Title: SYSTEMS AND METHODS FOR THE PRODUCTION OF HYDROGEN

Abstract: Systems and methods are provided for producing hydrogen, based on reacting CO with water, and reconverting the resulting carbon dioxide to CO and recycling the same. In one aspect of the invention, the system and method are coupled to a waste processing plant.
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
SYSTEMS AND METHODS FOR THE PRODUCTION OF HYDROGEN

FIELD OF THE INVENTION

This invention relates to the production of hydrogen. More specifically, the invention is concerned with the production of hydrogen from the gas products resulting from the processing of waste matter, in particular via pyrolyzation and/or gasification thereof. The invention is also concerned with the production of hydrogen from water using recirculated carbon monoxide.

BACKGROUND OF THE INVENTION

Waste processing systems for converting waste into, inter alia, product gases, are well known. The product gases comprise relatively large proportions of hydrogen, and in some systems, molecular hydrogen can be extracted by itself or in combination with other fuel gases. The hydrogen, whether harvested from the product gases by itself or included in a fuel gas, can constitute an important resource.

In a system developed by the Startech Environmental Corporation, a vessel is provided which converts waste into a molten material that can be removed from the vessel, and product gases, by means of a plasma torch system. The product gases are subjected to a ceramic filtration system which removes molecular hydrogen from the product gases.

In WO 2004/072210, an industrial process is disclosed in which combustible material from waste is thermally gasified by means of a plasma torch system, producing hydrogen and other technical gases. The hydrogen is enriched by means of catalytic combustion of carbon monoxide into carbon dioxide and hydrogen, and the hydrogen and carbon dioxide are separated from the other gases and removed from the industrial plant.

In US 6,686,556, waste material is converted into product gases including carbon dioxide and water, which are processed in a chamber comprising
incandescent coke into a fuel gas including carbon monoxide, hydrogen and hydrocarbons. The fuel gas is combusted in gas turbine generators to produce electricity. Exhaust gases from the turbine are processed in another chamber comprising incandescent coke, to convert the exhaust gases into hydrogen, carbon monoxide and some methane. The resulting fuel gas may be fed into the turbines, or alternatively the hydrogen removed and the carbon monoxide converted in another chamber to methane and oxygen, the oxygen being used in the turbines.

In WO 03/066779, product gases resulting from pyrolysis of waste contains hydrogen which may be separated and stored in nanotubes.

**SUMMARY OF THE INVENTION**

The present invention relates to a system for producing hydrogen, comprising:

- processing apparatus for processing waste into at least product gases based on at least one of pyrolysis and gasification of said waste, said product gases comprising at least carbon monoxide;

- post processing apparatus operatively connected to said processing apparatus and to a source of water, and adapted for producing hydrogen, said post-processing apparatus comprising first converting apparatus, separating apparatus and second converting apparatus, wherein:

  - said first converting apparatus comprises arrangement for receiving product gases from said processing apparatus and for receiving carbon monoxide from said second converting apparatus, and reaction arrangement for reacting carbon monoxide with water to produce output gases including hydrogen and carbon dioxide;

  - said separating apparatus configured for selectively separating at least hydrogen from said output gases received from said first converting apparatus, and for directing at least said carbon dioxide to said second converting apparatus;
said second converting apparatus configured for converting carbon
dioxide to carbon monoxide and for directing at least said carbon monoxide to
said first converting apparatus.

The waste processing apparatus typically comprises:
a waste converting chamber for accommodating a column of said waste,
said chamber having an upper part and a lower part;
at least one primary plasma torch arrangement for generating a hot gas jet
at an output end thereof and for directing said jet towards said lower part of said
chamber;
at least one waste inlet arrangement at said upper part of said chamber;
at least one liquid product outlet arrangement at said lower part for
removing liquid product from said chamber; and
at least one product gas outlet arrangement for directing product gases out
of said chamber and into said post processing arrangement.

The waste is comprises substantially solid waste, including for example at
least one of municipal waste and industrial waste.

The system preferably further comprises gas cleaning arrangement
upstream of said first converting apparatus, said gas cleaning arrangement being
adapted for removing predetermined components – such as for example one or
more of pitch, tar, dust, water, HCl, H2S, and so on - from said product gases,
and for subsequently directing said product gases to said first converting
apparatus.

The product gases typically further comprise at least one of H2, CO2, N2,
CnHm, wherein n and m are each integers.

The reaction arrangement typically comprises a suitable reaction vessel
configured for running therein a water-gas shift reaction in the presence of
suitable catalysts comprised therein. The catalysts may comprise a zinc-copper-
chromium catalyst, and wherein said water-gas shift reaction is run at a temperature typically in the range of about 350°C to about 380°C.

The second converting apparatus typically comprises a suitable UHF discharge device coupled to a DC electrical power source.

The first converting apparatus advantageously further comprises a suitable heat exchanger for cooling said output gases. The heat exchanger is typically further configured for preheating water from said water source prior to being reacted in said first converting apparatus.

The system may further comprise suitable hydrocarbon converter arrangement for converting hydrocarbons comprised in said product gases such as to provide hydrogen therefrom. The hydrocarbon converter arrangement typically comprises a suitable reaction vessel configured for carrying out therein a steam conversion reaction on said hydrocarbons in the presence of a suitable catalyst, e.g. an iron-chromium catalyst to produce hydrogen and carbon monoxide. The hydrogen produced by said hydrocarbon converter arrangement may be separated via said separating apparatus. A cooler may be provided for cooling gases output from said hydrocarbon converter prior to separating hydrogen therefrom.

Alternatively, the hydrocarbon converter arrangement comprises a suitable reaction vessel configured for carrying out therein a decomposition reaction for decomposing hydrocarbons to carbon and hydrogen.

The separation apparatus typically comprises at least one separation unit comprising membrane arrangement for separating hydrogen from said output gases by selectively allowing hydrogen to diffuse through said membrane. The separation apparatus may comprise further separation units for separating other gases from said output gases. One such separation unit may be adapted for separating carbon dioxide from said output gases, and for directing said carbon dioxide to said second converting apparatus. Other arrangement for separating the hydrogen and/or other desired gases may be provided, as described herein for example.
The present invention also relates to an apparatus for producing hydrogen, comprising:

first converting apparatus operatively connectable to a source of water, separating apparatus and second converting apparatus, wherein:

said first converting apparatus comprises arrangement for receiving carbon monoxide from said second converting apparatus, and reaction arrangement for reacting carbon monoxide with water to produce output gases including hydrogen and carbon dioxide;

said separating apparatus configured for selectively separating at least hydrogen from said output gases received from said first converting apparatus, and for directing at least said carbon dioxide to said second converting apparatus;

said second converting apparatus configured for converting carbon dioxide to carbon monoxide and for directing at least said carbon monoxide to said first converting apparatus.

The reaction arrangement comprises a suitable reaction vessel configured for running therein a water-gas shift reaction in the presence of suitable catalysts comprised therein, for example said catalysts may comprise a zinc-copper-chromium catalyst, and wherein said water-gas shift reaction is run at a temperature in the range of about 350°C to about 380°C.

The second converting apparatus typically comprises a suitable UHF discharge device coupled to a DC electrical power source.

The first converting apparatus typically further comprises a suitable heat exchanger for cooling said output gases, and the heat exchanger may be further configured for preheating water from said water source prior to being reacted in said first converting apparatus.

The separation apparatus comprises at least one separation unit typically comprising membrane arrangement for separating hydrogen from said output gases by selectively allowing hydrogen to diffuse through said membrane. Other
arrangement for separating the hydrogen may be provided, as described herein for example.

The apparatus further comprises a supply of carbon dioxide or carbon dioxide for maintaining the level of carbon monoxide within the apparatus within predetermined thresholds.

The present invention also relates to a method for producing hydrogen, comprising:

(i) processing waste into at least product gases based on at least one of pyrolysis and gasification of said waste, said product gases comprising at least carbon monoxide;

(ii) post processing said product gases by:

(a) receiving said product gases and providing output gases including hydrogen and carbon dioxide produced by suitably reacting carbon monoxide with water;

(b) selectively separating at least hydrogen from said output gases provided in (a);

(c) converting carbon dioxide contained in the output gases in step (b) to carbon monoxide and recycling at least said carbon monoxide to said product gases produced by said waste processing apparatus to be processed according to step (a);

(d) repeating steps (a) to (c).

In step (a), then carbon monoxide and steam are reacted together in a water-gas shift reaction to produce carbon dioxide and hydrogen, typically under the presence of suitable catalysts – for example a zinc-copper-chromium catalyst—the water-gas shift reaction being typically run at elevated temperatures, for example a temperature in the range of about 350°C to about 380°C.
In step (b), any suitable separation process may be used, for example based on using polymeric or metal diffusing membranes, physical absorption or adsorption processes, cryogenic methods, and so on.

Step (c) typically involves providing a suitable UHF discharge to carbon dioxide at below ambient pressure, typically increasing the gas temperatures to greater than 1000°C, and the conversion efficiency is kept as high as possible but within safety limits, for example at less than 40% by weight.

The method optionally further comprises converting hydrocarbons in the product gases to hydrogen and carbon (which is subsequently converted to carbon monoxide or dioxide) or carbon monoxide; the hydrogen is removed, and the carbon monoxide reacted with water to produce more hydrogen and carbon dioxide. The carbon dioxide may then be recycled in step (c).

The present invention also relates to a method for producing hydrogen, from water, comprising:

(a) providing a quantity of carbon monoxide;
(b) receiving carbon monoxide and providing output gases including hydrogen and carbon dioxide produced by reacting carbon monoxide with water;
(c) selectively separating at least hydrogen from said output gases provided in (b);
(d) converting carbon dioxide contained in the output gases in step (c) to carbon monoxide and recycling at least said carbon monoxide to be processed according to step (a);
(e) repeating steps (b) to (d).

In step (a), carbon monoxide may be provided already prepared, for example in pressurized containers, or alternatively may be provided by combusting coke or the like in a low oxygen atmosphere. Typically, though, a carbon dioxide supply, for example liquefied carbon dioxide with arrangement for gasifying an amount thereof on demand, is processed according to step (d), and applying steps (b) to (e) to the resulting carbon monoxide.
In step (b), then carbon monoxide and steam are reacted together in a water-gas shift reaction to produce carbon dioxide and hydrogen, typically under the presence of suitable catalysts – for example a zinc-copper-chromium catalyst. The water-gas shift reaction being typically run at elevated temperatures, for example a temperature in the range of about 350°C to about 380°C.

In step (c), any suitable separation process may be used, for example based on using polymeric or metal diffusing membranes, physical absorption or adsorption processes, cryogenic methods, and so on.

Step (d) typically involves providing a suitable UHF discharge to carbon dioxide at below ambient pressure, typically increasing the gas temperatures to greater than 1000°C, and the conversion efficiency is kept as high as possible but within safety limits, for example at less than 40% by weight.

At step (e) it is possible to check the amount of carbon monoxide in the system, and if below a threshold amount, for example due to leakage, additional carbon monoxide may be provided via step (a).

**BRIEF DESCRIPTION OF THE DRAWINGS**

In order to understand the invention and to see how it may be carried out in practice, a preferred embodiment will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

**Fig. 1** is a schematic representation of the system according to a first embodiment of a first aspect of the invention.

**Fig. 2** is a cross-sectional view of the waste processing plant of Fig. 1.

**Fig. 3** is a schematic representation of the post-processing arrangement of Fig. 1.

**Fig. 4** is a schematic representation of an embodiment of the hydrogen separation unit of Fig. 3.
**Fig. 5** is a schematic representation of a process for extracting hydrogen via physical absorption.

**Fig. 6** is a schematic representation of the system according to a first embodiment of the first aspect the invention.

**Fig. 7** is a schematic representation of the system according to a first embodiment of a second aspect of the invention.

**Fig. 8** is an alternative schematic representation of the system according to a first embodiment of a second aspect of the invention.

**Fig. 9** is a schematic representation of the method according to a first embodiment of a first aspect of the invention.

**DETAILED DESCRIPTION OF THE INVENTION**

Referring to **Fig. 1**, in a first aspect of the invention, a system for producing hydrogen according to a first embodiment of the present invention is generally designated with the numeral **150**, and comprises a waste processing plant **100** for processing waste, and post-processing arrangement **200** operatively connected thereto for producing hydrogen.

Referring to **Fig. 2**, the waste processing plant **100** is illustrated in more detail. It should be understood that the waste processing plant **100** illustrated in **Fig. 2** and described below is only illustrative, and any suitable waste processing plant may be used with the system **150** and that produces at least carbon monoxide (CO). The plant **100** is adapted for producing at least product gases, and typically also solid waste, such as for example slag and/or metal residues, and exemplary waste processing plants are described in US 6,763,772, US 6,820,564, US 6,807,913, WO 02/070412, WO 03/078897, and WO 03/069227, the contents of each of which are incorporated herein in their entirety. In these references, and also referring to **Fig. 2**, the plant **100** comprises a processing chamber **10**, in which a suitable feeding system **20** introduces waste to the chamber via an air lock arrangement **30**, typically comprising an upper valve **32**.
and a lower valve 34 defining a loading chamber 36 therebetween, the operation of which may be controlled by a human and/or automated controller (not shown). The waste may include solid, liquid or mixed waste, including medical, municipal, industrial, agricultural, and any other type of waste. Optionally, prior to providing the waste to the chamber 10, metallic waste such as iron and aluminium, and other recyclable materials including glass may be removed.

One or more plasma torches 40 connected to suitable electrical power, gas and coolant sources 45, are mounted in the chamber 10, typically via sealed sleeves, so that in operation, the torches 40 generate plumes of hot gases, directed into the bottom end of the column of waste 35. The hot gases support the temperature gradient set up in the chamber 10, and is sufficient for converting the waste into product gases that are channeled away from the chamber via outlet 50, and into a liquid material 33 that may include molten metal and/or slag, which may be periodically or continuously collected from the lower end of the chamber 10 via one or more outlets 60. Oxidising fluid source 70 provides oxidizing fluid such as oxygen, air or steam, typically at the lower end of the chamber 10 for converting carbon, produced in the process from organic waste, into product gases including CO and hydrogen (H₂).

Optionally, a disinfectant spraying system 31 may be provided for periodically or continuously spraying the inlet end or hop arrangement 39 with disinfectant, as required, particularly when medical waste is being processed by the plant 100.

Optionally, the said controller may be adapted to control the input of waste into the chamber 10, for example substantially as disclosed in WO 03/078897.

Optionally, the chamber 10 may comprise an oxidizing fluid distribution and mixing chamber incorporated therein, for example as disclosed in WO 02/070412.
Optionally, the processing plant 10 may further comprise a dedicated liquid waste feeding system (not shown), for example as disclosed in US 6,763,772.

Optionally, the plant 100 may further comprise a first decongesting system (not shown) for the removal of, and for the prevention of the formation of, bridging phenomena in the chamber 10, for example as disclosed in US 6,807,913.

Optionally, the plant 100 may further comprise a second decongestion system (not shown) for the removal of, and for the prevention of the formation of, unprocessed solid deposition within the chamber 10 and/or for dealing with high viscosity liquid product produced by the plant 100, for example as disclosed in US 6,820,564.

Optionally, the plant 100 may further comprise a recycling system (not shown) for recycling non-gaseous residues, such as for example flyash, generated by the plant 100, in order to reduce the eventual volume of residues, and to dispose of at least a part of the heavy metals produced by the plant 100, by encasing the compounds and complexes of metals in the slag melt, i.e., when the slag is still molten, for example substantially as disclosed in WO 03/069227.

The system 150 comprises a scrubber system 130, operatively connected to the outlet 50 for removing particulate matter and/or liquid droplets, including tar, pitch and dust for example, as well as any undesired gases (for example HCl, H₂S, and so on) from the product gas stream. Scrubbers capable of performing such tasks are well known and shall not be further described herein.

Referring to Fig. 3, the post-processing arrangement 200 is adapted for producing hydrogen from the product gases P produced by the gasification of the waste by means of the plant 100 and from water by reaction thereof with CO, and for enabling the hydrogen to be removed for further exploitation. The hydrogen may be removed after purification, or together with other combustible gases in a
hydrogen-enriched syngases. The product gases P, after being cleaned by the scrubber 130 and prior to post-processing by means of post-processing arrangement 200, typically comprise H₂, CO, CO₂, N₂, and hydrocarbons designated herein as CₙHₘ wherein n and m are each integers.

According to the invention, the post-processing arrangement 200 provides Hydrogen from four sources:-

(a) by direct extraction from the product gases P;
(b) by steam conversion of CO in the product gases;
(c) by steam conversion of CO recycled through the post-processing arrangement 200;
(d) by conversion of hydrocarbons CₙHₘ in the product gases.

Thus, post-processing arrangement 200 comprises a conduit or conduits for transporting the product gases P to a steam converter 230, in which carbon monoxide, from the product gases P and/or as recycled within the post-processing arrangement 200, as will be further described hereinbelow, is reacted with steam to produce hydrogen in a water-gas shift reaction:-

\[ H₂O + CO = H₂ + CO₂ \]  \hspace{1cm} (Eq. 1)

The water-gas shift reaction is typically run in the presence of suitable catalysts comprised in the steam converter 230 and at a suitable temperature, for example a zinc-copper-chromium catalyst at a temperature in the range of about 350°C to about 380°C. The water-gas shift reaction is exothermic, and the temperature of the resulting gases, designated P2 in Fig. 3, is higher than that of the pre-reacted gases, usually higher than 400°C, and typically between about 430°C and about 450°C. The output gases P2 have higher concentrations of H₂ and CO₂ than in the product gases P, but still contain the other original gases in P, notably N₂, CₙHₘ, as well as unreacted CO and H₂O. Steam converters are well known and are manufactured by many different companies, for example Linde, Uhde (Germany), Marubeni (Japan), KTI (England) and so on.
(Optionally, unwanted gases in P are removed therefrom prior to being channeled to the steam converter 230, for example using suitable membrane units, as described below, *mutatis mutandis*, so that only CO (and possibly also the H₂ in the product gases P) is supplied to the steam converter 230.)

Optionally, and advantageously, the output gases P₂ are passed through a suitable heat exchanger 240, in which steam from a suitable source 245, such as a steam generator, for example, is heated by the output gases P₂ prior to being supplied to the steam converter 230.

The output gases P₂ are then directed to a hydrocarbon converter 250 for converting hydrocarbons present in the output gases to hydrogen in any suitable manner. The hydrocarbon converter 250 may be based on steam reforming reactions, for example, in which the hydrocarbons are converted to hydrogen and carbon monoxide, exemplified as follows for methane and other hydrocarbons:-

\[
\text{CH}_4 + \text{H}_2\text{O} = 3\text{H}_2 + \text{CO} \quad \text{(Eq. 2)}
\]

\[
\text{C}_n\text{H}_m + n\text{H}_2\text{O} = (0.5 m + n)\text{H}_2 + n\text{CO} \quad \text{(Eq. 3)}
\]

The steam reforming reactions are typically run in the presence of a suitable catalyst, and at relatively high temperatures and pressures, for example an iron-chromium catalyst, at a temperature of between about 800°C to about 900°C, and at pressure in the order of about 2.5MPa absolute.

Accordingly, a suitable steam source, typically source 245 or alternatively a different source (not shown), provides steam for the reactions.

Such a process is known in the art, and is described in the following example publication, the contents of which are incorporated herein in their entirety by reference:- "Nuclear Hydrogen Energy and Technology", Part 3, pp. 92-95, published by Moscow Atomizdat, 1980.
Additionally or alternatively, the hydrocarbon converter 250 operates by decomposing the hydrocarbons into hydrogen and carbon, for example as follows for methane:

\[ \text{CH}_4 = 2\text{H}_2 + \text{C} \]

For this purpose, the hydrocarbon converter 250 may comprise a suitable plasma catalytic reactor, for example, for applying a plasma catalysis process for converting hydrocarbons to produce hydrogen. Such a process is based on subjecting the hydrocarbons to an electric plasma discharge rated at a frequency in the microwave range, and having suitable discharge energy for dissociating the C-C and C-H bonds the microwave plasma discharge acting as a catalyst.

Such a process is known in the art, and is described in the following two publications, the contents or which are incorporated herein in their entirety by reference:


The plasma for the catalytic process is typically provided by means of a suitable super-high-frequency plasma torch. Suitable plasma torches of this type are described in the following publications, the contents or which are incorporated herein in their entirety by reference:

(2) A.I. Babaritski, M.B. Babikov, E.N. Gerasimov et al. Properties of the catalytic pulsed microwave discharge at atmospheric pressure. “Spectroscopy of Non-Equilibrium Plasma at Elevated Pressures”, SPIE-4460, 2002 (The International Society for Optical Engineering);

(3) International patent application WO 2002/089536 “Method for plasma-catalytic conversion of fuels that can be used in an internal combustion engine or a gas turbine into a synthesis gas and the plasma-catalytic converter used for same”. 019255876-100161 Proprietor; David Systems & Technology S.L. Inventors: R. Balch Vizoro, B. Potapkin, V. Zhivotnov et al.


Furthermore, plasma torches configured for converting hydrocarbons into carbon and hydrogen are commercially available from many sources, for example: KVAERNER ENGINEERING S.A. (Norway); CONSULECTRA, EES, HGS (Germany); HOLDOR TOPSH (Holland).

The output gases P3 exiting the hydrocarbon converter 250 are thus further enriched in hydrogen, and also contain substantial amounts of carbon monoxide, which is recycled in the post-processing means 200, as will be further described herein. (Alternatively, the CO may be separated from the H2 and other gases, and the CO is directly channeled to the steam converter 230 for converting more steam into H2.) First, though, the output gases P3 are cooled in cooler 260
using any suitable heat exchanger system, for example, based on a water coolant supply 265. The cooler 260 reduces the temperature of the output gases to a temperature in the range of about 20°C to about 50°C, typically to about 25°C.

However, the output gases P2 from the steam converter 230 typically contain only small percentages of hydrocarbons, typically of the order of about 3% to about 4%, for example, and it may be more economical or preferred in some hydrogen production systems according to the invention to omit the said hydrocarbon converter 250 altogether. In such a case, the output gases P2 can be directed from the steam converter 230 or heat exchanger 240 directly to the next component in the post-processing arrangement 200, i.e., the hydrogen separator 270 (illustrated in Fig. 3 as dotted line 241) to extract the hydrogen, as well as these gaseous hydrocarbons which may optionally be taken off, stored and used (for example for combustion to generate heat or power) at some convenient point. Alternatively, it may be desired to use the post-processing arrangement to provide a fuel gas comprising hydrocarbons and that is hydrogen enriched, in which case the hydrocarbon converter 250 is omitted, and the output gas P2 further processed in the hydrogen extractor 270 to remove therefrom the fuel gases comprising the hydrocarbons together with the hydrogen. The remaining gases, typically N₂, CO and CO₂ are further processed, for example as described below regarding the hydrogen separating unit 270, mutatis mutandis.

Alternatively, the hydrocarbons present in the product gases P may be separated therefrom, for example using a suitable separating membrane unit, and the hydrocarbons routed directly to the hydrocarbon converter 250 (illustrated in Fig. 3 as dotted line 242), and the output gases from the heat exchanger 260 routed directly to the hydrogen separation unit 270.

Thus, the output gases P3 (or output gases P2 if the hydrocarbon converter 250 is omitted) are then directed to a hydrogen separating unit 270, which purifies the hydrogen (optionally together with hydrocarbons, or alternatively
and optionally also the hydrocarbons separately to the hydrogen) in the output
gases and diverts the hydrogen (and/or hydrocarbons) to a suitable storage
facility and/or to a consumer pipeline (not shown) and/or to a user facility.
Optionally, some of the hydrogen and/or hydrocarbons may be diverted for
power and/or heat for at least a part of the system 150.

The hydrogen separation unit 270 is based on diffusion separation
processes, and typically comprises a membrane separator of any suitable
configuration, though any other separation arrangements may be implemented
for separating and purifying the hydrogen in the output gases and optionally also
for separating hydrocarbon gases (together with or separately from the
hydrogen). For example, and referring to Fig. 4, the hydrogen separating unit 270
may comprise a series of membrane separating units, for example the three units
272, 274, 276 exemplified in Fig. 4, each of which separates out a particular
effluent of interest. For example, in the first separation stage unit 272 comprises
membrane 273 that is adapted for separating a first effluent, such as for example
nitrogen or hydrocarbon gases (from P2), which can then be channeled off and
stored or used. Suitable membranes for use as membrane 273 are well known,
and may comprise, for example, polysiloxan or other polymer flat composite
types or as marketed under the name "MEM", for example. The unit 272 may
have any suitable construction, for example comprising a plurality of separation
modules, each in the form of a cylindrical housing having an internal
cylindrically disposed membrane separating the housing into an outer and an
inner chamber. Raw gases are fed into the outer chamber and under pressure the
effluent is separated off into the inner chamber and removed from the unit. Many
other forms for unit 272 are possible within the spirit of the invention.

In the next stage, unit 274 comprises membrane 275 which is adapted for
separating out hydrogen, which is also channeled off and stored or used. Suitable
membranes for use as membrane 275 are also well known, and may comprise, for
example, polysulfon or other hollow fiber axisymmetric types, for example as
marketed under the name "Medal" by the company "Air Liquid" of Argentina.
The unit 274 may have any suitable construction, for example comprising a plurality of porous polymer fibers, with a suitable gas separating layer applied to the outer surface. The porous fibers have a complex asymmetric structure, and the polymer's density increases towards the outer surface of the fibers. As raw gas (or gas after being processed by the previous unit 272) is caused to flow parallel to the fibers, at least a part of the hydrogen in the gas is separated out and flows along the lumen of the fibers to be stored or used. The membrane unit 274 may optionally comprise a removable membrane cartridge construction, allowing membranes to be easily replaced.

The gas flow after unit 274 is further purified via unit 276, which comprise membrane 277 adapted for this purpose, and the remaining gases, designated P4 and comprising (typically a relatively low proportion of) CO and (typically a relatively high proportion of) CO2 are then directed to oxidizer 280. Unit 276 and membrane 277 may be similar to the other units and membranes of the hydrogen separation unit 270, as described herein mutatis mutandis. However, since not all the effluent gases in output gases P3 (or P2) are removed from the gas stream passing through the membranes, the third unit 276 recycles residual gases through the separator 270 continuously via feedback line 271 after having separated out output gases P4. A suitable compressor arrangement 273 pressurises the separator 270 and provides the required pressure head upstream of the first unit 272 to operate the separating membranes at optimum efficiencies.

The separating units 272, 274, 276 are configured for serially and selectively separating target gases from the input gas flow, in a predetermined sequence or order correlated to the properties of each membrane viz-a-viz the mixture of gases flowing through the unit 270e. These properties typically relate to the solubility of the gases and their capability of diffusing through the material of the membranes.

Without being restricted by theory, it is believed that separation of the gas mixtures is possible because of a difference between the partial pressures on the outer and inner surfaces of the hollow fiber membrane. The gases which can
penetrate the polymer membrane relatively quickly (for example H₂, CO₂, O₂, steam, higher hydrocarbons) are channeled to the lumens of the fibers and removed from the unit via one of the exit pipes. The other gases which penetrate through the membrane more slowly (for example CO, N₂, CH₄) are removed from the unit via a different exit pipe.

Membrane separation units have certain advantages over other separation systems, for example: low initial investment and maintenance costs; low energy consumption; simplicity of use and construction; reliability; operation thereof is potentially capable of being automated; flexibility in operation – e.g., scaling can be achieved by adding more units.

In one particular embodiment, a membrane separation unit 270 performs the function of preliminary enrichment of a particular target gas in a mixture, the target gas typically being H₂ (but for some separation units may comprise CO, CO₂, N₂, and so on), and an additional separation unit (not shown), for example based on cryogenic separation, or absorption separation, or adsorption separation (e.g. pressure swing adsorption) carries out final purification of the target gas.

Alternatively, metallic membranes may be used, for example based on Palladium alloys, for separating hydrogen to a high degree of purity. The process of separating hydrogen using Palladium alloy membranes is typically carried out at high temperatures, in the order of about 500°C to about 600°C, and high pressures, in the order of at least 2MPa. Examples of such membranes are manufactured by the firm Reb Research & Consulting of Ferndale, MI 48220.

Alternatively, one or more of the membrane separation units may be replaced with any other suitable separation arrangement. For example, separation processes based on physical absorption may be used. Referring to Fig. 5, in an exemple absorption separation unit 220, CO₂, CO and hydrocarbons may be separated from an inlet gas also comprising hydrogen in the separator regenerator unit 224. Part of the inlet gases, i.e., CO₂, CO and hydrocarbons, but not hydrogen, are dissolved in a suitable absorbent agent in absorber 221, and the
enriched absorbent agent is channeled to the separator regenerator unit 224 in which steam is used for heating the enriched agent. For example, CO can be removed using a mixture of aluminium tetrachloride and copper tetrachloride; CO₂ can be removed by using monoethanolamin (NH₂CH₂CH₂OH), for example.

The unwanted gases CO₂, CO and hydrocarbons come out of solution and are siphoned away at 227 via cooler 222 and compressor 223, while the absorbent agent is recycled to the absorber 221. Accordingly, the hydrogen in the absorber 221 becomes more and more purified, and the hydrogen can be removed from the absorber for use or storage.

Alternatively, suitable separation units based on physical adsorption methods, for example pressure swing adsorption (PSA) or short cycle heatless adsorption (SCA) may be used.

Alternatively, separation units based on cryogenic methods, or any other suitable methods may be used.

In oxidizer unit 280, air, oxygen or other oxidizer is provided from source 285 to convert the relatively small proportions of CO in P4 to CO₂, and the resulting output gas P5, comprising substantially pure CO₂ is directed to a carbon monoxide generator 290. Alternatively, though, the oxidizer unit 280 may be omitted, and instead the CO is separated from the CO₂, for example in separation unit 270 or another separating unit, the CO₂ being directed to the carbon monoxide generator 290, while the CO is recycled directly to the steam converter 230. The first option of converting the CO to CO₂ is typically more advantageous. Alternatively, the oxidizer unit 280 may be omitted, and the gas mixture including CO and CO₂ is directed to carbon monoxide generator 290.

Carbon monoxide generator 290 is adapted for generating carbon monoxide from carbon dioxide. In one embodiment, the said carbon monoxide generator 290 comprises a microwave plasma torch reactor or plasmatron which is based on providing non-equilibrium microwave supersonic discharges to the
CO₂, typically in the microwave frequency range of between about 0.9 to about 1.0 GHz, resulting in the conversion of CO₂ into CO and oxygen, according to the reaction:

\[ 2\text{CO}_2 = 2\text{CO} + \text{O}_2 \quad \text{(Eq. 4)} \]

Typically, a UHF discharge is maintained in the plasmatron for the purpose of breaking down the CO₂, and gas temperatures in the discharge can reach 1,500°C to about 2,000°C. The UHF discharge is maintained by a high power magnetron connected to a suitable DC electrical supply. Suitable heat exchangers and compressors are provided to maintain the pressure in the plasmatron below atmospheric. The conversion efficiency of the generator 290 is typically kept at between 35% to about 40% by weight, since after decomposition the gas mixture can become explosive if the CO₂ concentration in the mixture is below about 60% by weight.

Suitable plasma torch reactors for converting or reforming CO₂ to CO are disclosed in the following publications, the contents of which are incorporated herein by reference:-


R. I. Azizov, A. K. Vakar, V. K. Zhivotov et al. Non-equilibrium plasma chemical process of dissociation of CO₂ in supersonic Super high frequency discharge. Reports of the USSR Academy of Sciences, 1983, v.271, №1, p. 94-98. (The plasma torch used in the installation described in this reference works at the H₁₀ wave type in a rectangular wave duct. The charge chamber crosses the
wide wall of the wave duct. The wavelength of the microwave irradiation is 30 cm (0.9 GHz). Power of the plasma torch is 250 kW.)

The resultant output gases P6, comprising a mixture of CO₂, CO, and O₂ of varying proportions is directed to the steam converter 230, so that the CO from output gases P6 is reacted with steam to provide more hydrogen. Effectively, then, carbon monoxide is continually recycled in the post-processing unit 200, producing hydrogen from steam which is continuously provided via source 245. In addition, more CO is also continually provided to the CO recycling loop by the plant 100, and thus a state of equilibrium may be reached wherein the amount of CO recirculated via carbon monoxide generator 290 may be balanced against the working efficiency of said carbon monoxide generator 290 as well as the amount of CO being generated by the plant 100, and the rate at which steam is being supplied to the steam converter 230.

Optionally, a carbon dioxide separator (not shown) may be provided for removing excess CO₂ from the recycling loop past the carbon monoxide generator 290, and this CO₂ may be stored or sold as desired. Such a separator may be similar to separator 270, and may comprise, for example, a membrane separator, and is particularly adapted for separating CO₂ from the other output gases. Alternatively, any other suitable process may be applied for removing the excess CO₂, and many such processes are commonly used industrially for this purpose, including for example, chemosorption processes, which may be based on amines such as for example monomethanolamin and/or dimethanolamin, or alternatively may be alkaline-based; physical absorption processes (for example including the Selecscol process (i.e., using dimethilethir of polyethyleneglicol) or Fluor processes; cryogenic fractioning; and so on. Typically, a two-stage separation process ensures that a very high proportion of the CO₂ is separated out. Further optionally, an oxygen separator (not shown) may be provided for removing excess O₂ from the recycling loop past the carbon monoxide generator 290, and this O₂ may be stored, and/or sold. Alternatively, at least a part of the
oxygen generated by the CO generator 290 may be channeled to the plant 10 and/or to oxidizer unit 280 to be used as oxidizer.

Optionally, it is also possible to omit removal of effluents other than H2 at separator 270, such as for example N2, and to recycle the same to the steam converter 230.

One or more compressors (not shown), as well as valves and other suitable hardware, are provided at strategic locations in the system 200 to provide required pressure heads and safety and control apparatus such that gases are caused to flow within the system 200 in the desired directions therein. Similarly, a chimney, flue or stack (not shown) may be provided for venting excess gases and removing the same from the system 200.

A second embodiment of the invention is illustrated in Fig. 6 and comprises all of the elements and features as described with respect to the first embodiment, mutatis mutandis, with some differences as described below. Thus, similar components to the first embodiment are shown in Fig. 6 with the same reference numerals. The main distinctions between the second and first embodiments are that in the second embodiment, hydrogen is extracted at a number of separate stages. Thus, in the system 200' illustrated in Fig. 6, output gases from the waste processing plant 100, having been filtered and scrubbed by unit 130, are passed through a cooler 283, fed with water from source 286, and the gases are passed through a first separator unit 279a, typically a membrane separator unit as described for the first embodiment, mutatis mutandis, via compressor 282, to separate the hydrogen therein. Residual gases are then passed on to the steam converter 230, which converts CO in the residual gases to CO2 and H2, and to the hydrocarbon converter 250, which converts the hydrogen bound in the hydrocarbons to molecular H2. Another separating unit 279b, typically a membrane separator, separates out the hydrogen produced in these conversion units, and the residual gases are passed on to a suitable PSA unit (for example as provided by the Russian firm "GRASIS") or the like, coupled to a
third membrane separator 279c for removing substantially the remaining hydrogen gases produced by the system 200'. The residual gases are then passed on directly to the carbon monoxide generator 290, or alternatively the residual gases are first separated out so that only CO and CO2 are channeled to the carbon monoxide generator 290, which converts CO2 to CO and feeds this back to the steam converter unit 230 to continue with another hydrogen generation cycle.

Optionally, both for the first and second embodiments, a suitable separation unit for example a membrane separation unit, can be configured for separating CO from the corresponding gas mixture prior to being channeled to the steam converter 230, so that only CO (and possibly some CO2 and/or H2 only) is provided to the steam converter 230. For example, an absorption unit, typically similar to that illustrated in Fig. 5 may be used for the extraction of CO from the gas mixture. The gas mixture is input to an absorber unit containing a particular liquid absorbent that selectively absorbs CO. Selective absorption of CO can be provided with an absorbent liquid comprising a solution of mixed slats of copper and aluminium tetrachloride in aromatic hydrocarbons (e.g., in toluene). The absorption process can be carried out at moderate temperatures, such as about 40°C, and minimum positive gauge pressures. The remaining gases of the mixture, having been rid of the CO, are then removed from the unit, and after having been cleaned from residual absorbent (by condensers and filters, for example) and supplied to the next component in the system. The absorbent liquid, saturated with CO, is the heated via a heat exchanger to release the CO, and the regenerated absorbent liquid is channeled back to the absorbent unit via the heat exchanger. This desorption can be carried out by heating the absorbent, for example the aforesaid solution of mixed slats of copper and aluminium tetrachloride in aromatic hydrocarbons, up to a temperature of between about 120°C and about 140°C. Preferably, moisture is removed from the gas mixture prior to absorption of CO. The extracted CO is then purified from any remaining drops of absorbent, and supplied to the steam converter 230 for generating hydrogen and CO2 from steam.
Thus, the present invention provides a system for producing hydrogen from waste and also from water provided to the system, using the CO and \( \text{CO}_2 \) in the product gases from the plant 10 in a recycling loop to provide a high efficiency for hydrogen production.

In a second aspect of the invention, and referring to Figs. 7 and 8, a system and method are provided for the production of hydrogen from a supply of water.

Referring to Figs. 7 and 8, the system 400 according to this aspect of the invention is similar to the system 200 of the first aspect of the invention, and comprises a steam converter 430, optional heat exchanger 440, hydrogen separation units 470a, 470b, optional oxidizer unit (not shown) with oxygen supply (not shown), carbon monoxide generator 490, similar to the components described above for the system 200, \textit{mutatis mutandis}, i.e.:- steam converter 230, heat exchanger 240, hydrogen separation unit 270, oxidizer unit 280 with oxygen supply 285, carbon monoxide generator 290. Suitable conduits between the different components as illustrated in Figs. 7 and 8, and water is provided from a water source (not shown), similar to water source 245 as described above, \textit{mutatis mutandis}.

However, the system 400 differs from the system 200 of the first aspect of the invention in a number of ways. For example, a carbon monoxide source (not shown) provides an initial quantity of CO to the system 400, and replenishes the same with CO as required to compensate for any losses in CO; other than this, substantially the same quantity of CO is constantly recirculated through system 400 during operation thereof.

The carbon monoxide source may comprise any suitable arrangement for providing carbon monoxide, and may include, for example, a supply of CO, for example in pressurized bottles, a burner typically configured to burn coke or the like in an oxygen atmosphere in a manner such as to produce CO. If necessary
other product gases can be removed from the combustion process such that only CO is provided to the steam converter 430.

Alternatively, and in the present embodiment, CO\textsubscript{2} may be provided to the carbon monoxide generator 490, and the process started thereat (and of course, depletions in CO can also be corrected by topping up with CO\textsubscript{2} at the carbon monoxide generator 490). For this purpose, a liquid CO\textsubscript{2} storage tank 401 provides an initial quantity of gaseous CO\textsubscript{2} to the carbon monoxide generator 490 via gasifier 402, typically a heated diffuser arrangement. Excess gaseous CO\textsubscript{2} may be stored in storage tank 403. The carbon monoxide generator 490 comprises a plasma-chemical reactor 404 and a magnetron 406 comprising a waveguide system directed to said reactor 404, and connected to a suitable DC electrical supply 407. As with the first aspect of the invention, the carbon monoxide generator 490 is typically operated at a conversion efficiency of between about 35% to about 40% for safety reasons. From the carbon monoxide generator 490, the output gases, comprising CO, CO\textsubscript{2}, and O\textsubscript{2} are cooled via heat exchanger 440, which is connected to a vacuum pump 411 to reduce the pressure in the reactor 404 to below atmospheric. After the pump 411, the gas mixture is compressed via compressor 412 prior to being fed to a separation unit 470a, which comprises an additional compressor 413 for recirculating the gas mixtures through the separator 470a to boost the separating efficiency thereof. The separator 470a can be a membrane separator, or an absorption separator, for example as described above, mutatis mutandis, and separates out CO from the CO\textsubscript{2} and O\textsubscript{2}. The Oxygen can be converted to CO\textsubscript{2} via afterburner or combustor 418 and recycled to the carbon monoxide generator 490 via conduit 431 and non-return valve 405. Catalytic reactor 435 is provided for converting excess CO, that could not be separated out in the separator 470a, into CO\textsubscript{2}. The CO separated out by the separator unit 470a is channeled to the steam converter 430, which is fed steam from a suitable supply (not shown). The product gases from the steam converter, CO\textsubscript{2} and H\textsubscript{2}, are then channeled to a second separator unit 470b, which also comprises a compressor arrangement 417 the gas mixture through the
separations 470b to boost the separating efficiency thereof. The separator 470b can be a membrane separator, for example as described above, mutatis mutandis, and separates out H₂ from the CO₂.

Also, the system 400 provides hydrogen from a single source, the conversion of CO, which is continually recycled through the system 400. There is also no need in general for hydrocarbon converter or its associated cooler.

Optionally, the oxygen which is produced by the carbon monoxide converter or generator 490 can be removed and stored or sold, for example.

The compressors, as well as valves and other suitable hardware, are provided at strategic locations in the system 400 to provide required pressure heads and safety and control apparatus such that gases are caused to flow within the system 400 in the desired directions therein.

A suitable control system 419 is provided for monitoring and controlling the monoxide generator 490, and another control unit 420 for controlling and monitoring operation of the separation units 470a and 470b.

Thus, referring particularly to Fig. 9, the hydrogen production method according to a first embodiment, and generally designated with the numeral 300, comprises the following steps:-

Step 310 – providing a core quantity of carbon monoxide, typically CO₂ is provided by the carbon dioxide source 401 and converted to CO by the carbon monoxide generator 490.

Step 320 – reacting the carbon monoxide with water, typically in the form of steam, to produce hydrogen and carbon dioxide according to a water-gas shift reaction:-

\[ \text{H}_2\text{O} + \text{CO} = \text{H}_2 + \text{CO}_2 \]

This step is carried out substantially as described above via steam converter 430, the reaction product gases being cooled by the heat exchanger
440, which in turn advantageously preheats steam prior to being reacted in the steam converter 430.

Step 330 – the hydrogen produced in step 320 is separated from the carbon dioxide, as well as unreacted water and CO. Hydrogen separation is typically via suitable membranes, as described for the first aspect of the invention, mutatis mutandis.

Step 340 – the CO₂ in step 330 is converted back to carbon monoxide and recirculated so that step 320 may be reapplied to the CO. Typically, a carbon monoxide converter 490 is used for this reaction, and optionally, carbon monoxide left over in the gases leaving the hydrogen separation unit 470 may be first oxidized to CO₂, as described for the first aspect of the invention, mutatis mutandis.

Optionally, oxygen produced by the conversion of CO₂ to CO may be recirculated within the system to oxidize the residual CO left over after the hydrogen is separated in step 330.

Optionally, the quantity of CO remaining at step 340 is determined, and if depleted can be augmented as required at step 360.

Thus, according to this aspect of the invention, water is supplied to the system 400 via a suitable water source, and hydrogen is generated therefrom, the carbon monoxide required for the steam conversion reaction being continually recycled from CO₂ produced by the steam conversion reaction itself.

The system 400 may be incorporated into an apparatus having a water inlet and a hydrogen outlet, and may be configured for large scale use, for example industrial, hospital, household and other uses, or may be configured in a transportable configuration. For example, the system may be incorporated in a seafaring ship to produce hydrogen to power the ship from seawater, though the system would typically require suitable arrangement for purifying the water prior to being reacted with the carbon monoxide.
Thus, according to aspects of the invention, systems and methods are provided for producing hydrogen, based on reacting CO with water, and reconverting the resulting carbon dioxide to CO and recycling the same. In some aspects of the invention, the system and method are coupled to a waste processing plant.

In the method claims that follow, alphanumeric characters and Roman numerals used to designate claim steps are provided for convenience only and do not imply any particular order of performing the steps.

Finally, it should be noted that the word “comprising” as used throughout the appended claims is to be interpreted to mean “including but not limited to”.

While there has been shown and disclosed exemplary embodiments in accordance with the invention, it will be appreciated that many changes may be made therein without departing from the spirit of the invention.
CLAIMS:

1. A system for producing hydrogen, comprising:
   processing apparatus for processing waste into at least product gases
   based on at least one of pyrolysis and gasification of said waste, said product
   gases comprising at least carbon monoxide;
   post processing apparatus operatively connected to said processing
   apparatus and to a source of water, and adapted for producing hydrogen, said
   post-processing apparatus comprising first converting apparatus, separating
   apparatus and second converting apparatus, wherein:
   said first converting apparatus comprises an arrangement for receiving
   product gases from said processing apparatus and for receiving carbon
   monoxide from said second converting apparatus, and a reaction
   arrangement for reacting carbon monoxide with water to produce output
   gases including hydrogen and carbon dioxide;
   said separating apparatus configured for selectively separating at least
   hydrogen from said output gases received from said first converting
   apparatus, and for directing at least said carbon dioxide to said second
   converting apparatus;
   said second converting apparatus configured for converting carbon
   dioxide to carbon monoxide and for directing at least said carbon monoxide
   to said first converting apparatus.

2. A system according to claim 1, wherein said reaction arrangement
   comprises a suitable reaction vessel configured for running therein a water-gas
   shift reaction in the presence of suitable catalysts comprised therein.

3. A system according to claim 2, wherein said catalysts comprise a zinc-
copper-chromium catalyst, and wherein said water-gas shift reaction is run at a
   temperature in the range of about 350°C to about 380°C.
4. A system according to claim 3, wherein said first converting apparatus further comprises a suitable heat exchanger for cooling said output gases.

5. A system according to claim 4, wherein said heat exchanger is further configured for preheating water from said water source prior to being reacted in said first converting apparatus.

6. A system according to any one of claims 1 to 5, wherein said separation apparatus comprises at least one separation unit comprising a membrane arrangement for separating hydrogen from said output gases by selectively allowing hydrogen to diffuse through said membrane arrangement.

7. A system according to claim 6, wherein said separation apparatus comprises further separation units for separating other gases from said output gases.

8. A system according to claim 7, wherein one said separation unit is adapted for separating carbon dioxide from said output gases, and for directing said carbon dioxide to said second converting apparatus.

9. A system according to any one of claims 1 to 8, wherein said second converting apparatus comprises a suitable UHF discharge device coupled to a DC electrical power source.

10. A system according to claim 1, wherein said processing apparatus comprises:

   a waste converting chamber for accommodating a column of said waste, said chamber having an upper part and a lower part;

   at least one primary plasma torch arrangement for generating a hot gas jet at an output end thereof and for directing said jet towards said lower part of said chamber;

   at least one waste inlet at said upper part of said chamber;

   at least one liquid product outlet at said lower part for removing liquid product from said chamber; and

   at least one product gas outlet for directing product gases out of said chamber and into said post processing apparatus.
11. A system according to claim 10, wherein said waste comprises substantially solid waste.

12. A system according to claim 11, wherein said waste comprises at least one of municipal waste and industrial waste.

13. A system according to claim 1, further comprising a gas cleaning arrangement upstream of said first converting apparatus, said gas cleaning arrangement being adapted for removing predetermined components from said product gases, and for subsequently directing said product gases to said first converting apparatus.

14. A system according to claim 13, wherein said predetermined components include one or more of pitch, tar and dust.

15. A system according to claim 1, wherein said product gases further comprise at least one of H₂, CO₂, N₂, C₄H₈₉, wherein n and m are each integers.

16. A system according to any one of claims 1 to 15, further comprising a suitable hydrocarbon converter arrangement for converting hydrocarbons comprised in said product gases such as to provide hydrogen therefrom.

17. A system according to claim 16, wherein said hydrocarbon converter arrangement comprises a suitable reaction vessel configured for carrying out therein a steam conversion reaction on said hydrocarbons in the presence of a suitable catalyst to produce hydrogen and carbon monoxide.

18. A system according to claim 17, wherein said catalyst comprises an iron-chromium catalyst.

19. A system according to claim 17 wherein said hydrogen produced by said hydrocarbon converter arrangement is separated via said separating apparatus.

20. A system according to claim 19, further comprising a cooler for cooling gases output from said hydrocarbon converter prior to separating hydrogen therefrom.

21. A system according to claim 16, wherein said hydrocarbon converter arrangement comprises a suitable reaction vessel configured for carrying out
therein a decomposition reaction for decomposing hydrocarbons to carbon and hydrogen.

22. Apparatus for producing hydrogen, comprising:
first converting apparatus operatively connectable to a source of water, separating apparatus and second converting apparatus, wherein:
said first converting apparatus comprises a suitable arrangement for receiving carbon monoxide from said second converting apparatus, and a reaction arrangement for reacting carbon monoxide with water to produce output gases including hydrogen and carbon dioxide;
said separating apparatus configured for selectively separating at least hydrogen from said output gases received from said first converting apparatus, and for directing at least said carbon dioxide to said second converting apparatus;
said second converting apparatus configured for converting carbon dioxide to carbon monoxide and for directing at least said carbon monoxide to said first converting apparatus.

23. Apparatus according to claim 22, wherein said reaction arrangement comprises a suitable reaction vessel configured for running therein a water-gas shift reaction in the presence of suitable catalysts comprised therein.

24. Apparatus according to claim 23, wherein said catalysts comprises a zinc-copper-chromium catalyst, and wherein said water-gas shift reaction is run at a temperature in the range of about 350°C to about 380°C.

25. Apparatus according to claim 22, wherein said second converting apparatus comprises a suitable UHF discharge device coupled to a DC electrical power source.

26. Apparatus according to claim 23, wherein said first converting apparatus further comprises a suitable heat exchanger for cooling said output gases.
27. Apparatus according to claim 26, wherein said heat exchanger is further configured for preheating water from said water source prior to being reacted in said first converting apparatus.

28. Apparatus according to claim 22, wherein said separation apparatus comprises at least one separation unit comprising membrane arrangement for separating hydrogen from said output gases by selectively allowing hydrogen to diffuse through said membrane.

29. Apparatus according to claim 22, further comprising a supply of carbon dioxide or carbon dioxide for maintaining the level of carbon monoxide within the apparatus within predetermined thresholds.

30. A method for producing hydrogen, comprising:

   processing waste into at least product gases based on at least one of pyrolysis and gasification of said waste, said product gases comprising at least carbon monoxide;

   post processing said product gases by:

   (a) receiving said product gases and providing output gases including hydrogen and carbon dioxide produced by reacting carbon monoxide with water;

   (b) selectively separating at least hydrogen from said output gases provided in (a);

   (c) converting carbon dioxide contained in the output gases in step (b) to carbon monoxide and recycling at least said carbon monoxide to said product gases produced by said waste processing apparatus to be processed according to step (a);

   (d) repeating steps (a) to (c).

31. A method for producing hydrogen, comprising:

   (a) providing a quantity of carbon monoxide;
(b) receiving carbon monoxide and providing output gases including hydrogen and carbon dioxide produced by reacting carbon monoxide with water;

(c) selectively separating at least hydrogen from said output gases provided in (b);

(d) converting carbon dioxide contained in the output gases in step (c) to carbon monoxide and recycling at least said carbon monoxide to be processed according to step (a);

(e) repeating steps (b) to (d).
Providing a core quantity of carbon monoxide

Reacting carbon monoxide with steam to produce hydrogen and carbon dioxide according to a water-gas shift reaction -

\[ \text{H}_2\text{O} + \text{CO} = \text{H}_2 + \text{CO}_2 \]

Separating \( \text{H}_2 \) produced in step 320 from the \( \text{CO}_2 \) unreacted water and \( \text{CO} \)

Converting the \( \text{CO}_2 \) in step 330 to \( \text{CO} \) and recirculating \( \text{CO} \) to step 320 may be reapplied to the \( \text{CO} \)

Is the quantity of \( \text{CO} \) below minimum threshold?

No

Provide more \( \text{CO} \)

Yes

FIG. 9
**INTERNATIONAL SEARCH REPORT**

International application No
PCT/IL2006/000435

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C10J3/18  C01B3/16  C01B3/50  C01B31/18  C01B3/38

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
C10J  C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>A</td>
<td>WO 95/19407 A (RINECO CHEMICAL INDUSTRIES, INC) 20 July 1995 (1995-07-20) page 4, line 10 - line 23 page 9, line 34 - page 16, line 28 figure 1</td>
<td>1-31</td>
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[X] Further documents are listed in the continuation of Box C.  
[X] See patent family annex.

* Special categories of cited documents :

*A* document defining the general state of the art which is not considered to be of particular relevance

*E* earlier document but published on or after the international filing date

*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

*O* document referring to an oral disclosure, use, exhibition or other means

*P* document published prior to the international filing date but later than the priority date claimed

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*"X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

*"Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

*"A* document member of the same patent family

Date of the actual completion of the International search

19 July 2006

Date of mailing of the International search report

27/07/2006

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk
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Authorized officer

Harf-Bapin, E
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