

AN ELECTROLYSER SYSTEM AND METHOD FOR OPERATING AN ELECTROLYSER SYSTEM

TECHNICAL FIELD

[0001] The present invention relates to an electrolyser system and a method for operating an electrolyser system, in particular to improve its energy efficiency.

BACKGROUND ART

[0002] The following discussion of the background art is intended to facilitate an understanding of the present invention only. The discussion is not an acknowledgement or admission that any of the material referred to is or was part of the common general knowledge as at the priority date of the application.

[0003] Each document, reference, patent application or patent cited in this text is expressly incorporated herein in their entirety by reference, which means that it should be read and considered by the reader as part of this text. That the document, reference, patent application or patent cited in this text is not repeated in this text is merely for reasons of conciseness.

[0004] For hydrogen to contribute towards decarbonisation, it must be produced without CO₂ emissions; such production methods include 'Blue Hydrogen' which is produced from methane whilst employing Carbon Capture and Storage (CCS) and 'Green Hydrogen' which is produced by electrolysis using zero-emission electricity as an energy input.

[0005] Blue Hydrogen production methods are limited at present by the developmental status of CCS technology, with several high-profile CCS projects having experienced significant technical challenges.

[0006] Green Hydrogen production typically utilises intermittent renewable energy sources such as wind turbines and solar PV installations. Though possible with today's technology, Green Hydrogen is comparatively expensive partially due to the cost of the renewable energy inputs and the fact that

intermittent energy sources can only achieve partial utilisation of the associated hydrogen electrolyser(s).

[0007] The degree of electrolyser utilisation is limited by the capacity utilisation factors of the renewable energy inputs, capacity utilisation for onshore wind farms is approximately 40% whereas that of solar PV installations is approximately 30% (and more particularly approximately 25%). Furthermore, though the costs of wind turbines and solar PV have fallen considerably in the past decade, they remain relatively expensive sources of power when the costs of required grid transmission, grid storage and frequency control are included. In addition to this, and despite developments in battery technology, renewable energy remains subject to issues of intermittency as wind and solar resources are not 'always on' sources of energy.

[0008] The Applicant's International Patent Application No. PCT/AU2022/050157, the contents of which are hereby incorporated by reference for all purposes, describes processes and systems for producing hydrogen by electrolysis powered by baseload electricity produced from a waste heat to power system, advantageously an Organic Rankine Cycle (ORC) power generation system, recovering heat from exhaust gas. The hot exhaust gas may be produced by a gas turbine or diesel engine, conveniently forming part of a power plant, or from another large industrial waste heat source.

[0009] More generally, improvement of the electrical efficiency of electrolysis – not necessarily limited only to the production of hydrogen – would be desirable, particularly if energy consumption can be reduced in a manner that contributes to decarbonisation but without dependence on intermittent renewable energy sources.

[0010] The present invention has been developed against this background.

SUMMARY OF INVENTION

[0011] In one aspect, the present invention provides an electrolyser system, the electrolyser system comprising at least one electrolyser and having an

operating energy requirement generated by an energy source, said energy source including waste heat generated by a process comprising:

a waste heat to power system for recovering waste heat from the process to produce baseload electricity for supply to the at least one electrolyser; and

a heat exchange system for recovering waste heat from the process and transferring said recovered heat to the at least one electrolyser as thermal energy.

[0012] “Operating energy requirements” for an electrolyser system include an electricity requirement for conducting the electrolysis process, that is, in at least one electrolyser included within the electrolyser system. However, the electrolyser system may also require thermal energy to make an electrolysis process more efficient, for example by heating of a feed stream to increase the rate of electrolysis and production rate for a desired product of electrolysis. The electrolyser system may also include a process unit, such as a thermal water purification stage, which also has an energy requirement forming part of the operating energy requirements. Subject to the available amount of waste heat, as measured by its calorific value, efficiency is promoted by optimising, i.e. maximising, the use of the waste heat to meet the operating energy requirements of the electrolyser system. The higher the calorific value of the waste heat, the more duties it can supply energy to.

[0013] “Energy source” may include more than one source of energy, for example selected from the group consisting of mechanical, thermal and electrical energy.

[0014] Electricity may be supplied to the electrolyser system to conduct at least one of an electrochemical reaction and a further electrical requirement. The further electrical requirement is preferably selected from the group consisting of a heating requirement, a lighting requirement, a water purification requirement and a process control requirement dependent on the available amount of waste heat. In the case of a process control requirement, electricity may power an electronic control unit for the electrolyser system and/or waste heat to power system. The

electrical requirement may also include operation of pumps or valves within the electrolyser system.

[0015] Waste heat is generated by a process generating heat, typically an industrial process, conveniently heat generated by a combustion process for use, not necessarily exclusively, as a source of energy for electrolyser(s) in embodiments of the present invention. One useful source of waste heat would be a combustion process within a power plant. Exhaust gas streams from prime mover(s) within such a power plant are a particularly convenient source of waste heat whether captured directly or indirectly. Suitable prime movers may include gas turbines or internal combustion engines, such as diesel engines, though are not limited to such. Alternatively, waste heat may be generated or derived from non-combustion substantial sources of industrial waste heat, for example from smelting, calcination (for example of lithium containing ores), cement plants and other plants, such as oil refineries, producing heat from exothermic chemical reactions, are sources of waste heat and energy in embodiments of the present invention.

[0016] Waste heat may be generated by an electrolyser system itself and this may conveniently be utilised to optimise energy integration as described below.

[0017] Such a power plant may deliver electricity to the electrolyser system either directly or through co-generation, i.e. through the waste heat to power plant which converts waste heat from the power plant to electricity.

[0018] The heat exchange system desirably transfers recovered heat to an electrolyser stream. An electrolyser typically includes a feed stream to be subjected to electrolysis; and a product stream comprising the products of electrolysis. An electrolyser may include a plurality of feed streams and would typically have a plurality of product streams. For example, in the case of electrolysis of water or steam, hydrogen and oxygen are the products of electrolysis and are conveniently collected from the electrodes of an electrolyser as separate product streams. An electrolyser is preferably operated on a continuous or semi-continuous basis.

[0019] The feed stream(s) may advantageously be heated by heat from the waste heat source by the heat exchange system, optionally to form steam or a steam-water mixture. If desired, product stream(s) may also be heated by heat from the waste heat source by the heat exchange system. More typically, however, the product stream(s) would require cooling with heat being transferred to other electrolyser streams. For example, heat contained in a product stream – such as a hydrogen stream – could be used to heat a feed stream. Recycled hydrogen from at least one electrolyser may be included in the feed stream.

[0020] The electrolyser system may further comprise, in addition to the feed stream containing water and/or steam, at least one further inlet stream. The at least one inlet stream may also be heated by heat exchange with a waste heat stream, conveniently an exhaust gas from a combustion process as described above.

[0021] Energy efficiency of an electrolyser system, an electrolyser or downstream process utilising the product(s) of electrolysis may also be increased by heat exchange between selected electrolyser streams, for example between feed stream and product stream(s) where product stream(s) may preheat the feed stream while cooling the product stream. Heat exchanger(s) are provided as required for such heat exchange.

[0022] There are a range of potential electrolysis processes that may be conducted in an electrolyser according to embodiments of the invention. However, production of hydrogen either as fuel or as a feedstock in chemical manufacture, for example of ammonia, is one important potential application. In that case, the electrolyser system conducts electrolysis of water and/or steam to produce hydrogen and oxygen. It will be understood that electrolysis may be conducted for purposes other than, or additional to, hydrogen production.

[0023] In one embodiment useful for production of hydrogen, a feed stream containing water is fed to the electrolyser system. Water can be heated by such waste heat to generate steam which may be selected as a feed stream for the electrolyser system, indeed as a desirable feed stream for solid oxide electrolysis. Such a feed stream could also comprise a mixture of water and steam. Hydrogen

may be included within such a feed stream, for example as a recycle stream from the electrolyser(s).

[0024] Conveniently, where electrolysis is of a feed stream comprising water, steam or a mixture thereof, the heat exchanger may exchange heat between a product stream comprising hydrogen and the feed stream. In such heat exchange, the feed stream may be heated and the hydrogen product stream cooled. Such a product stream comprising hydrogen also typically contains some water which may be removed by condensation. In this embodiment, the heat exchanger partially cools the wet hydrogen stream which reduces the subsequent water condenser size and duty.

[0025] An electrolyser may – as alluded to above – comprise inlet streams additional to the feed stream. For example, a solid oxide electrolyser cell (SOEC) used for production of hydrogen typically includes a gaseous or pneumatic stream – typically comprising air – to sweep oxygen produced at the anode from the SOEC. Such a gaseous stream could also be heated with waste heat – for example an exhaust gas as described above – or by another heat source including an electrolyser process stream as described above.

[0026] Carbon dioxide could also be included within the feed stream so that a hydrogen-carbon monoxide-oxygen mixture or synthesis gas is produced at the cathode of the at least one electrolyser. Carbon dioxide is also conveniently sourced from exhaust gas, a proportion of which may be admixed with the feed stream. Other chemical components could be included within the feed stream to similar effect. Synthesis gas may be used as a feed to chemical production, for example for the production of a range of industrial chemicals or polymers.

[0027] The present method and system may be applied to any electrolyser type, whether solid oxide, alkaline or proton exchange membrane. Advantageously, the electrolyser system is applied to higher temperature electrolytic processes, in particular solid oxide electrolysis. In this embodiment, the electrolyser system comprises at least one solid oxide electrolyser with waste heat from the combustion process being utilised to provide heat to the solid oxide electrolyser to increase its efficiency by reducing electrical power input requirements. In this regard, solid oxide electrolysers typically operate in the

temperature range 600-1000°C and sourcing at least a portion of the heating requirement for solid oxide electrolysis from waste heat, in particular from exhaust gas from a combustion process, provides increased electrical efficiency and associated economic benefits as waste heat should be derived at low cost.

[0028] The electrolyser system is fully or partially supplied with electricity from the waste heat to power system which converts a portion of the waste heat from the process to electricity. Such electricity generation is possible on a continuous or baseload basis using systems and methods as described in the Applicant's co-pending International Patent Application No. PCT/AU2022/050157 (International Patent Publication No. WO2023023691), the contents of which are incorporated herein by reference. Preferably, the waste heat to power system includes an Organic Rankine Cycle (ORC) power generation system. Alternative power generation systems including, without limitation, supercritical CO₂ cycle systems (e.g. Brayton cycle) and Kalina cycle systems may be used as a waste heat to power system instead of an ORC power generation system.

[0029] Such waste to heat power systems conveniently directly or indirectly exchange heat between a hot stream containing the waste heat, conveniently an exhaust gas from a combustion process as described above, and a heat transfer fluid such as a thermal oil. Heat from a heated thermal oil may be converted to electricity in an ORC power generation system as described in PCT/AU2022/050157, the contents of which are incorporated herein by reference for all purposes.

[0030] The heated thermal oil may also conveniently be used for supplying heat to an electrolyser process stream. For example, the heated thermal oil may exchange heat with the feed stream with one embodiment comprising a water containing feed stream to form steam or at least higher temperature water. In another example, the heated thermal oil may exchange heat with an inlet stream – such as an inlet stream comprising air – to the electrolyser. In a further example, the heated thermal oil could exchange heat to drive a thermal water purification system, for example a vacuum evaporation system though not limited thereto, used to provide purified water or water-steam mixtures to the electrolyser. As

observed above, a preferred electrolyser system would include at least one solid oxide electrolysis cell.

[0031] The electrolyser system may itself be used to produce power in an embodiment in which the at least one electrolyser is reversible acting either to produce hydrogen; or acting as a fuel cell.

[0032] In another aspect, the present invention provides a method for operating an electrolyser system, the electrolyser system comprising at least one electrolyser and having an operating energy requirement comprising:

supplying waste heat generated by a process to the electrolyser system to meet at least a portion of the operating energy requirement;

recovering heat from the process to produce baseload electricity for supply to the at least one electrolyser; and

recovering heat, as required, from the process and enabling transfer of the recovered heat to the at least one electrolyser as thermal energy.

[0033] The electrolyser system, as described above, can be operated in a more electrically and thermally efficient manner because electricity requirements for the electrolyser(s) within the system – and in particular fuel and electricity energy requirements for heating and cooling for streams of the electrolyser system can be reduced through replacement by a waste heat source and/or converting waste heat from the waste heat source into electricity for use within the electrolyser system. There is no requirement for use of an intermittent energy source which is likely less efficient though the electrolyser system can still receive an additional renewable energy supply if required, possibly as a back up system. Such renewable energy supply would typically have a secondary role.

BRIEF DESCRIPTION OF THE DRAWINGS

[0034] Further features of the present invention are more fully described in the following description of several non-limiting embodiments thereof. This description is included solely for the purposes of exemplifying the present invention. It should not be understood as a restriction on the broad summary,

disclosure or description of the invention as set out above. The description will be made with reference to the accompanying drawings in which:

[0035] Figure 1 is a process flow diagram for a waste heat to power process and system for producing hydrogen in a prior electrolysis process.

[0036] Figure 2 is a process flow diagram for an Organic Rankine Cycle waste heat to power system included in the process and system of Figure 1.

[0037] Figure 3 is a process flow diagram for a solid oxide electrolyser system and process for preferred embodiments of the invention.

[0038] Figure 4 is a process flow diagram showing a first embodiment involving preheating by combustion exhaust of a water stream to be fed to the electrolyser system of Figure 3.

[0039] Figure 5 is a process flow diagram showing a second embodiment involving preheating by a thermal oil of a water stream to be fed to the electrolyser system of Figure 3.

[0040] Figure 6 is a process flow diagram showing preheating of an air inlet stream to the electrolyser system of Figure 3 according to a third embodiment of the present invention.

[0041] Figure 7 is a process flow diagram showing preheating of an air inlet stream to the electrolyser system of Figure 3 according to a fourth embodiment of the present invention.

[0042] Figure 8 is a process flow diagram showing use of waste heat for thermal water purification according to a fifth embodiment of the present invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0043] Referring now to Figure 1, this schematically shows a prior system and process 100 for producing hydrogen using electricity produced from waste heat in the exhaust gas from combustion in an open cycle gas turbine 22 supplied with

fuel in the form of natural gas 25. Examples of suitable gas turbines include: General Electric LM2500 (≈ 30 MW power rating), GE LM6000 (≈ 40 MW), and Solar Mars 100 (≈ 10 MW) gas turbines, with the Solar Mars 100 commonly being used in gas compressor stations. System 100 is used to take advantage of waste heat at a pipeline compressor station. However, it will be understood that a wide variety of power plants having open gas cycle gas turbines, internal combustion engines such as diesel engines or other combustion or non-combustion sources of industrial waste heat may be implemented according to embodiments of the present invention.

[0044] Natural gas 25 is combusted in a turbine combustor with air 26 (though oxygen 586 produced by electrolyser system 60 may also be used as an oxidant or for oxygen enrichment of air 25) during operation of the gas turbine 22 to produce electricity E and an exhaust gas 27 at a temperature of about 500°C with a mass flow of 130-143 kg/s. The typical gas turbine 22 operating temperature range is 430°C to 560°C although some gas turbines operate outside this range. Ordinarily, in an open cycle gas turbine arrangement, the exhaust gas 27 would simply be vented to atmosphere through vertically extending exhaust stack 35 with loss of utility of a valuable high-grade waste heat resource. Process and system 100 allows this value to be captured and a significant opportunity cost avoided.

[0045] Exhaust gas 27 is directed to a waste heat recovery unit (WHRU) 30 containing a heat exchanger 32 being a shell and tube heat exchanger, typically with finned tubes. Exhaust gas 27 flows on the shell side (hot) and heat transfer medium 42 on the tube side (cool).

[0046] WHRU 30 is here of integral design, formed within the vertically extending exhaust stack 35. Though not shown, an internal bypass is provided to allow a direct route to atmosphere for exhaust gas 27. A diverter valve arrangement 30a is provided at the bottom of WHRU 30 to direct exhaust gas 27 either for heat exchange in heat exchanger 32 or to be vented to atmosphere where heat transfer medium 42 cannot accept heat.

[0047] In the illustrated embodiment, diverter valve arrangement 30a directs flow of exhaust gas 27 past the heat exchanger 32 for counter-current heat

exchange with a heat transfer medium in the form of cool thermal oil 42 returning from the ORC power generation system 70 which is desirable and preferred in this embodiment, not least because of its low maintenance requirements and capacity to operate reliably without operator intervention to provide baseload power when coupled with an almost continuous heat source in the form of waste heat from gas turbine 22 when in operation. It will be understood that, in other embodiments, ORC power generation system 70 could be substituted with other types of power generation system; for example, a supercritical CO₂ Brayton cycle system or a Kalina cycle system.

[0048] Conveniently, the heat transfer medium is a thermal oil 42. The selected thermal oil has high stability and low vapour pressure at the required operating temperature of stream 40. Thermal oils are also preferred due to the low maintenance requirements and low design pressure of the heat recovery system in comparison to water/steam systems.

[0049] The flow of thermal oil 42 is driven by a pump 95 which is typically a centrifugal-type unit. Thermal oil flow rate may be controlled to achieve a desired level of heat transfer between exhaust gas 27 and thermal oil 42. For this purpose, a feedback control loop may be provided between hot thermal oil 40 temperature and flow rate. An expansion vessel 90 is situated upstream of the pump 95 to provide volume to accommodate thermal expansion.

[0050] In the illustrated embodiment, cool thermal oil 42 is not the working fluid for the ORC power generation system 70. Thus, the process 100 does not involve direct waste heat recovery from exhaust gas 27 but rather uses an indirect heat exchange using thermal oil 42 which, on return to the ORC power generation system 70 as heated thermal oil 40, further exchanges heat with the ORC working fluid 77 as shown in Figure 2. In some embodiments, direct waste heat recovery from exhaust gas 27 to ORC working fluid without use of the first or intermediate thermal oil 40, 42 may be adopted.

[0051] Following heat exchange between exhaust gas 27 and thermal oil 42, cooled exhaust gas 36 leaves the WHRU 30 and flows to atmosphere.

[0052] Hot thermal oil 40, heated by the exhaust gas 27, carries heat to ORC power generation system 70, where heat is transferred to an Organic Rankine Cycle (ORC) working fluid 77, conveniently cyclopentane (the ORC working fluid) in this embodiment. Cool thermal oil 42 flows through a return line including an expansion vessel 90 and pump 95 from ORC power generation system 70 to WHRU heat exchanger 32. The design and operation of ORC power generation system 70 is further described below. While cyclopentane is used as working fluid in this embodiment, a working fluid is selected to match the temperature profile of exhaust gas 27. Cyclopentane is useful for this purpose though other organic, including hydrocarbon and non-hydrocarbon, working fluid alternatives are available. Without limitation, suitable alternative ORC working fluids to cyclopentane may be selected from the group consisting of: silicon fluids (siloxanes), hydrocarbons (e.g. cyclohexane, n-pentane, iso-pentane, n-butane, isobutane) and old and new generation refrigerants.

[0053] Referring now to Figure 2, the operation of ORC power generation system 70 will now be described. ORC power generation system 70 embodies a closed-loop thermodynamic process that converts waste heat, as recovered from exhaust gas 27 (see Figure 1), in the heated first thermal fluid 40, to electricity for powering electrolyser 60.

[0054] The ORC working fluid 77, undergoes a series of phase, temperature and volume changes through the various stages of the thermodynamic process (i.e. the Organic Rankine Cycle) and ORC power generation system 70. ORC power generation system 70 includes, in series, preheater 76, evaporator 71, expansion turbine 72 for driving electricity generator 79, recuperator 73 and condenser 74. Turbine 72 may be bypassed by cyclopentane line 78, if required.

[0055] In this embodiment, preheater 76 is a shell and tube heat exchanger with thermal oil 402 flowing on the shell side and cyclopentane 77c flowing through the tubes. The function of preheater 76 is to receive high-pressure cyclopentane 77c in the liquid phase from the recuperator 73 and raise the cyclopentane temperature to its boiling point at the selected operating pressure.

[0056] In this embodiment, evaporator 71 is a kettle-type heat exchanger with a tube bundle submerged in liquid cyclopentane 77a.

[0057] Recuperator 73 is a shell and tube heat exchanger with low-pressure cyclopentane vapour 77b on the shell side and high-pressure cyclopentane liquid 77d flowing through the tubes.

[0058] Condenser 74 is here air-cooled which is desirable for water conservation in an arid location but it will be understood that it may be water cooled or cooled by another refrigerant subject to economics. Refrigerant systems may have benefit in terms of fine adjustment of condenser temperature. In the air-cooled condenser (ACC) 74 embodiment, cyclopentane flows through a multiple tube bundle of ACC 74 with air flowing over the exterior of the finned tubes. The ACC 74 may comprise multiple identical modules. Airflow over the tube bundle is conveniently driven by fans. Cyclopentane vapour from the recuperator 73 is distributed between the ACC modules by an inlet header 74a which runs across the full length of ACC 74. The inlet header 74a acts as a manifold which distributes the cyclopentane vapour into the multiple tube bundles. Each tube bundle flows across the ACC fans to the far side of the air-cooled condenser 74 where condensed liquid cyclopentane is collected in the outlet header 74b. Collection of liquid cyclopentane in the outlet header 74b provides suction head for ORC pump 75.

[0059] The ORC power generation system 70 operates as follows:

- (1) High pressure cyclopentane in the liquid phase 77a flows to evaporator 71 where heat is exchanged from the thermal oil 40 into the cyclopentane, evaporating the cyclopentane to produce high pressure, high temperature vapour in line 77. Cooled thermal oil 402 flows back via preheater 76 to the heat exchanger of WHRU 30 as cool thermal oil 42. In some embodiments, a superheater (not shown) may be included downstream of the evaporator 71 to further increase the temperature of cyclopentane vapour in line 77.
- (2) High pressure, high temperature cyclopentane vapour 77 flows to the expansion turbine 72 where it expands to a low pressure generating rotational motion within the expansion turbine 72 which drives the electricity generator 79 and produces electrical power which is used in the electrolyser 60. Cyclopentane working fluid

77b leaves the expansion turbine 72 as a low pressure, superheated vapour 77b.

- (3) Low pressure, superheated cyclopentane vapour 77b flows to recuperator 73 where superheat is removed prior to condensation of the vapour in the ACC 74. The recuperator 73 is an economizer which transfers superheat from the low-pressure cyclopentane 77b into the high pressure cyclopentane liquid 77d before it enters the preheater 76 as high pressure cyclopentane liquid 77c.
- (4) Low pressure, low temperature vapour 77e from recuperator 73, flows to condenser 74 where the vapour is cooled further and condenses into the liquid phase, with air providing a heat sink for the condensation process. The cyclopentane leaves the ACC 74 as low-pressure liquid cyclopentane 77f.
- (5) Low pressure, low temperature liquid cyclopentane 77f flows to pump 75 where its pressure is increased to the ORC cycle high pressure for delivery as high pressure, low temperature liquid cyclopentane 77d to recuperator 73.
- (6) High pressure, low temperature cyclopentane liquid 77d flows to the recuperator 73 where heat is transferred to the liquid cyclopentane from the medium temperature cyclopentane vapour 77b flowing from the expansion turbine 72 exhaust. High pressure, medium temperature liquid 77c, heated in recuperator 73, flows to the preheater 76.
- (7) High pressure, medium temperature liquid 77c flows to the preheater 76 where its temperature is increased to the boiling point at the operating pressure through heat exchange with the thermal oil 402 leaving the evaporator 71. High pressure, saturated liquid cyclopentane then flows to the evaporator, completing the cycle.

[0060] The cycle of thermal process stages (1) to (7) continues for as long as the WHRU 30 is coupled with the ORC power generation system 70 to generate

power. It will be understood that pipeline 10 typically operates continuously and, similarly, compressor 20 must also operate continuously to transport purified natural gas through pipeline 10 as typically must the WHRU 30. It follows that electricity generator 79 can supply electricity 80 continuously to the electrolyser 60 to enable production of hydrogen 450 with baseload power and without the recognised intermittency issues of solar or wind power though, in embodiments, such power sources can be used, as a secondary source, in combination with power produced by the ORC power generation system 70 to supply electrolyser 60 with baseload electricity or power 80.

[0061] It will be understood that the ORC power generation system 70 generates alternating current (AC) electricity for supply to electrolyser 60 which operates with DC electricity. A rectifier (not shown) is used to convert the AC electrical output from electricity generator 79 to DC electricity 80.

[0062] Hydrogen 450 is produced by electrolysis of water 62 at the cathode 67 of electrolyser 60 powered by electricity 80 generated from waste heat recovered from exhaust gas 27 by the Organic Rankine Cycle (ORC) power generation system 70. Electrolyser 60 may be sized accordingly in preferred embodiments. As electricity 80 is generated continuously, i.e. at base load, for the reasons described above, the consequence is a lower production cost for hydrogen 450 than for hydrogen produced from electricity generated from intermittently available renewable resources such as solar and wind power.

[0063] Oxygen is also produced at the anode 66 of electrolyser 60, an anode compartment being separated from the cathode 67 compartment by a suitable membrane 65 and/or exported from the compressor station 120 site if demand exists. Oxygen 586 can also be used as an oxidant for the gas turbine 22 combustor, directed as an oxygen stream to storage or export or vented directly to atmosphere with no deleterious environmental impact.

[0064] Water 62 should be demineralised for electrolysis and is, in this embodiment, pre-treated by filtration and reverse osmosis 9 (not shown), to reduce total dissolved solids (from a likely brackish or saline water source) prior to delivery to the electrolyser 60. Water purification methods other than reverse osmosis may be appropriate and used in other embodiments.

[0065] The electrolysis process may be more efficient at elevated temperatures, particularly for solid oxide electrolysis though alkaline electrolysis may also operate more efficiently with higher temperature water streams. In this case, heat can be sourced from elsewhere in the process 100, preferably the cool thermal oil 42 returned from ORC power generation system 70, this heat being optionally used to preheat demineralised water prior to delivery to electrolyser 60. A further alternative source of heat for heating water 62 is exhaust gas 27 and a suitable heat exchanger, for example a shell and tube heat exchanger, may be used to enable such heat exchange.

[0066] Hydrogen 450 is captured and delivered to applications, whether for pipeline use or otherwise, as required. Detailed description is provided in the Applicant's International Publication No. WO2023023691 incorporated by reference and is therefore omitted here.

[0067] Referring to Figures 3 to 8, there is described an electrolyser system 400 comprising at least one electrolyser 460 according to one embodiment of the present invention. The at least one electrolyser 460 operates by Solid Oxide Electrolysis (SOE) to produce hydrogen and oxygen. Unlike alkaline electrolysis, SOE requires higher energy input to allow the electrolyser 460 – which in the following description is referred to as a solid oxide electrolysis cell (SOEC) – to operate at a temperature of 600-1000°C. This requires heating of the electrolyser 460 to that temperature range and, conventionally, provides an operating energy requirement that presents a significant cost.

[0068] Although one SOEC 460 is shown for the electrolyser systems 400 of each of Figures 3 to 8, it will be understood that a plurality of SOEC(s) 460 could be included in those electrolyser systems 400 dependent on hydrogen demand and the availability of energy to provide the operating energy requirement of SOEC(s) 460.

[0069] Referring first to Figure 3, SOEC 460 of electrolyser system 400 is fed with a first process stream 405 which may comprise water and/or steam. The first process stream 405 is heated in steam recuperator 406 and steam trim heater 407 to a selected input temperature to the SOEC 460 of heated first process

stream 405a. The steam trim heater 407 has a power requirement Q_1 to enable heating to an optimum temperature for operation of SOEC 460.

[0070] Hydrogen is produced at the cathode of electrolyser 460 and thus a second process stream 420 contains a mixture of hydrogen and steam. Second process stream 420 is directed first to steam recuperator 406 allowing a degree of heating of first process stream 405 by heat exchange between the two process streams 405 and 420 as the hydrogen containing process stream 420, having been discharged from the SOEC 460 (operating temperature range 600-1000°C), is at a higher temperature. Consequentially, second process stream 420 is cooled.

[0071] Second process stream 420 is then split into two streams 423 and 426. Stream 423 is directed through hydrogen recycle blower 424 to provide a hydrogen recycle stream 425 that is blended with the first process stream 420.

[0072] Stream 426 is cooled in water condenser 427 to cause further water condensation with water being removed in knock-out vessel 470 as stream 472.

[0073] Hydrogen 450, from which water has been separated, is then directed to further processing, e.g. drying or to an end use – whether as a fuel for fuel cell vehicles (FCV) or as a feedstock, for example for production of ammonia. Hydrogen 450 has high purity.

[0074] Oxygen is produced at the anode of electrolyser 460 and thus a third process stream 580 contains oxygen. Oxygen in third process stream 580 is in admixture with air used to sweep oxygen from the electrolyser 460. To that end, an air input stream 590 is directed to SOEC 460.

[0075] Air input stream 590 is generated by a suitable blower or blower arrangement (not shown) and is heated by air recuperator 582 and air trim heater 587 to a selected input temperature to the SOEC 460 of heated air input stream 590a.

[0076] Third process stream 580 is directed first to air recuperator 582 allowing a degree of heating of air input stream 590 by heat exchange between

the two streams 580 and 590 as the oxygen containing process stream 580, having been discharged from the SOEC 460 (operating temperature range 600-1000°C), is at a higher temperature. Consequentially, third process stream 580 is cooled.

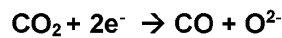
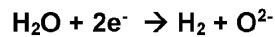
[0077] Third process stream 580 is then split into two streams 583 and 586. Stream 583 is directed through air recycle blower 584 to provide an air recycle stream 585 that is blended with the air input stream 590. Stream 580 is an oxygen rich air stream which may be discharged or used as an oxidant stream for a combustor, for example for gas turbine 22.

[0078] As is the case with electrolyser 60 described above, SOEC 460 is fed with direct current electricity 80 generated from waste heat recovered from exhaust gas 27 by the Organic Rankine Cycle (ORC) power generation system 70 as described above. A high voltage alternating current electricity supply 695 is reduced in a step down transformer 697 and rectified by rectifier 699 to provide direct current electricity to SOEC 460.

[0079] Solid oxide electrolysis system 400, as shown in Figure 3, is simplified. For example, heat recovery systems in practice are likely to be more complex and utilise a heat exchange system comprising a plurality of heat exchangers to maximise heat recovery and thermal efficiency. Such a heat exchange system may require numerous heat exchangers.

[0080] In addition to the above, it will be apparent that other steps to a more energy efficient electrolyser system 400 have been taken by energy integration within the electrolyser system 400 itself. That is, process streams (i.e streams 580 and 420) discharged from SOEC 460 are conveniently used to heat process and input streams (i.e streams 405, 590) to SOEC 460. This reduces power generation requirements for electrolyser system 400 and allows a higher energy efficiency electrolyser system 400.

[0081] Although the electrolyser system 400 of Figure 3 is used for production of hydrogen, in an alternative embodiment, first process stream 405, 405a may also include carbon dioxide. SOEC 460 then allows for production of both hydrogen and carbon monoxide according to the following reactions:



Hydrogen and carbon monoxide are produced in admixture, as synthesis gas or “syngas” at the cathode of SOEC 460.

[0082] Oxygen gas is produced at the anode of SOEC 460 in this embodiment.

[0083] Carbon monoxide is a useful gas that can be further processed to form synthetic hydrocarbons which may be used, for example, as fuels or chemical feedstocks. Synthetic hydrocarbons are considered carbon neutral if the carbon dioxide feed has been captured from an exhaust stream from a combustion process and would otherwise have been released to atmosphere.

[0084] As shown in the embodiments of Figures 4 to 8, the operating energy requirement of SOEC 460 and electrolyser system 400 is provided – at least in part – by waste heat generated by a combustion process, in this embodiment in an open cycle gas turbine 22. To that end, electrolysis system 400 is located close to a power plant including one or more open cycle gas turbines 22 which combust natural gas 25 with air or oxygen enriched air 26 to drive a turbine and produce electricity E. Other fuels may be used and power plants may, less desirably, include prime movers other than open cycle gas turbines. As referenced above with respect to Figures 1 and 2, the source of waste heat may be high temperature exhaust gas 27 from open cycle gas turbine 22 where used for supplying power to a gas compressor station 120. However, many other power plant arrangements are known as understood in the art and embodiments may be directed to these. Other industrial sources generating substantial quantities of waste heat may also be employed as an energy source.

[0085] The use of waste heat, however derived from a combustion process, allows a portion of the operating energy requirement for SOEC 460 to be met and increased energy efficiency and an energy cost saving for operation of SOEC 460. As described below, with reference to Figures 4 to 8, there are a number of options for use of such waste heat within the electrolyser system 400. Desirably,

the options would be used in combination though the constraint is the available amount of waste heat. Typically, sources of energy other than waste heat would also be required to efficiently operate electrolyser system 400.

[0086] Referring to Figure 4, the heat of exhaust gas stream 27 is used both to directly heat demineralised water stream 404 and to indirectly provide heat to ORC system 70, indirectly through production of a heated thermal oil stream 40, for production of electricity 80 as described above. Electricity 80 can be used in electrolyser system 400 and, in particular, by SOEC 460. Such direct heating of demineralised water stream 404 allows formation of a first process stream 405 comprising water, a mixture of steam and water or steam alone. The heating of demineralised water stream 404 by exhaust gas 27 allows the heating duty of steam trim heater 407 to be reduced from Q_1 to Q_2 providing an energy cost saving both in terms of reduced process heating and reduced electricity requirements.

[0087] Referring to Figure 5, water stream 404 is not heated directly by exhaust gas 27 but rather by heated thermal oil 42 in heat exchanger 402.

[0088] Referring to Figure 6, the heat of exhaust gas stream 27 is used both to directly heat input air stream 590 and to indirectly provide heat to ORC system 70, indirectly through production of a heated thermal oil stream 40, for production of electricity 80 as described above. Electricity 80 is again used in electrolyser system 400 and, in particular, by SOEC 460. The heating of input air stream 590 by exhaust gas 27 allows the heating duty of air trim heater 587 to be reduced from Q_{1A} to Q_{2A} providing an energy cost saving both in terms of reduced process heating and reduced electricity requirements.

[0089] Referring to Figure 7, input air stream 590 is not heated directly by exhaust gas 27 but rather by heated thermal oil 42 in heat exchanger 402A to form heated input air stream 590a.

[0090] Referring to Figure 3, water present in first process stream 405, 405a should be extremely pure and demineralised to avoid fouling of the SOEC 460 and protect SOEC 460 efficiency and longevity. Even if a source of potable water were to be available at the location of electrolyser system 400, further water

purification would likely be required. Suitable water purification technologies include, without limitation: thermal water purification, reverse osmosis (RO) and capacitive deionisation.

[0091] In preferred embodiments, thermal water purification is used. Thermal water purification itself can be further sub-divided into multiple categories: vacuum evaporators (VE), vacuum mechanical vapour compression (VMVC), mechanical vapour compression (MVC), multi-stage flash (MSF) separation and multi-effect distillation (MED).

[0092] Figure 8 shows a scheme for capturing waste heat from exhaust gas 27 for thermal water purification stage 410. Brackish feed water stream 404 is not heated directly by exhaust gas 27 but rather by heated thermal oil 42 in thermal water purification stage 410 to form demineralised water stream 412. Heat is captured from the heated thermal oil 42 to operate a vacuum evaporator forming part of thermal water purification stage 410. The result is benefit in terms of reduced process heating and reduced electricity requirements for electrolyser system 400.

[0093] Although the above embodiments involve solid oxide electrolysis, where most benefit is expected because of the operating temperature range (600-1000°C), the principles may be applied to different electrolysis methods and configurations. For example, the principles are also applicable to alkaline electrolysis.

[0094] Hydrogen 450, produced according to the principles described above for processes 100 and 400, may be further compressed by a compressor and stored in high pressure gas in a pressure vessel or in liquefied form in a storage vessel with a hydrogen fuel offtake to supply hydrogen for use in high-purity applications such as for zero-emission fuel in heavy vehicles, industrial or mining equipment or aircraft. Alternative embodiments in which hydrogen is used on-site as a fuel for vehicles or for blending with natural gas in a pipeline are also possible. Such embodiments may involve storage of gaseous or liquid hydrogen in appropriately configured accumulators.

[0095] In further embodiments, hydrogen may be used as a feedstock for other chemical processes, e.g. reacted with nitrogen – by the Haber process – to form ammonia either as a form of storage of hydrogen or as a fuel, for example for shipping. Hydrogen may also be used in other chemical production processes.

[0096] In still further embodiments, synthesis gas produced in electrolyser systems of embodiments of the invention may be used as fuel or as an intermediate in chemical production. Exhaust gas 27 may be used as a hot source of carbon dioxide for production of synthesis gas in SOEC 460.

[0097] Amongst other advantages, the system and processes according to the invention enable energy efficient and productive utilisation of waste heat produced from gas turbines, diesel engine exhausts or other substantial industrial sources of waste heat, in particular those used in remote locations 120 by cost-effectively generating zero-emission hydrogen 450 through other electrolysis processes, for example producing synthesis gas as described above may be operated according to embodiments of the invention. There are three salient benefits, namely 1) low-cost baseload zero-emission electricity reducing hydrogen (and other) production cost; 2) maximisation of electrolyser utilisation, further reducing hydrogen production cost; and 3) hydrogen delivery to a pipeline or storage facility conveniently located adjacent to hydrogen production facilities producing hydrogen locally avoiding need for, amongst other things, high pressure hydrogen compression and liquefaction or other chemical transformation required for long distance transportation thereby eliminating associated cost, energy and safety concerns.

[0098] Modifications and variations to the electrolyser systems and electrolysis processes described in this specification may be apparent to the skilled reader of this disclosure. Such modifications and variations are within the scope of the present invention.

[0099] Throughout this specification, unless the context requires otherwise, the word "comprise" or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

CLAIMS

1. An electrolyser system, the electrolyser system comprising at least one electrolyser and having an operating energy requirement generated by an energy source, said energy source including waste heat generated by a process, comprising:
 - a waste heat to power system for recovering heat from the process to produce electricity for supply to the at least one electrolyser; and
 - a heat exchange system for recovering heat from the process and enabling transfer of said recovered heat to the at least one electrolyser as thermal energy.
2. The electrolyser system of claim 1, wherein said electricity is supplied to conduct at least one of an electrochemical reaction and a further electrical requirement.
3. The electrolyser system of claim 2, wherein said further electrical requirement is selected from the group consisting of a heating requirement, a lighting requirement, a water purification requirement and a process control requirement dependent on the available amount of waste heat.
4. The electrolyser system of any one of the preceding claims, wherein waste heat from said at least one electrolyser is recovered by said heat exchange system.
5. The electrolyser system of any one of the preceding claims, wherein said waste heat is generated by combustion in a power plant comprising one or more prime movers selected from the group consisting of gas turbines and internal combustion engines.
6. The electrolyser system of claim 5, wherein said power plant also supplies electricity to at least one electrolyser.
7. The electrolyser system of any one of the preceding claims, wherein said heat exchange system transfers said recovered heat to an electrolyser stream.
8. The electrolyser system of claim 7, wherein said electrolyser stream is a feed stream.

9. The electrolyser system of claim 7 or 8, wherein said electrolyser stream, following heating by said heat exchange system, includes steam, optionally as a steam-water mixture.
10. The electrolyser system of claim 8 or 9, wherein said feed stream includes hydrogen recycled from said at least one electrolyser.
11. The electrolyser system of claim 7, further comprising at least one further inlet stream to which said heat exchange system transfers said recovered heat.
12. The electrolyser system of claim 11, wherein said inlet stream is a gaseous stream, preferably an air stream.
13. The electrolyser system of claim 7, wherein said electrolyser stream is a product stream.
14. The electrolyser system of any one of the preceding claims, wherein said at least one electrolyser is a solid oxide electrolytic cell.
15. The electrolyser system of any one of the preceding claims comprising a plurality of electrolyser streams including a feed stream and one or more product streams comprising one or more heat exchangers for exchanging heat between selected electrolyser streams.
16. The electrolyser system of claim 15, wherein said selected electrolyser streams include a feed stream and at least one product stream.
17. The electrolyser system of claim 16, wherein said product stream comprises water, the electrolyser system comprising a condenser for removing water, heat exchange between the feed stream and the product stream allowing water condensation.
18. The electrolyser system of claim 6, wherein said at least one electrolyser produces hydrogen while said power plant is operating.
19. The electrolyser system of claim 18, coupled with an ammonia plant to which said hydrogen is a feed stream.
20. The electrolyser system of claim 8, wherein said feed stream includes carbon dioxide and a product stream comprises a hydrogen-carbon monoxide-oxygen mixture.

21. The electrolyser system of claim 20, wherein said carbon dioxide is sourced from exhaust gas from said combustion process, said feed stream including a proportion of said exhaust gas.
22. The electrolyser system of claim 20 or 21, wherein said product stream is directed as a feed to chemical production.
23. The electrolyser system of claim 14, wherein said solid oxide electrochemical cell is reversibly operable as a fuel cell.
24. The electrolyser system of any one of the preceding claims, wherein said waste heat to power system is selected from the group consisting of an Organic Rankine Cycle, supercritical CO₂ cycle and Kalina cycle power generation systems.
25. The electrolyser system of claim 24, wherein said power system is an Organic Rankine Cycle system in which a heated thermal oil supplies heat to an electrolyser process stream.
26. The electrolyser system of claim 25, wherein said electrolyser process stream is a feed stream or an inlet stream.
27. The electrolyser system of claim 24, wherein said power system is an Organic Rankine Cycle system in which a heated thermal oil exchanges heat to drive a thermal water purification system.
28. The electrolyser system of claim 27, wherein said thermal water purification system is a vacuum evaporation system for supplying purified water or water-steam mixtures to the electrolyser system.
29. A method for operating an electrolyser system, the electrolyser system comprising at least one electrolyser and having an operating energy requirement generated by an energy source, said energy source including waste heat generated by a process comprising:
 - recovering heat from the process to produce baseload electricity for supply to the at least one electrolyser; and
 - recovering heat from the process and transferring said recovered heat to the at least one electrolyser as thermal energy.