carbon monoxide and carbon dioxide are obtained from coal-burning plants.

9. The processes according to claims **1**, **2** and **3** using hot air and any other form of energy as may be available from the coal-burning plants, e.g. electric energy in off-peak production.

10. The processes according to claims **4**, **5**, **6** and **7** using hot hydrogen as produced in processes claimed in **1**, **2**, and **3**.

11. The processes according to claims **4**, **5**, **6** and **7** using hot air and any other form of energy as may be available from the coal-burning plants, e.g. electric energy in off-peak production.

12. In all previous claims, coal-burning power plant is specified but the invention also provides that natural gas-based power plants can also be subjected to similar treatment.

13. In all previous claims, coal-burning power plant is specified but the invention also provides that energy for the claims **1-7** may also be obtained from nuclear power plants.

14. In all previous claims, coal-burning power plant is specified but the invention also provides that energy for the claims **1-7** may also be obtained from alternate energy sources such as hydroelectricity and wind and solar energy.

15. In all previous claims, where sodium compounds are used, sodium may be replaced potassium.

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