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- (71) **Applicant** (for all designated States except US): **INVISTA TECHNOLOGIES S.A R.L.** [LU/CH]; Zweigniederlassung St. Gallen, Kreuzackerstrasse 9, 9000 St. Gallen (CH).
- (72) **Inventors:** **FORSYTH, Stewart**; 102 Yearsley Place, Wilmington, Delaware 19808 (US). **RENNER, Martin J.**; 710 North Market Street, Hallettsville, Texas 77964 (US). **LIU, Aiguo**; 907 Lincoln Square, Apartment J, Elk Grove Village, Illinois 60007 (US). **STAHLMAN, Brent J.**; 1701 Victoria Station Drive, Apartment 708, Victoria, Texas 77901 (US).
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(54) **Title:** SYSTEM AND METHOD FOR RECYCLING IN AN ANDRUSSOW PROCESS

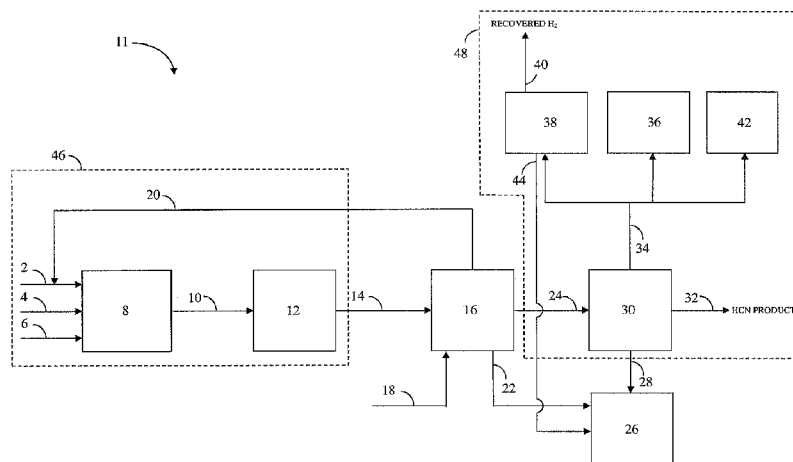


FIG. 1

(57) **Abstract:** A method and a system for utilizing waste produced during production of hydrogen cyanide are described herein.

SYSTEM AND METHOD FOR RECYCLING IN AN ANDRUSSOW PROCESS

CROSS-REFERENCE TO RELATED APPLICATION

[001] This application claims the benefit of priority to U.S. Provisional Patent Application Serial No. 61/738,895 entitled “SYSTEM AND METHOD FOR RECYCLING IN AN ANDRUSSOW PROCESS,” filed December 18, 2012, the disclosure of which is incorporated herein in its entirety by reference.

TECHNICAL FIELD

[002] The present disclosure is directed to a recycling scheme for the Andrussow process for the production of hydrogen cyanide (HCN) from methane, ammonia, and oxygen.

BACKGROUND

[003] The Andrussow process is used for gas phase production of hydrogen cyanide (HCN) from methane, ammonia, and oxygen over a platinum-containing catalyst. Ammonia, methane, and oxygen are fed into a reactor and heated to a reaction temperature in the presence of a catalyst that comprises platinum. The methane can be supplied from natural gas, which can be further purified. Hydrocarbons having two carbons, three carbons, or more can be present in natural gas. While air can be used as a source of oxygen, the reaction can also be carried out with oxygen-enriched air or undiluted oxygen (e.g., an oxygen Andrussow process). The reactor off-gas containing HCN can be sent through an ammonia absorption process to remove unreacted ammonia. This can be accomplished by contacting with an ammonium phosphate solution, phosphoric acid or sulfuric acid to remove the ammonia. From the ammonia absorber the product off-gas can be sent through an HCN absorber where cold water can be added to entrain the HCN. The HCN-water mixture can be sent to a cyanide stripper where HCN can be separated from the water and other materials.

[004] Various aspects of the Andrussow process are described in the following articles: N.V. Trusov, *Effect of Sulfur Compounds and Higher Homologues of Methane on Hydrogen Cyanide Production by the Andrussow Method*, Rus. J. of Applied Chemistry, Vol. 74, No. 10, pp. 1693–97 (2001); Clean Development Mechanism (CDM) Executive Board, United Nations Framework Convention on Climate Change (UNFCCC), *Clean Development Mechanism Project Design Document Form (CDM PDD)*, Ver. 3, (Jul. 28, 2006), available online at

http://cdm.unfccc.int/Reference/PDDs_Forms/PDDs/PDD_form04_v03_2.pdf; Gary R. Maxwell et al., *Assuring process safety in the transfer of hydrogen cyanide manufacturing technology*, J. of Hazardous Materials, Vol. 142, pp. 677–84 (2007); Eric. L. Crump, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, *Economic Impact Analysis For the Proposed Cyanide Manufacturing NESHAP* (May 2000), available online at <http://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P100AHG1.PDF>, the disclosures of which are incorporated by reference as if reproduced herein.

SUMMARY

[005] The problem of thermal waste and material waste in an Andrussow process is solved or improved by recovering energy from heat generated from the reaction producing HCN and recovering energy from burning the gaseous waste stream. The present disclosure is directed to methods for utilizing waste produced during an Andrussow process (e.g., during an oxygen-enriched or oxygen Andrussow process). The present disclosure also provides systems that can operate during production of hydrogen cyanide and reduce the amount of energy or material that is wasted during an Andrussow process.

[006] Some problems of using oxygen-enriched or substantially pure oxygen feedstreams are readily understood. For example, oxygen-enriched and substantially pure oxygen feedstreams are more expensive than air. Oxygen-enriched and substantially pure oxygen feedstreams can include concentrated oxygen sources and produce waste streams that contain high levels of hydrogen. Thus, added care is used to avoid problems relating to the use of pure oxygen as the gaseous oxygen feed stream. For example, safety concerns, equipment design, equipment maintenance, and operating conditions that are not generally used or needed in an air Andrussow process can be needed for dealing with safety issues raised by combining hydrogen recovery with an oxygen-enriched or oxygen Andrussow process.

[007] Very few oxygen-enriched or oxygen Andrussow manufacturing facilities exist or have been built. In addition to the more readily apparent concerns associated with oxygen-enriched or oxygen Andrussow manufacturing facilities such as those described above, there are a multitude of additional problems that are not readily or widely understood.

[008] For example, an oxygen-enriched or oxygen Andrussow process is more sensitive to variations in concentration of reactants than in an Andrussow process that employs air.

Variations in concentration or flow rate of reactants in an oxygen-enriched or oxygen Andrussov process can cause larger changes in the efficiency of the process than are observed in an air Andrussov process. An oxygen-enriched or oxygen Andrussov process is more sensitive to changes in a heating value (British Thermal Units (BTU)) of the feed gas; small variations in the composition of the feedstream can cause greater temperature fluctuations in the reactor than would be observed for similar feedstream compositions in an air Andrussov process. Local variations in the concentration of reactants traveling past the catalyst can cause temperature variations in the catalyst bed, such as hot spots, which can reduce the life of the catalyst as compared to an air Andrussov process. The presence of about 78 vol% nitrogen in air serves to dilute the gas mixture in an air Andrussov process and can reduce the production of by-products and the need for heightened control of the reaction. The gaseous waste stream of an air Andrussov process (e.g., the stream after the HCN recovery), has a low heating value such that the stream would need to be supplied with a fuel gas (e.g., natural gas) to complete combustion. Therefore, the air Andrussov process gaseous waste stream is not meaningful as a fuel gas.

[009] Heat transfer from the effluent of an oxygen-enriched or oxygen Andrussov process poses more problems than observed for an air Andrussov process. The effluent from an oxygen-enriched or oxygen Andrussov process is more concentrated than for an air Andrussov process. While cooling such a concentrated effluent is best done quickly to stop reactants from forming by-products, the effluent should not be cooled to the point of HCN condensation because the HCN has a greater propensity for polymerization when condensed.

[010] An oxygen-enriched or oxygen Andrussov process tends to proceed in a more concentrated fashion than an air Andrussov process. As such, an oxygen-enriched or oxygen Andrussov process tends to generate a higher concentration of all products, including by-products. Hence, the reactor and associated equipment for an oxygen-enriched or oxygen Andrussov process is more susceptible to the build-up of impurities in the system that can more easily be flushed out of the equipment employed in an air Andrussov process. The greater rate of by-product build-up can lead to increased rates of corrosion as well as more frequent shut down and maintenance of various parts of the process. Equipment that can be significantly affected by by-product build-up, corrosion and related problems include, for example, heat recovery system(s), the reactor(s), the ammonia recovery system(s), and the HCN recovery system(s).

[011] Although the equipment needed for production of an equivalent amount of HCN can be more compact (i.e., smaller) for an oxygen-enriched or oxygen Andrussov process than for an air Andrussov process, many manufacturers would choose to operate an air Andrussov process to avoid the problems associated with an oxygen-enriched or oxygen Andrussov process. The problems associated with combining an oxygen-enriched or oxygen Andrussov process with utilizing waste produced during the oxygen-enriched or oxygen Andrussov process are not well understood and the difficulties are of sufficient magnitude that most manufacturers would not attempt such a combination.

[012] However, the benefits can be surprisingly large. Various examples of the present disclosure can generate energy from waste such as thermal waste and material waste, produced during the production of HCN from an oxygen-enriched or oxygen Andrussov process. For example, co-generation units can be utilized after the reactor and after HCN recovery to generate electricity and heat. The various examples can reduce the cost of producing HCN during an oxygen-enriched or oxygen Andrussov process by recycling the generated heat and electricity back into the process thereby minimizing the amount of externally supplied energy and minimize the amount of material waste. The benefits described with respect to the oxygen-enriched or oxygen Andrussov process were not plausible in an air Andrussov process.

[013] The conversion of ammonia and methane to HCN is an endothermic reaction, but in an Andrussov process the reaction is converted to an exothermic catalytic reaction by using ammonia, methane, oxygen, and a suitable catalyst, such as a Pt-containing catalyst. Producing HCN via the Andrussov process can occur at reaction temperatures greater than 800 °C, for example, about 800 to 2,500 °C or 1,000 to about 1,500 °C. Supplying energy to heat the reactant feed streams to the reaction temperature can be costly. Additionally, if the heat generated by the reaction is not recaptured and converted to energy, the generated heat can be considered thermal waste. Additionally, recovering the heat generated can decrease the temperature of the product stream and prevent components of the product stream from forming by-products. In various examples, the present disclosure can recover a portion of the heat and generate both electricity and heat, which can be recycled back into the process. For example, a co-generation unit can be utilized to generate steam and electricity. Recycling the electricity and heat back into the process can reduce the amount of externally supplied energy, minimize the amount of heat waste, and improve the overall efficiency of the process.

[014] In various examples, material waste (e.g., chemical waste) can be produced during the production of HCN. For example, in an oxygen Andrussov process about 40,000 standard cubic feet (scf) of waste gas can be produced for 1,000 pounds (lbs) of HCN and 235 BTU/scf can be lost. As discussed herein, as the oxygen percentage in the feed gas increases (e.g., in an oxygen Andrussov process), the hydrogen and other combustible components (such as carbon monoxide increases) such that the gaseous waste stream can be used as a fuel. In various examples, the present disclosure can convert the chemical waste into energy. For example, a co-generation unit can be utilized in a gaseous waste stream from an oxygen or oxygen-enriched Andrussov process and generate heat and electricity. By recovering energy from material waste, the various examples of present disclosure can reduce the amount of material wasted during the production of HCN and can produce HCN more efficiently than other processes (e.g., an air Andrussov process). For example, the various examples can reduce the overall cost of producing hydrogen cyanide by reducing the amount of externally supplied energy and minimize the amount of material waste.

[015] In various examples, the present disclosure provides a method of utilizing waste produced during production of hydrogen cyanide. The method can include burning a gaseous waste stream for primary energy generation, wherein the gaseous waste stream is from a reactor configured to produce hydrogen cyanide, and the gaseous waste stream is substantially free of hydrogen cyanide. The method can include contacting a heat recovery unit with heat for secondary energy generation, where the heat is generated by a reactor during production of the hydrogen cyanide. In various examples, the method can include both burning the gaseous waste stream for primary energy generation and contacting a heat recovery unit with heat for secondary energy generation. The primary or secondary energy generation can include heat transfer, steam generation, electricity generation or a combination thereof.

[016] In various examples, the present disclosure provides a system for producing hydrogen cyanide via the Andrussov process. The system includes a reactor configured for producing hydrogen cyanide from a reaction mixture comprising methane, ammonia and oxygen in the presence of a catalyst comprising platinum, wherein the reactor is also configured to supply the reaction mixture with sufficient oxygen to generate a gaseous waste stream that has at least 59 volume percent hydrogen after removal of ammonia and recovery of hydrogen cyanide. The system can include a first cogeneration unit configured to burn the gaseous waste stream as a

fuel for primary energy generation, wherein the gaseous waste stream is substantially free of hydrogen cyanide. The system can include a second cogeneration unit configured to absorb heat from the reactor for secondary energy generation. In various examples, the system can include both the first cogeneration unit and the second cogeneration unit.

[017] In various examples, the present disclosure provides a method. The method can include adjusting a reaction mixture comprising methane, ammonia and oxygen to provide the reaction mixture with sufficient oxygen to generate a gaseous waste stream that has at least 59 volume percent hydrogen in the gaseous waste stream after removal of ammonia and recovery of hydrogen cyanide. The method can further include burning the gaseous waste stream for energy generation.

[018] These and other examples and features of the present methods and devices will be set forth in part in the following Detailed Description. This Summary is intended to provide an overview of the present subject matter, and is not intended to provide an exclusive or exhaustive explanation. The Detailed Description below is included to provide further information about the present systems and methods.

BRIEF DESCRIPTION OF THE FIGURES

[019] In the drawings, which are not necessarily drawn to scale, like numerals describe substantially similar components throughout the several views. The drawings illustrate generally, by way of example, but not by way of limitation, various examples discussed in the present document.

[020] **FIG. 1** is a flow diagram of a process for the production of hydrogen cyanide (HCN) via the Andrussov process, in accordance with various examples.

[021] **FIG. 2** is a more detailed flow diagram of a portion from process 11 of **FIG. 1**, in accordance with various examples.

[022] **FIG. 3** is a more detailed flow diagram of a portion of the process of **FIG. 1** for the production of HCN, in accordance with various examples.

DETAILED DESCRIPTION

[0001] Reference will now be made in detail to certain claims of the disclosed subject matter. While the disclosed subject matter will be described in conjunction with the enumerated

claims, it will be understood that they are not intended to limit the disclosed subject matter to those claims. On the contrary, the disclosed subject matter is intended to cover all alternatives, modifications, and equivalents, which can be included within the scope of the presently disclosed subject matter as defined by the claims. The following detailed description includes references to the accompanying drawings, which form a part of the detailed description. The drawings show, by way of illustration, specific examples in which the invention may be practiced.

[0002] References in the specification to “one example,” “an example,” etc., indicate that the example described can include a particular feature, structure, or characteristic, but every example may not necessarily include the particular feature, structure, or characteristic.

Moreover, such phrases are not necessarily referring to the same example. Further, when a particular feature, structure, or characteristic is described in connection with an example, it is submitted that it is within the knowledge of one skilled in the art to affect such feature, structure, or characteristic in connection with other examples whether or not explicitly described.

[023] The term "about" can allow for a degree of variability in a value or range, for example, within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range. When a range or a list of sequential values is given, unless otherwise specified any value within the range or any value between the given sequential values is also disclosed.

[024] The term “air” as used herein refers to a mixture of gases with a composition approximately identical to the native composition of gases taken from the atmosphere, generally at ground level. In some examples, air is taken from the ambient surroundings. Air has a composition that includes approximately 78% nitrogen, 21% oxygen, 1% argon, and 0.04% carbon dioxide, as well as small amounts of other gases.

[025] As used herein, an air Andrussov process uses air as the oxygen-containing feedstream, having approximately 20.95 mol% oxygen.

[026] An oxygen-enriched Andrussov process uses an oxygen-containing feed stream having about 21 mol% oxygen to about 26%, 27%, 28%, 29%, or to about 30 mol% oxygen, such as about 22 mol% oxygen, 23%, 24%, or about 25 mol% oxygen.

[027] As used herein, an oxygen Andrussov process uses an oxygen-containing feed stream having about 26 mol% oxygen, 27%, 28%, 29%, or about 30 mol% oxygen to about 100 mol% oxygen. An oxygen Andrussov process can also use an oxygen-containing feed stream

having about 35 mol% oxygen, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95%, or about 100 mol% oxygen.

[028] The term “substantially free” as used herein refers to less than about 1 wt%, less than about 0.5 wt%, and less than about .10 wt%.

[029] This disclosure describes methods and systems for utilizing waste produced during production of hydrogen cyanide (HCN) from an Andrussov process. The methods and systems of the present disclosure can safely solve the problems of wasteful loss of heat and material from an oxygen-enriched or oxygen Andrussov process by use of the methods and systems described herein. The methods and systems can involve burning a gaseous waste stream for the generation of energy. The methods and systems of the present disclosure can also involve generating energy from the heat given off from the reaction for producing HCN. In various examples, the energy generated from waste can be used and recycled back into the process for producing HCN. Thus, the methods and systems of the present disclosure can reduce the amount of energy or material in an Andrussov process that is waste.

[030] During an Andrussov process, reactant gas feedstreams including a gaseous ammonia feedstream, a gaseous methane feedstream and a gaseous oxygen feedstream react to form a product stream that contains hydrogen cyanide and water. As discussed herein, the synthesis of hydrogen cyanide by the Andrussov method (see, for example, Ullmann's Encyclopedia of Industrial Chemistry, Volume 8, VCH Verlagsgesellschaft, Weinheim, 1987, pp. 161–162) can be carried out in the vapor phase over a catalyst that comprises platinum or platinum alloys, or other metals. Catalysts suitable for carrying out the Andrussov process were discovered and described in the original Andrussov patent, published as U.S. Pat. No. 1,934,838, and elsewhere. In Andrussov's original work, he disclosed that catalysts can be chosen from oxidation catalysts that are infusible (solid) at the working temperature of around 1000°C; he included platinum, iridium, rhodium, palladium, osmium, gold or silver as catalytically active metals either in pure form or as alloys. He also noted that certain base metals, such as rare earth metals, thorium, uranium, and others, could also be used, such as in the form of infusible oxides or phosphates, and that catalysts could either be formed into nets (screens), or deposited on thermally-resistant solid supports such as silica or alumina.

[031] In subsequent development work, platinum-containing catalysts have been selected due to their efficacy and to the heat resistance of the metal even in gauze or net form.

For example, a platinum-rhodium alloy can be used as the catalyst, which can be in the form of a metal gauze or screen such as a woven or knitted gauze sheet, or can be disposed on a support structure. In an example, the woven or knitted gauze sheet can form a mesh-like structure having a size from 20-80 mesh, e.g., having openings with a size from about 0.18 mm to about 0.85 mm. A catalyst can comprise from about 85 wt% to about 90 wt% platinum (Pt) and from about 10 wt% to about 15 wt% rhodium (Rh). A platinum-rhodium catalyst can also comprise small amounts of metal impurities, such as iron (Fe), palladium (Pd), iridium (Ir), ruthenium (Ru), and other metals. The impurity metals can be present in trace amounts, such as about 10 ppm or less.

[032] A broad spectrum of possible embodiments of the Andrussov method is described in German Patent 549,055. In one example, a catalyst comprising a plurality of fine-mesh gauzes of Pt with 10% rhodium disposed in series is used at temperatures of about 800 to 2,500° C, 1,000 to 1,500° C, or about 980 to 1050° C. For example, the catalyst can be a commercially-available catalyst, such as a Pt-Rh catalyst gauze available from Johnson Matthey Plc, London, UK, or a Pt-Rh catalyst gauze available from Heraeus Precious Metals GmbH & Co., Hanau, Germany.

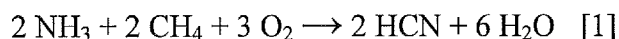
[033] Andrussov processes can be performed using a variety of sources for the gaseous oxygen feedstream. For example, the gaseous oxygen feedstream can be pure oxygen, mixtures of oxygen with inert gases, as well as mixtures of air and oxygen. In general, a greater percentage of oxygen in the gaseous oxygen feedstream will give rise to a greater percentage of hydrogen in the gaseous waste stream. For example, an Andrussov process that employs a gaseous oxygen feedstream that is substantially pure oxygen can yield a gaseous waste stream with as much as 70-80 vol % hydrogen. However, an Andrussov process that employs air as its gaseous oxygen feedstream has substantially less hydrogen in its gaseous waste stream, for example, as little as 15-18 vol%. As discussed herein, the gaseous waste stream of an air Andrussov process that has not been supplemented with fuel gas is not generally useful as a fuel gas. Hence, burning the gaseous waste stream to generate energy in an oxygen-enriched or substantially pure oxygen Andrussov process having more than 55 vol % of oxygen in the oxygen feed stream may be more economically attractive than burning the gaseous waste stream in an air Andrussov process. For example, the gaseous waste stream from an air Andrussov process will need to be supplemented with a fuel gas in order to include enough fuel to be useful for energy generation (e.g., via a cogeneration unit).

[034] As used herein, an air Andrussov process uses air as the oxygen-containing feedstream, having approximately 20.95 vol% oxygen. An oxygen-enriched Andrussov process uses an oxygen-containing feed stream having about 21 vol% oxygen to about 26%, 27%, 28%, 29%, or to about 30 vol% oxygen, such as about 22 vol% oxygen, 23%, 24%, or about 25 vol% oxygen.

[035] An oxygen Andrussov process uses an oxygen-containing feed stream having about 26 vol% oxygen, 27%, 28%, 29%, or about 30 vol% oxygen to about 100 vol% oxygen. An oxygen Andrussov process can also use an oxygen-containing feed stream having about 35 vol% oxygen, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 95%, or about 100 vol% oxygen.

[036] In various examples, the oxygen-containing feedstream in an oxygen-enriched Andrussov process, or in an oxygen Andrussov process with an oxygen-containing feedstream having less than 100 vol% oxygen, can be generated by mixing air with oxygen, by mixing oxygen with any suitable gas or combination of gases, or by removing one or more gases from an oxygen-containing gas composition such as air.

[037] **FIG. 1** is a flow diagram of a process **11** for the production of hydrogen cyanide (HCN) via the Andrussov process, in accordance with various examples. In the example process **11**, a HCN synthesis system **8** includes one or more unit operations configured to produce HCN. In various examples, the HCN synthesis system **8** is supplied with an ammonia (NH₃) stream **2**, a methane (CH₄) stream **4**, and an oxygen stream **6** (which includes oxygen gas (O₂)). The three feed streams **2**, **4**, **6**, are mixed and reacted in a plurality of reactors to be converted to hydrogen cyanide and water in the presence of a suitable catalyst according to Equation 1:



[038] The resulting product stream **10** from the HCN synthesis system **8** can be fed into a thermal waste utilization system **12** (discussed in further detail in **FIG. 2**). The reaction of Equation 1 for producing HCN using the Andrussov process is exothermic and generates heat. If the heat is not recaptured, the generated heat can be considered thermal waste. Additionally, by removing the heat from the product stream **10**, the process **11** can minimize the amount of by-product formation. The thermal waste utilization system **12** can include one or more unit operations configured to utilize the thermal waste and generate energy. In various examples, the energy generated by the thermal waste utilization system **12** can include heat transfer, steam

generation, electricity generation or a combination thereof. In one example, the thermal waste utilization system **12** generates steam. The generated steam can be used to recuperatively pre-heat one or more of the reactant feed streams, for example, streams **2**, **4**, and **6**, which can reduce the amount of externally supplied heat that elevates the temperature of the feed streams **2**, **4**, and **6** to the reaction temperature. In one example, the thermal waste utilization system **12** generates electricity. The generated electricity can be used to supplement the electricity needs of the process **11** for producing HCN.

[039] After heat has been removed from product stream **10**, a resulting reduced-temperature product stream **14** can be fed into an ammonia recovery system **16**. The composition of stream **14** and stream **10** are substantially the same, but stream **14** has a lower temperature than stream **10**. The ammonia recovery system **16** can include one or more unit operations configured to recover unreacted NH_3 . Ammonia can be recovered by NH_3 absorption via contacting with one or more of phosphoric acid (H_3PO_4), sulfuric acid (H_2SO_4), and an ammonium phosphate solution, that can absorb NH_3 from the product stream **10**. In the example shown in **FIG. 1**, a phosphoric acid stream **18** is added to the ammonia recovery system **16** to absorb NH_3 . In the case of an H_3PO_4 solution, ammonia can be removed from the resulting ammonium phosphate solution using one or more strippers to separate the NH_3 from the H_3PO_4 . The NH_3 can be recycled back to the NH_3 feed stream **2** via an NH_3 recycle stream **20**. The H_3PO_4 and other waste can be purged as a wastewater stream **22**, while an NH_3 -stripped HCN stream **24** can be fed to an HCN recovery system **30**.

[040] The HCN recovery system **30** can include one or more unit operations configured to separate and purify HCN from the NH_3 -stripped HCN stream **24**. As a result of the HCN recover system **30**, a purified HCN product stream **32** is produced. The HCN recovery system **30** can also produce a gaseous waste stream **34** and a wastewater stream **28**. Wastewater stream **28** from the HCN recovery system **30** can be fed into wastewater treatment system **26**. Waste water treatment system **26** can further process wastewater streams **22**, **28**, for example, by further treatment, storage, or disposal. Prior to being fed to the waste water treatment system **26**, either or both of wastewater streams **22** and **28** can be processed to recover additional ammonia, which can be recycled back to the ammonia recovery system **16**.

[041] In various examples, process **11** can include a material waste utilization system **36** that generates energy from waste. The gaseous waste stream **34** can include a variety of gases

including hydrogen, unreacted methane, carbon dioxide, carbon monoxide, water, nitrogen, a variety of organonitriles, and trace amounts of HCN. Flaring the gaseous waste stream **34** is wasteful and creates material waste.

[042] In various examples, the gaseous waste stream **34** can be fed to a material waste utilization system **36**, an H₂ recovery system **38**, a flare **42**, or combinations thereof. In various examples, the gaseous waste stream **34** can be diverted, in whole or in part, from the material waste utilization system **38** and to the H₂ recovery system **38** and/or the flare **42**. In various examples, the gaseous waste stream **34** can be divided between the material waste utilization system **36**, the H₂ recovery system **38**, and the flare **42**.

[043] In various examples, the material waste utilization system **38** can be configured to burn the gaseous waste stream **34** and generate energy. The energy generated can include electricity generation, steam generation, heat transfer and combinations thereof. In an embodiment(s), where electricity is generated, the generated electricity can be used to supplement the external supply of electricity for the production of HCN. In various examples, the material waste utilization system **38** can capture a portion of the heat generated from burning the gaseous waste stream **34** and be recycled to preheat the feed stream reactants.

[044] The H₂ recovery system **38** can be configured to recover hydrogen from the gaseous waste stream **34**. The recovered H₂ **40** can be stored or further processed. For example, the recovered H₂ **40** can be employed for hydrogenation. As discussed herein, a portion of the gaseous waste stream **34** can be sent to the flare **42**. The flare **42** can be used to destroy any excess gases produced. However, the various examples minimize flaring and thereby minimize the material waste produced during the production of HCN, as discussed herein.

[045] **FIG. 2** is a more detailed flow diagram of portion **46** from process **11** of **FIG. 1**, in accordance with various examples. As shown in **FIG. 2**, only one reactor **66** is illustrated for simplicity. However, a plurality of reactors **66** can be connected in series and used to produce HCN. The reactor **66** can include a catalyst bed. The catalyst bed can comprises a catalyst material that is capable of catalyzing Reaction 1, such as a catalyst comprising platinum (Pt). In an embodiment, the catalyst bed comprises a platinum and rhodium (Rh) catalyst, such as a catalyst comprising about 85 wt% to about 95 wt% Pt and about 5 wt% to about 15 wt% Rh, such as 85/15 Pt/Rh, 90/10, or 95/5 Pt/Rh. The catalyst of the catalyst bed can also comprise small amounts of metal impurities, such as iron (Fe), palladium (Pd), iridium (Ir), ruthenium

(Ru), and other metals. The impurity metals can be present in trace amounts, such as about 10 parts per million (ppm) or less.

[046] The catalyst bed can be formed with the catalyst, such as the Pt-Rh catalyst described above, on a support structure, such as a woven or knitted gauze sheet, a corrugated catalyst structure, or a supported catalyst structure. In an example, the woven or knitted gauze sheet can form a mesh-like structure having a size from 20-80 mesh, e.g., having openings with a size from about 0.18 mm to about 0.85 mm. The amount of catalyst that is present in the catalyst bed can depend on the feed rate of the reaction mixture **64** being feed to the reactor **66**. In an embodiment, the mass of catalyst in the catalyst bed is from about 0.4 grams (g) to about 0.6 g per feed rate, in pounds per hour, of the reaction mixture being fed to the reactor **66**. The catalyst of the catalyst bed can be a commercially-available catalyst, such as a Pt-Rh catalyst gauze available from Johnson Matthey Plc, London, UK, or a Pt-Rh catalyst gauze available from Heraeus Precious Metals GmbH & Co., Hanau, GERMANY.

[047] The HCN synthesis system **8** (illustrated in **FIG. 1**) can include operations for preparing each feed stream, e.g., the NH_3 stream **2**, the CH_4 stream **4**, and the oxygen stream **6**, to be at desired conditions in order to effectuate reaction according to Equation 1 and to produce HCN. For example, the NH_3 feed stream **2**, which can be fed as a liquid, can be vaporized by an ammonia vaporizer **56** that can vaporize the liquid NH_3 stream **2** into an NH_3 vapor stream **58**. The NH_3 vapor stream **58** can be further heated in an NH_3 super heater **54** to form a superheated NH_3 vapor **60**.

[048] In various examples, the CH_4 stream **4** can be provided as a hydrocarbon feed comprising natural gas, biogas, substantially pure methane or mixtures thereof. In one embodiment, the CH_4 stream **4** is in the form of a natural gas feed. The composition of the natural gas feed can be a majority CH_4 with small percentages of other hydrocarbons. In an embodiment, the natural gas feed **4** can be about 90 wt% to about 97 wt% CH_4 , about 3 wt% to about 10 wt% ethane (C_2H_6), about 0 wt% to about 5 wt% propane (C_3H_8), about 0 wt% to about 1 wt% butane (C_4H_{10} , either in the form of isobutene, n-butane or a combination thereof), and trace amounts of higher hydrocarbons and other gases. The natural gas feed can also be purified to comprise a more pure source of methane. In an embodiment, a purified natural gas feed can comprise about 99.9% CH_4 and less than about 0.1 wt% other hydrocarbons (which are primarily ethane). The natural gas feed can be heated by a gas heater **52**.

[049] The oxygen stream 6 can be pressurized, such as with a compressor 50 (e.g., an air compressor). The oxygen stream 6 can be provided as an oxygen-rich or substantially pure oxygen feeds stream. For example, such an oxygen stream 6 can contain at least about 25 vol% oxygen, at least about 30 vol% oxygen, at least about 40 vol% oxygen, at least about 50 vol% oxygen, at least about 60 vol% oxygen, at least about 70vol % oxygen, at least about 80 vol% oxygen, at least about 90 vol% oxygen, at least about 95% oxygen, at least about 98% oxygen. Substantially pure oxygen can also be employed as the oxygen stream 6.

[050] The three feed streams 2, 4, 6, can be combined in preheater 62, where the preheater 62 can assist in heating the reaction mixture to the reaction temperature. In various examples, the preheater 62 can include a gas mixer that is configured to form a reaction mixture feed stream 64 comprising gaseous ammonia, methane, and oxygen gas. In various examples, preheater 62 may contact one or more of the three feed streams 2, 4, and 6, before forming the reaction mixture feed stream 64, with heat (e.g., steam 72) that is generated from a cogeneration unit 74 using thermal waste from the reactor 66. As illustrated in process 11, the feed streams 2, 4, 6 are combined prior to entering the reactor 66. In some examples, the mixing can occur within a mixing zone of the reactor 66 before entering a reactor zone of reactor 66. In some examples, a portion of the product stream 10 leaving the reactor 66 can be recovered in a storage tank 68 and sent back to the preheater 62 by a stream 69.

[051] As discussed herein, a portion of the heat possessed by the product stream 10 leaving the reactor 66 can be recovered and recycled. In various examples, the heat waste utilization system 12 can include the cogeneration unit 74 that includes a boiler 70 and a generator 78 (e.g., a heat-activated generator) configured to generate both electricity and heat. The product stream 10 can enter the boiler 70 and the heat energy contained in the product stream 10 can be used to create steam. For example, the generated heat of the product stream 10 can be contacted with the water to make steam.

[052] As discussed herein, the preheater 62 may receive a portion of the steam 72 generated from boiler 70 to heat the feed streams 2, 4, 6. As illustrated in FIG. 2, the three feed streams 2, 4, 6 are mixed and heated within the preheater 62. The preheater 62 can reduce the amount of externally supplied energy to heat the feed streams to the reaction temperature, as compared to a process that does not include the preheater 62.

[053] The cogeneration unit **74** of the heat waste utilization system **12** can include a generator **78** (e.g., a heat-activated generator) configured to generate electricity from the heat generated by the boiler **70**. A portion of the steam **76** can be fed to the generator **78** to generate electricity. The electricity can be used in the process **11** for producing HCN, which reducing the amount of externally supplied energy.

[054] In various examples, the product stream **10** from the reactor **66** can have a first temperature. After the product stream **10** has passed through the co-generation unit **74**, the reduced temperature product stream **14** can have a second temperature, where the second temperature is less than the first temperature. In various examples, the first temperature can be about 1000 °C to about 1300 °C and the second temperature of the reduced temperature product stream **14** can be about 450 °C to about 240 °C . As discussed herein, the cogeneration unit **74** can quickly absorb the heat and reduce the heat of the product stream **10** to minimize by-products.

[055] As illustrated in **FIG.2**, a single boiler **70** and generator **78** is used to generate steam and electricity. In some examples, another boiler (not shown) can be used to remove additional heat from the reduced temperature product stream **14** prior to entering the ammonia recovery system **16**. For example, the reduced temperature product stream **14** can enter an additional boiler that could create additional steam that can be recirculated back into the process. In various examples, heat generation may be more advantageous than electricity. In that example, the boiler **70** can be utilized without the generator **78** to product steam.

[056] The heat waste utilization system **12** can be employed in an air Andrussov process, an enriched-oxygen Andrussov process, and an oxygen Andrussov process. However, it may be more advantageous to utilize the heat waste utilization system **12** in an enriched-oxygen or an oxygen Andrussov process due to the increased concentration of combustible components. Thus, the risk of igniting the product stream **12** or producing by-products in the product stream are reduced.

[057] **FIG. 3** is a more detailed flow diagram of portion **48** of the process of **FIG. 1** for the production of HCN, in accordance with various examples. As discussed herein, after the removal of ammonia in the HCN recovery system **30** (illustrated in **FIG. 1**), the NH₃-stripped HCN stream **24** enter the HCN recovery system **30**. The HCN recovery system **30** can contact stream **24** with water to entrain the HCN. The HCN-water mixture can be sent to a cyanide

stripper where excess waste is removed from the liquid. In addition, the HCN-water mixture may also be sent through a fractionator to concentrate the HCN. The HCN product stream **32** can be stored in tanks or used directly for synthesis of other compounds.

[058] After removal of ammonia and hydrogen cyanide from an Andrussov product stream **10** (as illustrated in **FIG. 1**), a gaseous waste stream **34** remains that contains a variety of gases including hydrogen, unreacted methane, carbon dioxide, carbon monoxide, water, nitrogen, a variety of organonitriles, and trace amounts of HCN. The gaseous waste stream **34** should not have any detectable ammonia present. The amounts of these gases in the gaseous waste stream **34** can vary depending upon Andrussov reaction conditions. Variables that can affect the composition of the gaseous waste stream **34** include the amount of oxygen in the Andrussov reaction, the ratios of methane to ammonia, the temperature of the reactor, the catalyst effectiveness, flow rates into and through an Andrussov reactor, and the like. For example, when pure oxygen is used as a reactant in an Andrussov process and reaction conditions generally optimized, up to about 75 vol % hydrogen can be present in the gaseous waste stream, but when air is employed as a source of oxygen for the Andrussov reaction, only about 1.5 vol% hydrogen may be present in the waste product stream.

[059] The gaseous waste stream **34** can advantageously contain lower amounts of nitrogen than are present in air. For example, the gaseous waste stream **34** can contain less than about 60% nitrogen, less than about 50% nitrogen, less than about 40% nitrogen, less than about 30% nitrogen, less than about 20%, or less than about 10%.

[060] As discussed herein, an Andrussov process having an oxygen stream **6** (as illustrated in **FIG. 1**) that contains more than 55 vol % oxygen can produce a gaseous waste stream **34** having a heat value that enables the gaseous waste stream **34** to be burned at a temperature that can generate steam without supplementing the gaseous waste stream **34** with fuel gas. Therefore, the methods and systems disclosed herein can be particularly advantageous when the gaseous waste stream **34** includes energy rich components, such as hydrogen and carbon monoxide, that have a heat value of greater than 182 BTU/scf. For example, the methods and systems of the present disclosure can generate energy (e.g., heat and electricity) by utilizing the energy-rich components of the gaseous waste stream **34**. In an example, the gaseous waste stream **34** can include about 78 vol% hydrogen and 11 vol% carbon monoxide when pure oxygen is used as the oxygen stream **6**. In general, the gaseous waste stream **34** will contain only

residual amounts of HCN. Removal of HCN is typically substantially complete not only so that valuable HCN is not lost to the waste water, but also for health and environmental concerns, and because significant amounts of HCN can complicate processing of the waste water.

[061] The material waste utilization system 36 can include a cogeneration unit 90. In one example, cogeneration unit 90 can include a boiler 80 and a generator 82 (e.g., an electrical generator) configured to burn the waste effluent and generate energy (e.g., heat and electricity). Other cogeneration units can be employed. In some examples, the material waste utilization system 36 can also include a water extraction unit (not shown) configured to remove liquid water from the gaseous waste stream 34 before the gaseous waste stream 34 is burned as fuel in the cogeneration unit 90.

[062] The cogeneration unit 90 can receive and burn the gaseous waste stream 34 as fuel to produce thermal energy. For example, the boiler 80 can receive and burn the gaseous waste stream 34. The heat generated from the combustion of the gaseous waste stream 34 can be contacted with water to generate heat (e.g., steam). A portion of the steam 88 can be recirculated back into the process. A portion of the steam 92 can be fed to the generator 82 to generate electricity from the thermal energy. The generator 82 can transform thermal energy into rotational energy that can produce electricity. The electricity can be used in the process 11 for producing HCN.

[063] The material waste utilization system 36 can include one or more detectors 84 configured to quantify levels of hydrogen cyanide, methane, hydrogen, carbon monoxide or a combination thereof in the gaseous waste stream 34. The material waste utilization system 36 can also include a diverter 86 to channel the gaseous waste stream 34 between the material waste utilization system 36, a hydrogen recovery system 38, and a flaring system 42. The detector 84 can monitor for energy rich components such as hydrogen and carbon monoxide. In various examples, the diverter 86 can divert the gaseous waste stream 34 from the cogeneration unit 90 when a hydrogen concentration is below a threshold value. For example, when the concentration of hydrogen is equal to or less than about 55 vol% of the gaseous waste stream 34 the diverter 86 can divert the gaseous waste stream from the cogeneration unit 90. In an example where the hydrogen concentration is equal to or less than 55 vol%, the gaseous waste stream 34 does not have a heat value that can generate steam without the addition of supplemental fuel gas. Thus, the diverter 86 can channel the gaseous waste stream 34 to the hydrogen recovery system 38

and/or the flare 42. In some examples, the diverter 86 can split the gaseous waste stream 34 such that a portion enters the cogeneration unit 90, the hydrogen recovery 38, and the flare 42, while the amount sent to the flare can be minimized.

[064] In one example where the material waste utilization system 70 is employed, the oxygen stream 6 can include more than 55 vol% oxygen. In further examples where the material waste utilization system 70 is employed, the oxygen stream 6 includes at least 65 vol % oxygen to about 100 % vol oxygen. As discussed herein, the oxygen stream 6 that includes more than 55 vol% oxygen can generate a gaseous waste stream 34 that has a heat value great enough to generate steam when burned, without supplementing the gaseous waste stream 34 with fuel gases.

[065] Various factors can determine whether the entire or a portion of the gaseous waste stream 34 is sent to the cogeneration unit 90, the hydrogen recovery 38, and or the flare 42. For example, a hydrogen demand can determine whether a portion of the gaseous waste stream 34 is sent to the hydrogen recovery 38. For example, at a minimum the portion of the gaseous waste stream 34 that is sent to the hydrogen recovery 34 should be enough to satisfy the hydrogen demand. In other examples, more of the gaseous waste stream 34 can be sent to the hydrogen recovery 38 and the recovered hydrogen can be stored. Other factors may include the cost of hydrogen, steam and electricity. For example, a cost analysis of the hydrogen recovery 38 versus the cogeneration 90 can be compared.

[066] In examples employing a flare 42, a minimum flow to the flare 42 is needed. The methods and systems of the present disclosure can minimize any amount beyond the minimum flow needed. For example, a majority of the gaseous waste stream 34 is preferentially sent to the hydrogen recovery 38, the cogeneration unit, or combinations thereof. Thus, the present methods and systems can reduce material waste by either converting the material waste into energy (e.g., heat and/or electricity) or recovering a portion of the material. In other examples, the gaseous waste stream 34 can be used as a pilot gas (not shown). Pilot gases do not require a very high heat value since it is only used to sustain a flame.

[067] In an example, a portion or the entire gaseous waste stream 34 can be channeled to the hydrogen recovery system 38. The recovered hydrogen stream 98 can be stored for future processing or sale, sent to additional hydrogen processing units, recycled to a point upstream or downstream, used to supplement a flare 42, hydrogenations reactions, or combinations thereof,

as discussed further below. However, if the gaseous waste stream **34** has less than about 40 vol % hydrogen, the hydrogen recovery system **42** may not be economical.

EXAMPLES

[068] The present disclosure can be better understood by reference to the following examples which are offered by way of illustration. The present disclosure is not limited to the examples given herein.

Comparative Example 1: Comparison Air and Oxygen Andrussov Process Waste Gas Compositions

[069] This Example illustrates that an Andrussov process that uses a highly enriched source of oxygen generally produces a waste stream with higher hydrogen content than one that employs air as an oxygen source.

[070] A 4 inch internal diameter stainless steel reactor with ceramic insulation lining inside is used for pilot scale test. Forty sheets of 90 wt% Pt/10 wt% Rh 40 mesh gauze from Johnson Matthey (USA) are loaded as catalyst bed. Perforated alumina tile is used for catalyst sheet support. The total flow rate is set at 2532 SCFH (standard cubic foot per hour). Hydrogen cyanide is produced via two separate Andrussov processes. One process is an oxygen Andrussov process that employs a gaseous reaction mixture that includes 35 vol% methane, 38 vol% ammonia and 27 vol% substantially pure oxygen. A second process is an air Andrussov process employs about 17 vol% methane, 19 vol% ammonia and 64 vol% air. A platinum-containing catalyst is used for both processes.

[071] Ammonia is separately removed from each of the product streams in a process involving absorption into an ammonium phosphate stream. Hydrogen cyanide is then removed from the ammonia-depleted product stream in a process involving acidified water, thereby separately generating a hydrogen cyanide product and a gaseous waste stream for each of the processes.

[072] The composition of the gaseous waste streams from the oxygen and air processes, after ammonia and HCN removal are shown below in Table 1.

Table 1: Gaseous Waste Stream Composition

Simulation results	O₂	Air
Component	% (v/v)	% (v/v)
H ₂	78.78	16.74
N ₂	5.43	76.33
CO	11.18	4.43
Ar	0.17	0.48
O ₂	0.09	0.00
CH ₄	1.03	0.83
CO ₂	0.99	0.29
NH ₃	0.00	0.00
HCN	0.13	0.05
acrylonitrile	0.00	0.00
acetonitrile	0.05	0.01
propionitrile	0.00	0.00
H ₂ O	2.14	0.91
H ₂ SO ₄	0.00	0.00
H ₂ PO ₄	0.00	0.00
Total	100	100

[073] As illustrated, an Andrussov process that employs highly enriched oxygen as a source of the oxygen-containing feedstream generates significantly more hydrogen than an Andrussov process that employs air as a source of the oxygen-containing feedstream.

Comparative Example 2: Waste Generated During an Oxygen Andrussov Process

[074] This Example can illustrate the amount of waste generated during production of hydrogen cyanide.

[075] Hydrogen cyanide is produced via an Andrussov process from a gaseous reaction mixture that includes 35 vol% methane, 38 vol% ammonia and 27 vol% substantially pure oxygen, in the presence of a platinum catalyst. The methane feed stream, the ammonia feed stream, and the oxygen feed stream are fed into a reactor containing a platinum catalyst. A 4 inch internal diameter stainless steel reactor with ceramic insulation lining inside is used for pilot scale test. Forty sheets of 90 wt% Pt/10 wt% Rh 40 mesh gauze from Johnson Matthey (USA) are loaded as catalyst bed. Perforated alumina tile is used for catalyst sheet support. Total flow rate is set at 2532 SCFH (standard cubic foot per hour).

[076] As the reaction proceeds a gaseous waste stream is continually produced that contains hydrogen cyanide, unreacted ammonia, waste gases and other products. After removal of the hydrogen cyanide and the unreacted ammonia, a gaseous waste stream that is free of hydrogen cyanide can contain a mixture of gases such as hydrogen, unreacted methane, carbon dioxide, carbon monoxide, water, nitrogen, a variety of organonitriles, and trace amounts of HCN, and therefore includes energy-rich gases such as hydrogen, methane and carbon monoxide. In the example, the gaseous waste stream can be sent to flare to thoroughly dispose of the components of the gaseous waste stream. In this example, approximately 40,000 scf of waste gas is produced for 1,000 lbs HCN. Additionally, 258 BTU/scf is lost after the HCN recovery.

Example 1: Hydrogen Content in the Gaseous Waste Stream

[077] This Example illustrates how the hydrogen content of the gaseous waste stream varies in Andrussov processes using reactant oxygen-containing feedstreams with different amounts of oxygen.

[078] Hydrogen cyanide is produced via a series of separate Andrussov processes performed as described for Comparative Example 1. However, each process is performed using a different reactant oxygen-containing feedstream, where the content of oxygen in the feedstream is varied between about 20.9 vol% to about 100 vol% oxygen, as shown in Table 2.

[079] Ammonia is separately removed from each of the product streams in a process involving absorption into an ammonium phosphate stream. Hydrogen cyanide is then removed from the ammonia-depleted product stream in a process involving acidified water, thereby separately generating a hydrogen cyanide product and a gaseous waste stream for each of the processes.

[080] The composition of the gaseous waste streams from Andrussov processes run with oxygen-containing feedstreams having different oxygen contents are shown below in Table 2.

Table 2:
Waste Gas Stream BTU Value as Oxygen Percentage Increases

Reactant Feed stream (Percent vol/vol O₂)	Waste Gas Stream (Percent vol/vol H₂)	Waste Gas Stream (Percent CO)	Waste Gas Stream BTU/SCF)	Valuable as Fuel (Yes/No)
Air (20.95%)	16.7	4.43	67.6	No
25% Oxygen	21.2	5.28	83.2	No
35% Oxygen	32.3	7.11	120.3	No
45% Oxygen	42.6	8.53	153.3	No
55% Oxygen	51.8	9.56	181.5	No
65% Oxygen	59.6	10.3	205.0	Yes
75% Oxygen	66.3	10.7	224.4	Yes
80% Oxygen	69.2	10.9	232.7	Yes
85% Oxygen	71.9	11.0	240.3	Yes
90% Oxygen	74.4	11.1	247.1	Yes
95% Oxygen	76.7	11.2	253.3	Yes
Pure Oxygen	78.8	11.2	258.9	Yes

[081] In table 2, the waste gas stream refers to the volume percent of Hydrogen in the waste stream after ammonia and HCN have been removed. Additionally, “valuable” refers to whether the waste gas stream is capable of being used as a fuel gas (e.g., combustion) to generate steam without the addition of natural gas.

[082] Example 2: Oxygen Andrussov Process Utilizing an Energy Recapturing System

[083] This Example illustrates the configuration of an energy recapturing system that includes a heat waste utilization system and a material waste utilization system operating during production of hydrogen cyanide via an oxygen Andrussov Process.

[084] A 4 inch internal diameter stainless steel reactor with ceramic insulation lining inside is used for pilot scale test. Forty sheets of 90 wt% Pt / 10 wt% Rh 40 mesh with from Johnson Matthey (USA) are loaded as catalyst bed. Perforated alumina tile is used for catalyst sheet support. The total flow rate is set at 2532 SCFH (standard cubic foot per hour). Hydrogen cyanide is produced via an Andrussov process from a gaseous reaction mixture that includes 35 vol% methane, 38 vol% ammonia and 27 vol% substantially pure oxygen, in the presence of a platinum-containing catalyst. The product stream is contacted with a cogeneration unit and generates electricity and steam. A portion of the steam can be recirculated back to preheat feedstreams of the reaction mixture to minimize an amount of externally supplied heat. Additionally the electricity can be recirculated back into the process and minimize the amount of externally supplied electricity.

[085] As the reaction proceeds a gaseous waste stream is continually produced that contains hydrogen cyanide, unreacted ammonia, waste gases and other products. After removal of the ammonia and hydrogen cyanide a gaseous waste stream is generated. In this example, amount sent to the flare is minimized. Additionally, the gaseous waste stream has a heat value of greater than 258 BTU/scf and be sent to a cogeneration unit of a material waste utilization system. In this example, approximately 258 BTU/scf is recovered in the gaseous waste stream after the HCN recovery. During optimal operating conditions, such energy capturing units such as the heat waste utilization system and the material waste utilization system can generate greater than 100 % of the energy required for the manufacture of hydrogen cyanide by the process described.

[086] The above Detailed Description is intended to be illustrative, and not restrictive. For example, the above-described examples (or one or more elements thereof) can be used in combination with each other. Other examples can be used, such as by one of ordinary skill in the art upon reviewing the above description. Also, various features or elements can be grouped together to streamline the disclosure. This should not be interpreted as intending that an

unclaimed disclosed feature is essential to any claim. Rather, inventive subject matter can lie in less than all features of a particular disclosed embodiment. Thus, the following claims are hereby incorporated into the Detailed Description, with each claim standing on its own as a separate embodiment. The scope of the invention should be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled.

[087] In the event of inconsistent usages between this document and any documents so incorporated by reference, the usage in this document controls.

[088] In this document, the terms “a” or “an” are used, as is common in patent documents, to include one or more than one, independent of any other instances or usages of “at least one” or “one or more.” In this document, the term “or” is used to refer to a nonexclusive or, such that “A or B” includes “A but not B,” “B but not A,” and “A and B,” unless otherwise indicated. In this document, the terms “including” and “in which” are used as the plain-English equivalents of the respective terms “comprising” and “wherein.” Also, in the following claims, the terms “including” and “comprising” are open-ended, that is, a system, device, article, composition, formulation, or process that includes elements in addition to those listed after such a term in a claim are still deemed to fall within the scope of that claim. Moreover, in the following claims, the terms “first,” “second,” and “third,” etc. are used merely as labels, and are not intended to impose numerical requirements on their objects.

[089] Method examples described herein can be machine or computer-implemented, at least in part. Some examples can include a computer-readable medium or machine-readable medium encoded with instructions operable to configure an electronic device to perform methods or method steps as described in the above examples. An implementation of such methods or method steps can include code, such as microcode, assembly language code, a higher-level language code, or the like. Such code can include computer readable instructions for performing various methods. The code may form portions of computer program products. Further, in an example, the code can be tangibly stored on one or more volatile, non-transitory, or non-volatile tangible computer-readable media, such as during execution or at other times. Examples of these tangible computer-readable media can include, but are not limited to, hard disks, removable magnetic disks, removable optical disks (e.g., compact disks and digital video disks), magnetic cassettes, memory cards or sticks, random access memories (RAMs), read only memories (ROMs), and the like.

[090] The Abstract is provided to comply with 37 C.F.R. §1.72(b), to allow the reader to quickly ascertain the nature of the technical disclosure. It is submitted with the understanding that it will not be used to interpret or limit the scope or meaning of the claims.

[091] Although the invention has been described with reference to exemplary examples, workers skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

[092] Specific enumerated statements [1] to [31] provided below are for illustration purposes only, and do not otherwise limit the scope of the disclosed subject matter, as defined by the claims. These enumerated statements encompass all combinations, sub-combinations, and multiply referenced (e.g., multiply dependent) combinations described therein.

Statements

[093] [1.] A method of utilizing waste produced during production of hydrogen cyanide via the Andrussov process comprising:

(a) burning a gaseous waste stream for primary energy generation, wherein the gaseous waste stream is from a reactor configured to produce hydrogen cyanide, and the gaseous waste stream is substantially free of hydrogen cyanide;

(b) contacting a heat recovery unit with heat for secondary energy generation, where the heat is generated by a reactor during production of the hydrogen cyanide; or

(c) a combination thereof.

[094] [2.] The method of statement [1], wherein the primary or secondary energy generation comprises heat transfer, steam generation, electricity generation or a combination thereof.

[095] [3.] The method of statement [1] or [2], wherein the primary or secondary energy generation is steam generation and electricity generation.

[096] [4.] The method of any one of statements [1]-[3], further comprising prior to burning the gaseous waste stream, adjusting a reaction mixture comprising methane, ammonia and oxygen to provide a reaction mixture with sufficient oxygen to generate at least about 59 volume percent hydrogen in the gaseous waste stream after removal of ammonia and recovery of hydrogen cyanide.

[097] [5.] The method of statement [4], wherein the sufficient oxygen is supplied as an oxygen-containing feedstream comprising more than 55 volume percent oxygen.

[098] [6.] The method of any one of statements [1]-[5], wherein the gaseous waste stream comprises about 60 volume percent oxygen to about 78 volume percent oxygen and about 10 volume percent carbon monoxide to about 15 volume percent carbon monoxide.

[099] [7.] The method of any one of statements [1]-[6], wherein the gaseous waste stream comprises less than about 50 volume percent nitrogen.

[0100] [8.] The method of any one of statements [1]-[7], wherein the gaseous waste stream comprises a heat value of greater than 182 British Thermal Unit per square cubic feet (BTU/scf).

[0101] [9.] The method of any one of statements [1]-[8], wherein the gaseous waste stream comprises a heat value of about 205 BTU/scf to about 260 BTU/scf.

[0102] [10.] The method of any one of statements [1]-[9], wherein the gaseous waste stream is not supplemented with a fuel gas.

[0103] [11.] The method of any one of statements [1]-[10], wherein burning the gaseous waste stream includes contacting the gaseous waste stream with a first cogeneration unit.

[0104] [12.] The method of statement [11], wherein the first cogeneration unit comprises a first boiler and an electrical generator, the first boiler configured to generate steam and the electrical generator configured to generate electricity.

[0105] [13.] The method of any one of statements [1]-[12], wherein the heat recovery unit is a second cogeneration unit.

[0106] [14.] The method of statement [13], wherein the second cogeneration unit includes a second boiler and a heat-activated generator, the second boiler configured to generate steam and the heat-activated generator configured to generate electricity.

[0107] [15.] The method of statement [13], wherein contacting the heat recovery unit with heat further includes contacting a product stream from the reactor with the second cogeneration unit, wherein the product stream has a first temperature prior to contacting the second cogeneration unit and the product stream has a second temperature after contacting the second cogeneration unit, the first temperature great than the second temperature.

[0108] [16.] The method of any one of statements [1]-[15], wherein the hydrogen cyanide is produced in a reaction mixture of methane, ammonia and oxygen in the presence of a catalyst comprising platinum, wherein the reaction mixture has more than about 55 volume percent oxygen.

[0109] [17.] The method of statement [16], wherein the methane is provided in a methane-containing hydrocarbon feed.

[0110] [18.] The method of statement [16] or [17], wherein the methane is provided as a hydrocarbon feed comprising natural gas, biogas, substantially pure methane or mixtures thereof.

[0111] [19.] The method of any one of statements [16]-[18], wherein the methane is provided as natural gas.

[0112] [20.] The method of any one of statements [16]-[19], wherein the methane is provided as substantially pure methane.

[0113] [21.] The method of any one of statements [16]-[20], wherein the oxygen is provided as an enriched-oxygen feed, a substantially pure oxygen feed, or any combination thereof.

[0114] [22.] The method of any one of statements [1]-[21], wherein ammonia has been substantially removed from the gaseous waste stream.

[0115] [23.] The method of any one of statements [1]-[22], wherein water has been substantially removed from the gaseous waste stream.

[0116] [24.] The method of any one of statements [1]-[23], wherein the gaseous waste stream comprises hydrogen, methane or mixtures thereof.

[0117] [25.] A system for producing hydrogen cyanide via the Andrussow process, comprising:

(a) a reactor configured for producing hydrogen cyanide from a reaction mixture comprising methane, ammonia and oxygen in the presence of a catalyst comprising platinum, wherein the reactor is also configured to supply the reaction mixture with sufficient oxygen to generate a gaseous waste stream that has at least 59 hydrogen after removal of ammonia and recovery of hydrogen cyanide;

(b) a first cogeneration unit configured to burn the gaseous waste stream as a fuel for primary energy generation, wherein the gaseous waste stream is substantially free of hydrogen cyanide; and/or

(c) a second cogeneration unit configured to absorb heat from the reactor for secondary energy generation.

[0118] [26.] The system of statement [25], wherein the sufficient oxygen is supplied as an oxygen-containing feedstream comprising more than 55 volume percent oxygen.

[0119] [27.] The system of any of statements [25] or [26], wherein the gaseous waste stream comprises about 60 volume percent oxygen to about 78 volume percent oxygen and about 10 volume percent carbon monoxide to about 15 volume percent carbon monoxide.

[0120] [28.] The system of any one of statements [25]-[27], wherein the gaseous waste stream comprises less than about 50 volume percent nitrogen.

[0121] [29.] The system of any one of statements [25]-[28], wherein the gaseous waste stream comprises a heat value of greater than 182 BTU/scf.

[0122] [30.] The system of any one of statements [25]-[29], wherein the gaseous waste stream comprises a heat value of about 205 BTU/scf to about 260 BTU/scf.

[0123] [31.] The system of any one of statements [25]-[30], wherein the gaseous waste stream is not supplemented with a fuel gas.

[0124] [32.] The system of any one of statements [25]-[31], further comprising:

(d) a first heat transfer system configured to absorb heat from the first cogeneration unit and recycle the heat; and/or

(e) a second heat transfer system configured to absorb heat from the second cogeneration unit and recycle the heat to warm at least one of the methane, ammonia and oxygen fed into the reactor.

[0125] [33.] The system of any one of statements [25]-[32], further comprising a detector for quantifying levels of hydrogen cyanide, methane, hydrogen, carbon monoxide or a combination thereof in the gaseous waste stream.

[0126] [34.] The system of statement [33], further comprising a valve operably linked to the detector, wherein the valve is configured divert the gaseous waste stream from the first cogeneration unit when a hydrogen concentration below a threshold value is detected in the gaseous waste stream.

[0127] [35.] The system of statement [33], further comprising a valve operably linked to the detector, wherein the valve is configured to divert the gaseous waste stream from the first cogeneration unit when a set value of combustible components is below a threshold value.

[0128] [36.] The system of statement [35], wherein the threshold value is based on a heat content value of the gaseous waste stream.

[0129] [37.] The system of statement [33], wherein the methane is a hydrocarbon feed comprising natural gas, syngas, biogas, substantially pure methane or mixtures thereof.

[0130] [38.] The system of statement [33], wherein the methane is natural gas.

[0131] [39.] The system of statement [33], wherein the methane is substantially pure methane.

[0132] [40.] The system of statement [33], wherein the oxygen is provided an enriched-oxygen feed, a substantially pure oxygen feed, or any combination thereof.

[0133] [41.] The system of any one of statements [25]-[40], wherein ammonia has been substantially removed from the gaseous waste stream.

[0134] [42.] The system of any of statements [25]-[41], wherein water has been substantially removed from the gaseous waste stream.

[0135] [43.] The system of any one of statements [25]-[42], wherein the waste effluent comprises hydrogen, methane or mixtures thereof.

[0136] [44.] A method, comprising:

(a) adjusting a reaction mixture comprising methane, ammonia and oxygen to provide the reaction mixture with sufficient oxygen to generate a gaseous waste stream that has at least 59 volume percent hydrogen in the gaseous waste stream after removal of ammonia and recovery of hydrogen cyanide; and

(b) burning the gaseous waste stream for energy generation.

[0137] [45.] The method of statement [44], wherein the energy generation comprises steam generation, electricity generation, or a combination thereof.

[0138] [46.] The method of statement [44], wherein the energy generation comprises steam generation and electricity generation via a cogeneration unit.

[0139] [47.] The method of any one of statements [44]-[46], wherein the sufficient oxygen is supplied as an oxygen-containing feedstream comprising more than 55 volume percent oxygen.

[0140] [48.] The method of any one of statements [44]-[47], wherein the gaseous waste stream comprises about 59 volume percent hydrogen to about 78 volume percent hydrogen, about 12 volume percent carbon monoxide to about 15 volume percent carbon monoxide, about 0.7 volume percent carbon dioxide to about 1.5 volume percent carbon dioxide, about 3 volume percent nitrogen to about 5 volume percent nitrogen, about 1 volume percent methane to about 2.0 volume percent methane, about 0.01 volume percent organonitriles to about 0.1 volume percent organonitriles, about 0.01 volume percent HCN to about 0.05 volume percent HCN, about 3 volume percent water to about 5 volume percent water, and combinations thereof.

[0141] [49.] The method of any one of statements [44]-[48], wherein the gaseous waste stream comprises less than about 50 volume percent nitrogen.

[0142] [50.] The method of any one of statements [44]-[49], wherein the gaseous waste stream comprises a heat value of greater than 182 BTU/scf.

[0143] [51.] The method of any one of statements [44]-[50], wherein the gaseous waste stream comprises a heat value of about 205 BTU/scf to about 260 BTU/scf.

[0144] [52.] The method of any one of statements [44]-[51], wherein the gaseous waste stream is not supplemented with a fuel gas.

CLAIMS

What is claimed is:

1. A method of utilizing waste produced during production of hydrogen cyanide via the Andrussov process comprising:
 - (a) burning a gaseous waste stream for primary energy generation, wherein the gaseous waste stream is from a reactor configured to produce hydrogen cyanide, and the gaseous waste stream is substantially free of hydrogen cyanide;
 - (b) contacting a heat recovery unit with heat for secondary energy generation, where the heat is generated by a reactor during production of the hydrogen cyanide; or
 - (c) a combination thereof.
2. The method of claim 1, wherein the primary or secondary energy generation comprises heat transfer, steam generation, electricity generation or a combination thereof.
3. The method of claim 1 or 2, wherein the primary or secondary energy generation is steam generation and electricity generation.
4. The method of any one of claims 1-3, further comprising:

prior to burning the gaseous waste stream, adjusting a reaction mixture comprising methane, ammonia and oxygen to provide a reaction mixture with sufficient oxygen to generate at least about 59 volume percent hydrogen in the gaseous waste stream after removal of ammonia and recovery of hydrogen cyanide.
5. The method of claim 4, wherein the sufficient oxygen is supplied as an oxygen-containing feedstream comprising more than 55 volume percent oxygen.
6. The method of any one of claims 1-5, wherein the gaseous waste stream comprises about 60 volume percent oxygen to about 78 volume percent oxygen and about 10 volume percent carbon monoxide to about 15 volume percent carbon monoxide.

7. The method of any one of claims 1-6, wherein the gaseous waste stream comprises less than about 50 volume percent nitrogen.
8. The method of any one of claims 1-7, wherein the gaseous waste stream comprises a heat value of greater than 182 British Thermal Unit per square cubic foot (BTU/scf).
9. The method of any one of claims 1-8, wherein the gaseous waste stream comprises a heat value of about 205 BTU/scf to about 260 BTU/scf.
10. The method of any one of claims 1-9, wherein the gaseous waste stream is not supplemented with a fuel gas.
11. The method of any one of claims 1-10, wherein burning the gaseous waste stream includes contacting the gaseous waste stream with a first cogeneration unit.
12. The method of claim 11, wherein the first cogeneration unit comprises a first boiler and an electrical generator, the first boiler configured to generate steam and the electrical generator configured to generate electricity.
13. The method of any one of claims 1-12, wherein the heat recovery unit is a second cogeneration unit.
14. The method of claim 13, wherein the second cogeneration unit includes a second boiler and a heat-activated generator, the second boiler configured to generate steam and the heat-activated generator configured to generate electricity.
15. The method of claim 13, wherein contacting the heat recovery unit with heat further includes:
 - contacting a product stream from the reactor with the second cogeneration unit, wherein the product stream has a first temperature prior to contacting the second cogeneration unit and

the product stream has a second temperature after contacting the second cogeneration unit, the first temperature great than the second temperature.

16. The method of any one of claims 1-15, wherein the hydrogen cyanide is produced in a reaction mixture of methane, ammonia and oxygen in the presence of a catalyst comprising platinum, wherein the reaction mixture has more than about 55 volume percent oxygen.

17. The method of claim 16, wherein the methane is provided in a methane-containing hydrocarbon feed.

18. The method of claim 16 or 17, wherein the methane is provided as a hydrocarbon feed comprising natural gas, biogas, substantially pure methane or mixtures thereof.

19. The method of any one of claims 16-18, wherein the methane is provided as natural gas.

20. The method of any one of claims 16-19, wherein the methane is provided as substantially pure methane.

21. The method of any one of claims 16-20, wherein the oxygen is provided as an enriched-oxygen feed, a substantially pure oxygen feed, or any combination thereof.

22. The method of any one of claims 1-21, wherein ammonia has been substantially removed from the gaseous waste stream.

23. The method of any one of claims 1-22, wherein water has been substantially removed from the gaseous waste stream.

24. The method of any one of claims 1-23, wherein the gaseous waste stream comprises hydrogen, methane or mixtures thereof.

25. A system for producing hydrogen cyanide via the Andrussov process, comprising:
- (a) a reactor configured for producing hydrogen cyanide from a reaction mixture comprising methane, ammonia and oxygen in the presence of a catalyst comprising platinum, wherein the reactor is also configured to supply the reaction mixture with sufficient oxygen to generate a gaseous waste stream that has at least 59 hydrogen after removal of ammonia and recovery of hydrogen cyanide;
 - (b) a first cogeneration unit configured to burn the gaseous waste stream as a fuel for primary energy generation, wherein the gaseous waste stream is substantially free of hydrogen cyanide; and/or
 - (c) a second cogeneration unit configured to absorb heat from the reactor for secondary energy generation.
26. The system of claim 25, wherein the sufficient oxygen is supplied as an oxygen-containing feedstream comprising more than 55 volume percent oxygen.
27. The system of any of claims 25 or 26, wherein the gaseous waste stream comprises about 60 volume percent oxygen to about 78 volume percent oxygen and about 10 volume percent carbon monoxide to about 15 volume percent carbon monoxide.
28. The system of any one of claims 25-27, wherein the gaseous waste stream comprises less than about 50 volume percent nitrogen.
29. The system of any one of claims 25-28, wherein the gaseous waste stream comprises a heat value of greater than 182 BTU/scf.
30. The system of any one of claims 25-29, wherein the gaseous waste stream comprises a heat value of about 205 BTU/scf to about 260 BTU/scf.
31. The system of any one of claims 25-30, wherein the gaseous waste stream is not supplemented with a fuel gas.

32. The system of any one of claims 25-31, further comprising:
- (d) a first heat transfer system configured to absorb heat from the first cogeneration unit and recycle the heat; and/or
 - (e) a second heat transfer system configured to absorb heat from the second cogeneration unit and recycle the heat to warm at least one of the methane, ammonia and oxygen fed into the reactor.
33. The system of any one of claims 25-32, further comprising a detector for quantifying levels of hydrogen cyanide, methane, hydrogen, carbon monoxide or a combination thereof in the gaseous waste stream.
34. The system of claim 33, further comprising a valve operably linked to the detector, wherein the valve is configured divert the gaseous waste stream from the first cogeneration unit when a hydrogen concentration below a threshold value is detected in the gaseous waste stream.
35. The system of claim 33, further comprising a valve operably linked to the detector, wherein the valve is configured to divert the gaseous waste stream from the first cogeneration unit when a set value of combustible components is below a threshold value.
36. The system of claim 35, wherein the threshold value is based on a heat content value of the gaseous waste stream.
37. The system of claim 33, wherein the methane is a hydrocarbon feed comprising natural gas, syngas, biogas, substantially pure methane or mixtures thereof.
38. The system of claim 33, wherein the methane is natural gas.
39. The system of claim 33, wherein the methane is substantially pure methane.
40. The system of claim 33, wherein the oxygen is provided an enriched-oxygen feed, a substantially pure oxygen feed, or any combination thereof.

41. The system of any one of claims 25-40, wherein ammonia has been substantially removed from the gaseous waste stream.
42. The system of any of claims 25-41, wherein water has been substantially removed from the gaseous waste stream.
43. The system of any one of claims 25-42, wherein the waste effluent comprises hydrogen, methane or mixtures thereof.
44. A method, comprising:
- (a) adjusting a reaction mixture comprising methane, ammonia and oxygen to provide the reaction mixture with sufficient oxygen to generate a gaseous waste stream that has at least 59 volume percent hydrogen in the gaseous waste stream after removal of ammonia and recovery of hydrogen cyanide; and
 - (b) burning the gaseous waste stream for energy generation.
45. The method of claim 44, wherein the energy generation comprises steam generation, electricity generation, or a combination thereof.
46. The method of claim 44, wherein the energy generation comprises steam generation and electricity generation via a cogeneration unit.
47. The method of any one of claims 44-46, wherein the sufficient oxygen is supplied as an oxygen-containing feedstream comprising more than 55 volume percent oxygen.
48. The method of any one of claims 44-47, wherein the gaseous waste stream comprises about 59 volume percent hydrogen to about 78 volume percent hydrogen, about 12 volume percent carbon monoxide to about 15 volume percent carbon monoxide, about 0.7 volume percent carbon dioxide to about 1.5 volume percent carbon dioxide, about 3 volume percent nitrogen to about 5 volume percent nitrogen, about 1 volume percent methane to about 2.0

volume percent methane, about 0.01 volume percent organonitriles to about 0.1 volume percent organonitriles, about 0.01 volume percent HCN to about 0.05 volume percent HCN, about 3 volume percent water to about 5 volume percent water, and combinations thereof.

49. The method of any one of claims 44-48, wherein the gaseous waste stream comprises less than about 50 volume percent nitrogen.

50. The method of any one of claims 44-49, wherein the gaseous waste stream comprises a heat value of greater than 182 BTU/scf.

51. The method of any one of claims 44-50, wherein the gaseous waste stream comprises a heat value of about 205 BTU/scf to about 260 BTU/scf.

52. The method of any one of claims 44-51, wherein the gaseous waste stream is not supplemented with a fuel gas.

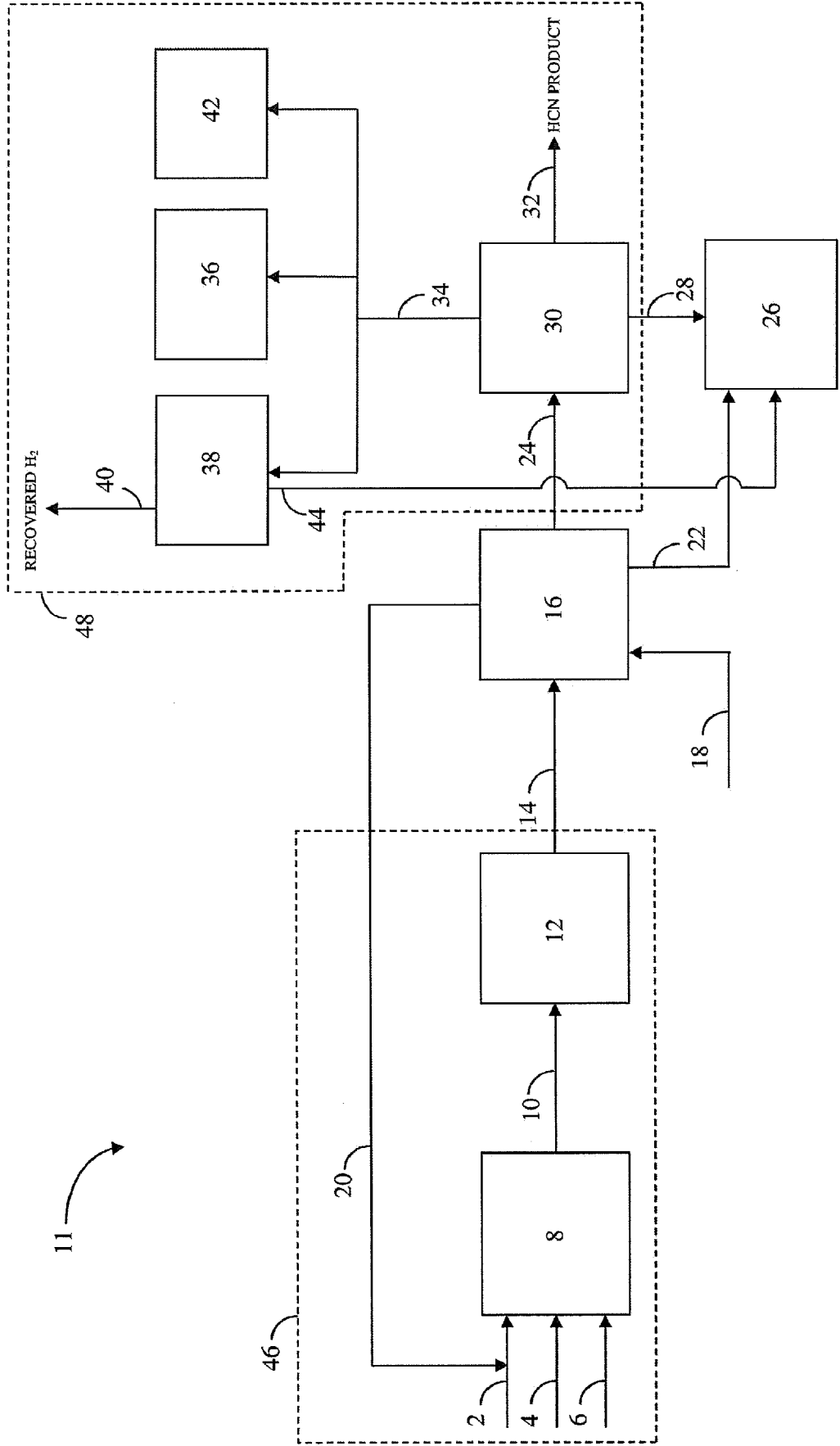


FIG. 1

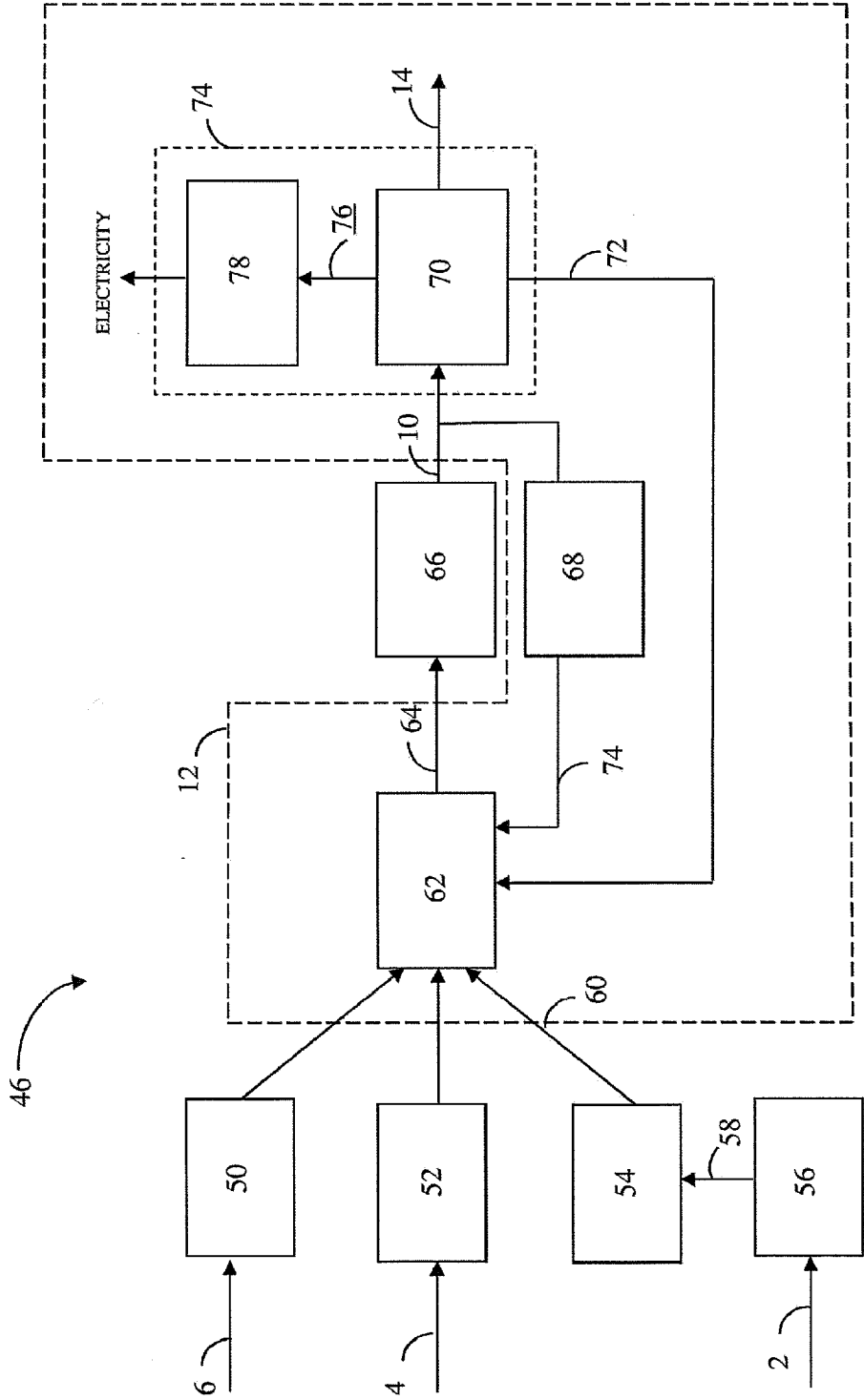


FIG. 2

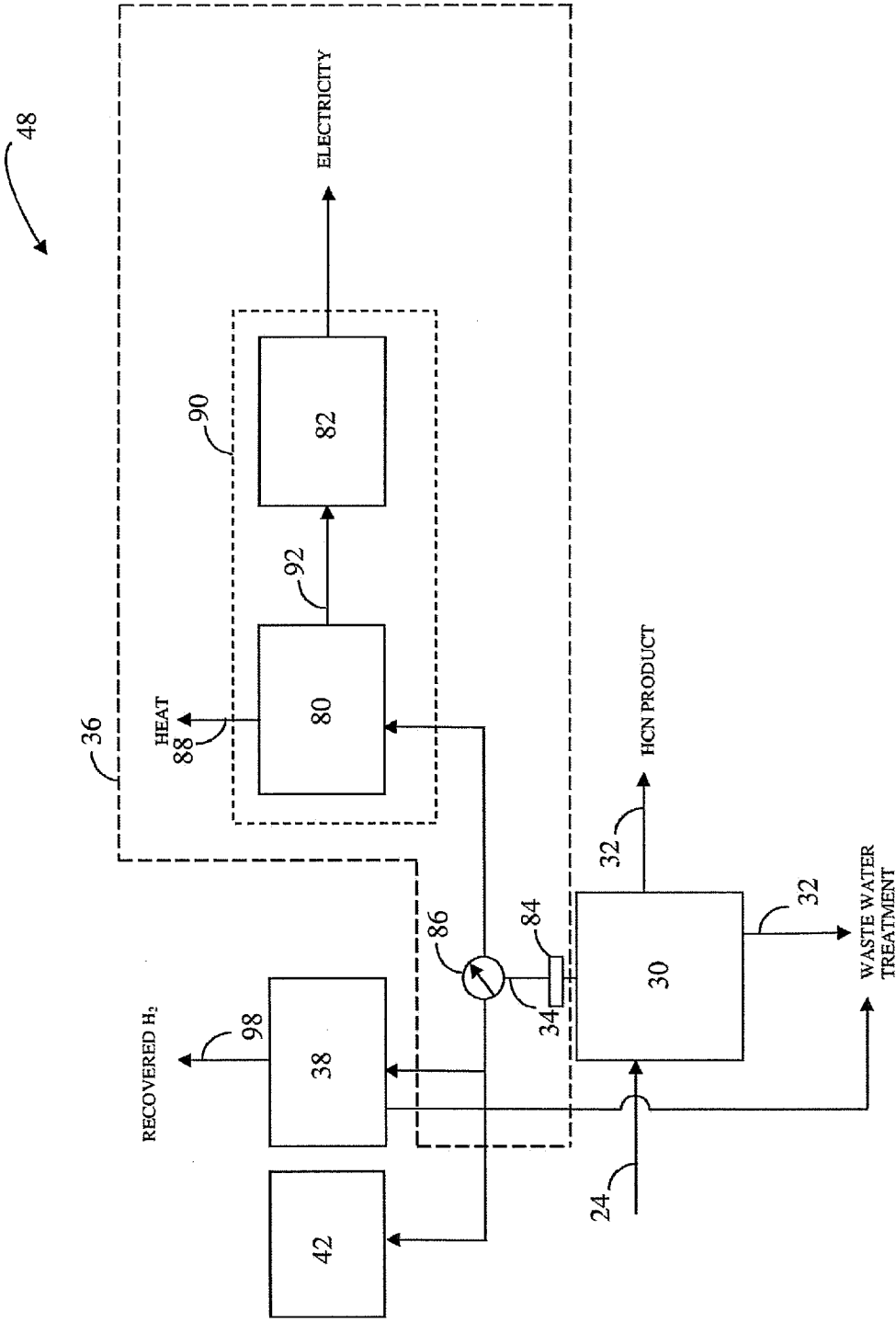


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/074515

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01C3/02 F23G7/06
ADD.

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)

C01C F23G

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 practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/084767 A1 (EVONIK DEGUSSA GMBH [DE]; FINKELDEI CASPAR HEINRICH [DE]; ZACCHI PABLO) 28 June 2012 (2012-06-28)	1-3, 10-15, 22-32, 41-43
Y	page 4, lines 6-14; figure 2	4-9,
A	page 5, line 5 - page 6, line 5	16-21, 44-52
Y	-----	33-40
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A	paragraphs [0004] - [0007], [0031], [0040], [0043], [0047]	1-3, 10-15, 22-43
	----- -/-	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"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

"&" document member of the same patent family

Date of the actual completion of the international search

7 April 2014

Date of mailing of the international search report

15/04/2014

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Werner, Håkan

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/074515

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	column 2, line 25 - column 3, line 37; figures 1-3 column 4, lines 27-47 column 5, lines 32-50 -----	5-9, 16-23, 33-40, 44-52
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Y	column 4, lines 3-27; figures 1,8 column 6, line 66 - column 7, line 16	4-9, 16-21, 44-52
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