

## CO<sub>2</sub> CYCLE FOR CARBON CAPTURE

### Field of Invention

- 5 The present disclosure generally relates to carbon capture, and more particularly relates to CO<sub>2</sub> cycle for carbon capture in power production systems.

### Background

- 10 The listing or discussion of a prior-published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

There is a global urgency to combat climate change and global warming due to the rise in  
15 atmospheric CO<sub>2</sub> concentration. One key solution is to adopt low- or zero-carbon electricity as the dominant source of power by 2050. In order to achieve this goal, the power generation sector, which is responsible for ~50% of all anthropogenic CO<sub>2</sub> emissions, must utilise carbon capture and storage (CCS) technologies to supply affordable low-carbon electricity at large scales. CCS is a scheme for reducing the emission of CO<sub>2</sub> from large stationary sources  
20 (including power plants, natural gas processing plants, hydrogen production plants, industrial furnaces, blast furnaces in the steel industry, kilns in the cement industry, municipal solid waste incinerators, etc.) whilst maintaining the use of carbonaceous fuels (e.g. coal and biomass). With CCS, conventional power plants will be able to generate low-carbon electricity at reasonable costs (US\$40 – 100/tCO<sub>2</sub> avoided, or US\$50 – 200/MWh). Compared to other  
25 means to reduce the carbon footprint of an industrialised economy (e.g. using renewable energy sources), CCS presents a highly affordable solution for rapid, large-scale decarbonisation.

The prerequisite of the CCS scheme is the separation of CO<sub>2</sub> from industrial process streams  
30 to produce a stream of concentrated (close to 100%) CO<sub>2</sub>, which is easier to compress, liquefy, transport and utilise than raw, dilute CO<sub>2</sub>-containing flue gases. For CO<sub>2</sub> capture, three approaches exist: post-combustion capture, pre-combustion capture, and oxy-combustion. Regardless of the approaches used, carbon capture processes essentially involve gas separation and are ubiquitously associated with substantial energy penalty, which can account  
35 for 10 – 35% of the thermal energy input to the power plants. In the case of post-combustion and pre-combustion capture, energy penalties arise from the separation of CO<sub>2</sub> from

combustion flue gas and syngas, respectively. For oxy-fuel combustion, the energy penalty arises from the separation of oxygen from air, often by cryogenic distillation.

In oxy-fuel combustion, a pure stream of oxygen devoid of nitrogen is used as the oxidant.

- 5 Therefore, the flue gas contains mostly CO<sub>2</sub> and steam. Combustion in a N<sub>2</sub>-free environment also avoids NO<sub>x</sub> formation. After water condensation, the product is a CO<sub>2</sub> stream of high purity that can be readily transported or stored for sequestration and utilisation.

- 10 Maximizing efficiency is a primary objective in the design and operation of thermal power cycles. To achieve this goal, engineers and researchers have proposed various approaches, such as optimizing thermal fluid pressure and temperature levels, employing more efficient heat exchangers, and leveraging advanced materials for components.

- 15 Recent advancements in materials science and engineering have facilitated the development of components and systems capable of withstanding increasingly elevated temperatures and pressures, thereby enabling enhanced thermal efficiency. Notably, the ability to surpass steam pressures exceeding 35 MPa and temperatures surpassing 700 °C (i.e., ultra-supercritical steam) constitutes a significant breakthrough in thermal power generation technology. Alternatively, novel power cycles using thermal fluids other than steam have been proposed and developed. Among these novel cycles, supercritical CO<sub>2</sub> cycles (sCO<sub>2</sub>) have garnered considerable attention as an efficient and sustainable alternative to conventional thermal power cycles, partly owing to the distinctive properties of supercritical CO<sub>2</sub> such as superior heat transfer characteristics and higher energy density.

- 25 Specifically, the sCO<sub>2</sub> cycle offers several advantages over other power cycles, e.g. the steam Rankine cycle. Firstly, the critical point of CO<sub>2</sub> is much lower in temperature and pressure than those of water, i.e. it is much easier for CO<sub>2</sub> to achieve supercritical state. Secondly, sCO<sub>2</sub> is inert and non-corrosive to the turbine material, unlike water-steam mixtures; this lifts the restrictions on the turbine inlet temperature and pressure, allowing higher cycle efficiencies. 30 Thirdly, the specific power level (power output per unit fuel) and the fluid density of sCO<sub>2</sub> are high, making it possible for sCO<sub>2</sub> plants to employ more compact turbomachinery. As a result, the smaller size of sCO<sub>2</sub> turbines also means that they require less cooling water than conventional steam turbines, which often rely on large cooling utilities. Therefore, the overall system size and water usage are significantly reduced, making sCO<sub>2</sub> cycles a more 35 environmentally friendly option.

Given the advantages explained above, sCO<sub>2</sub> cycles have gained significant attention and are being developed for deployment in various energy applications, including concentrated solar power, waste heat recovery, and nuclear power plants. The Allam cycle, one of the embodiments of a trans-critical CO<sub>2</sub> power cycles, is an oxyfuel combustion-based technology, which uses CO<sub>2</sub> as the thermal fluid. The typical process flowsheet of the Allam cycle is illustrated in Fig. 1. As shown in Fig. 1, the Allam cycle includes:

- 1a. natural gas feed, entering the fuel compressor;
- 2a. fuel compressor;
- 3a. compressed natural gas feed, exiting the fuel compressor and entering the combustion chamber along with (4a) and (5a);
- 4a. recycled supercritical mixture of CO<sub>2</sub> and O<sub>2</sub>, exiting the recuperator and entering the combustion chamber along with (3a) and (5a);
- 5a. recycled supercritical CO<sub>2</sub> coolant mixture, exiting the recuperator and entering the combustion chamber along with (3a) and (4a);
- 6a. combustion chamber;
- 7a. hot flue gas products of combustion, exiting the combustion chamber and entering the supercritical turbine along with (8a);
- 8a. recycled supercritical CO<sub>2</sub> coolant mixture, exiting the recuperator and entering the supercritical turbine along with (7a);
- 9a. supercritical CO<sub>2</sub> turbine;
- 10a. expanded gas mixture, exiting the supercritical CO<sub>2</sub> turbine and entering the recuperator as hot gas;
- 11a. recuperator;
- 12a. cooled expanded gas mixture, exiting the recuperator and entering the water condenser;
- 13a. condenser;
- 14a. condensed water discharged from the water condenser;
- 15a. high purity CO<sub>2</sub> stream, exiting the water condenser and being split into (17a) and (18a);
- 16a. stream splitter;
- 17a. CO<sub>2</sub> emissions captured from the combustion of fossil fuel which can be safely processed, transported and stored/utilised;
- 18a. recycled CO<sub>2</sub> from the emissions of combustion, entering the gas compressor;
- 19a. gas compressor;
- 20a. compressed CO<sub>2</sub> gas, exiting the gas compressor and entering the CO<sub>2</sub> cooler;
- 21a. gas cooler;
- 22a. cooled compressed CO<sub>2</sub> liquid, exiting the CO<sub>2</sub> cooler and entering the pump;

- 23a. CO<sub>2</sub> pump;
- 24a. pumped CO<sub>2</sub> liquid, split into (26a) and (27a)
- 25a. stream splitter
- 26a. part of pure CO<sub>2</sub> to be used as coolant;
- 5 27a. part of pure CO<sub>2</sub> to be gasified and mixed with pure O<sub>2</sub>;
- 28a. CO<sub>2</sub> gasifier;
- 29a. CO<sub>2</sub> gas to be mixed with pure CO<sub>2</sub>;
- 30a. air feed to the air separation unit;
- 31a. air separation unit;
- 10 32a. N<sub>2</sub> by-product of air separation unit;
- 33a. pure O<sub>2</sub>;
- 34a. stream splitter;
- 35a. mixed stream of CO<sub>2</sub> and O<sub>2</sub>;
- 36a. supercritical CO<sub>2</sub> compressor;
- 15 37a. supercritical mixture of CO<sub>2</sub> and O<sub>2</sub>;
- 38a. liquid CO<sub>2</sub> pump;
- 39a. high pressure CO<sub>2</sub> liquid;
- 40a. stream splitter;
- 41a. part of high pressure CO<sub>2</sub> liquid sent to recuperator to gasify to be used as coolant
- 20 flow in combustion chamber; and
- 42a. part of pumped CO<sub>2</sub> liquid recycle sent to recuperator to gasify to be used as coolant
- in turbine.

As illustrated in Fig. 1, there is a combustion chamber 6a, and an air separation unit (ASU)

25 31a. The key feature of the Allam cycle is the combustion of fuel at a high pressure in the presence of a mixture of supercritical CO<sub>2</sub> (sCO<sub>2</sub>) and O<sub>2</sub>; the latter is supplied by a cryogenic ASU. The flue gas, also in supercritical state, is expanded through a sCO<sub>2</sub> turbine to generate electricity. As such, the Allam cycle avoids the use of a steam Rankine cycle (with steam turbine); this reduces the physical footprint of the entire process (e.g. a sCO<sub>2</sub> turbine is only

30 10% the size of a conventional steam turbine of the same wattage). The absence of nitrogen in the Allam cycle also completely eliminate any potential for NO<sub>x</sub> emission, which has been a major pollutant in conventional nature gas combined cycle (NGCC) power plants.

The performance of the Allam cycle depends on the temperature and pressure at which the

35 hot combustion flue gas enters the turbine. The optimal values for turbine inlet temperature (TIT) and pressure have been determined to be 1000 – 1200 °C and 200 – 400 bar, respectively, for achieving high working efficiency.

The design components of this cycle present several challenges, one of which is the heat recuperator section responsible for managing multiple hot and cold streams. This section encounters a significant pressure gradient between the different streams, requiring a large heat transfer area. Additionally, the presence of CO<sub>2</sub> and condensing water in the hot side poses a risk of equipment corrosion. Furthermore, there is a notable imbalance between the heat required by the high pressure recycle streams and the heat supplied by the low-pressure turbine exhaust. To address this imbalance, external heat sources such as the ASU air compressors or the CO<sub>2</sub> recycle compressors can be introduced into the recuperator. However, this adds complexity to the overall process and diminishes the novelty of flexible operation.

In addition to the high efficiency of the supercritical CO<sub>2</sub> cycle, the oxygen supply to the Allam cycle must be produced by economical and renewable methods. The current technology for supplying oxygen to the Allam cycle is cryogenic air distillation. However, even an optimized cryogenic air separation process imposes an energy penalty that is equivalent to 5 – 16 % of the LHV of the fuel consumed, i.e. an efficiency reduction of 5 – 16% points. The scale of this energy penalty is comparable to those of competing carbon capture technologies, such as post-combustion capture by amine scrubbing. In addition, cryogenic air separation is capital-intensive and requires substantial land space.

There have been attempts to develop non-cryogenic and non-adsorption-based methods of air separation, including temperature swing absorption using alkali metal nitrates and nitrites, electrolytic methods and thermochemical splitting of water. However, these methods did not lead to large-scale deployment owing to inherent difficulties related to their thermodynamic feasibility and low throughputs.

Therefore, there exists a need for new power production systems for improving the thermodynamic performance of the overall scCO<sub>2</sub>-based power generation scheme with inherent CO<sub>2</sub> capture.

### Summary of Invention

It has been surprisingly found that one can incorporate an air separation technology that is driven by high temperature through a highly recuperative cycle to enable CO<sub>2</sub>-driven power generation. As such, the current invention uses this high temperature air separation technology to replace typical air separation technologies (cryogenic air separation) that are

used in conventional systems. Aspects and embodiments of the invention are provided in the following numbered clauses.

1. A power production system, comprising:
  - 5 a combustor configured to combust a fuel stream and an oxygen-enriched supercritical CO<sub>2</sub> stream to produce a combustion stream;
  - a supercritical CO<sub>2</sub> turbine configured to expand the combustion stream to provide a first discharge stream;
  - a condenser configured to receive the first discharge stream and provide a recycled
  - 10 CO<sub>2</sub> stream;
  - a high-temperature air separation system comprising:
    - an oxidation reactor configured to house an oxygen carrier
    - material in a reduced state, the oxidation reactor configured to receive
    - compressed air and in use produce a depleted air stream and the
    - 15 oxygen carrier material in an oxidised state;
    - a hot air turbine configured to expand the depleted air stream to provide a second discharge stream;
    - a reduction reactor configured to house the oxygen carrier material in an oxidised state, the reduction reactor configured to receive the
    - 20 recycled CO<sub>2</sub> stream and in use produce an oxygen-enriched CO<sub>2</sub> stream and the oxygen carrier material in a reduced state;
    - a means or apparatus to transfer the oxygen carrier material from the oxidation reactor to the reduction reactor and *vice versa* when housed therein;
  - 25 a compressor configured to receive the oxygen-enriched CO<sub>2</sub> stream to produce an oxygen-enriched supercritical CO<sub>2</sub> stream; and
  - a recuperator configured to interact with:
    - the first discharge stream from the supercritical CO<sub>2</sub> turbine and reduce its
    - temperature;
    - 30 the recycled CO<sub>2</sub> stream and increase its temperature;
    - the oxygen-enriched CO<sub>2</sub> stream and reduce its temperature; and
    - the oxygen-enriched supercritical CO<sub>2</sub> stream and increase its temperature.
2. The power production system according to Clause 1, wherein in an initial state, the
- 35 oxygen carrier material is present in one or both of:
  - (i) the oxidation reactor in a reduced state; and
  - (ii) the reduction reactor in an oxidised state.

3. The power production system according to Clause 2, wherein the oxygen carrier material is a material capable of cyclically taking up and releasing gaseous oxygen in substantially concentrated CO<sub>2</sub> at a temperature of from 500 to 700 °C and a pressure of from 100 kPa to 10,000 kPa, optionally wherein the oxygen carrier material is selected from one or more of MnO<sub>2</sub>, Co<sub>2</sub>O<sub>3</sub>, CuO, mixed-metal oxides (e.g. CaMnO<sub>3</sub> and SrFeO<sub>3</sub>), composites thereof, and solid solutions thereof.
4. The power production system according to Clause 2 or Clause 3, wherein the oxygen carrier material is in a solid form, optionally wherein the oxygen carrier material is in particulate form, further optionally wherein the oxygen carrier material further comprises one or more catalysts and promoters (e.g. selected from one or more of the group consisting of Au, Ag, CeO<sub>2</sub> and ZrO<sub>2</sub>) to enhance the rates of the uptake and release of oxygen.
5. The power production system according to any one of the preceding clauses, wherein the high-temperature air separation system is a chemical looping apparatus.
6. The power production system according to any one of the preceding clauses, wherein the means or apparatus to transfer the oxygen carrier material from the oxidation reactor to the reduction reactor and *vice versa* is selected from one or more of the group consisting of a circulating fluidised beds system, a moving beds system, a parallel packed beds system, a rotating disc system and an oxygen permeating membrane separation system.
7. The power production system according to any one of the preceding clauses, wherein one or more of the following apply:
- (a) the system further comprises a fuel compressor to compress a fuel and provide the compressed fuel to the combustor;
  - (b) the system further comprises an air compressor to compress air and provide the compressed air to the oxidation reactor of the high-temperature air separation system; and
  - (c) the system further comprises a means or apparatus to remove a portion of the recycled CO<sub>2</sub> stream, optionally wherein the means or apparatus is a valve.
8. A method of power generation comprising:
- mixing a fuel stream and an oxygen-enriched supercritical CO<sub>2</sub> stream together and
  - introducing the mixed stream into a combustor operating at a pressure of up to 30,000 kPa;
  - combusting the fuel to provide a combustion stream comprising CO<sub>2</sub> and one or more secondary components;

- expanding the combustion stream across a supercritical CO<sub>2</sub> turbine to generate power and provide a first discharge stream comprising CO<sub>2</sub> and one or more secondary components, the supercritical CO<sub>2</sub> turbine having an inlet for receiving the combustion stream and an outlet for release of the first discharge stream, where the combustion stream is provided to the
- 5 supercritical CO<sub>2</sub> turbine inlet at a temperature of from 1,000 to 1,500 °C;
- withdrawing heat from the first discharge stream by passing the first discharge stream through a recuperator to provide a cooled first discharge stream;
- passing the cooled first discharge stream through a condenser to remove one or more secondary components that are present in the cooled first discharge stream to provide a
- 10 recycled CO<sub>2</sub> stream;
- heating the recycled CO<sub>2</sub> stream by passing the recycled CO<sub>2</sub> stream through the recuperator to provide a heated recycled CO<sub>2</sub> stream having a temperature of from 500 to 900 °C;
- passing the heated recycled CO<sub>2</sub> stream through a high-temperature air separation
- 15 system that is operating at a temperature of from 500 to 900 °C and a pressure of up to 10,000 kPa, to provide an oxygen-enriched CO<sub>2</sub> stream;
- withdrawing heat from the oxygen-enriched CO<sub>2</sub> stream by passing the oxygen-enriched CO<sub>2</sub> stream through the recuperator to provide a cooled oxygen-enriched CO<sub>2</sub> stream;
- 20 compressing the cooled oxygen-enriched CO<sub>2</sub> stream to provide an oxygen-enriched supercritical CO<sub>2</sub> stream; and
- heating the oxygen-enriched supercritical CO<sub>2</sub> stream for introduction to the combustor, wherein
- the high-temperature air separation system operates by:
- 25 introducing a compressed air stream into an oxidation reactor comprising an oxygen carrier material in a reduced state to provide a depleted air stream and the oxygen carrier material in an oxidised state;
- expanding the depleted air stream across a hot air turbine to generate power and provide a second discharge stream; and
- 30 transporting the oxygen carrier material in an oxidised state to a reduction reactor operating at a pressure of from 100 kPa to 10,000 kPa where it meets the heated recycled CO<sub>2</sub> stream to provide the oxygen-enriched CO<sub>2</sub> stream and the oxygen carrier material in a reduced state, which is transported back to the oxidation reactor for re-oxidation, and wherein
- 35 the one or more secondary components comprise water.

9. The method according to Clause 8, wherein a product CO<sub>2</sub> stream is withdrawn from the recycled CO<sub>2</sub> stream prior to passing through the recuperator.
10. The method according to Clause 9, wherein the product CO<sub>2</sub> stream comprises  
5 substantially all of the CO<sub>2</sub> formed by combustion of the fuel.
11. The method according to any one of Clauses 8 to 10, wherein the said combustion is carried out at a temperature of from about 1,200° C to about 5,000° C.
- 10 12. The method according to any one of Clauses 8 to 11, wherein the fuel comprises one or more of hydrogen, a hydrocarbon gas, and carbon monoxide, optionally wherein the fuel is mixed with one or more diluents selected from H<sub>2</sub>O, and an inert gas (e.g. N<sub>2</sub> and Ar)
13. The method according to any one of Clauses 8 to 12, wherein the oxygen carrier  
15 material is a material capable of cyclically taking up and releasing gaseous oxygen in substantially pure CO<sub>2</sub> at a temperature of from 500 to 700 °C and a pressure of from 100 kPa to 10,000 kPa.
14. The method according to Clause 13, wherein the oxygen carrier material is selected  
20 from one or more of MnO<sub>2</sub>, Co<sub>2</sub>O<sub>3</sub>, CuO, mixed-metal oxides (e.g. CaMnO<sub>3</sub> and SeFeO<sub>3</sub>), composites thereof, and solid solutions thereof.
15. The method according to Clause 13 or Clause 14, wherein the oxygen carrier material is in a solid form, optionally wherein the oxygen carrier material is in particulate form, further  
25 optionally wherein the oxygen carrier material further comprises one or more catalysts to facilitate the uptake and release of oxygen.
16. The method according to any one of Clauses 8 to 15, wherein the recycled CO<sub>2</sub> stream is a substantially pure CO<sub>2</sub> stream, optionally wherein the recycled CO<sub>2</sub> stream is from 98 to  
30 99 mol% CO<sub>2</sub>.
17. The method according to any one of Clauses 8 to 16, wherein one or both of the first discharge stream and the recycled CO<sub>2</sub> stream are maintained at a pressure of from 2,500 to 5,000 kPa, such as about 3,000 kPa.  
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18. The method according to any one of Clauses 8 to 17, wherein the high-temperature air separation system is a chemical looping apparatus.

19. The method according to any one of Claims 8 to 18, wherein the means or apparatus to transfer the oxygen carrier material from the oxidation reactor to the reduction reactor and *vice versa* is selected from one or more of the group consisting of a circulating fluidised beds system, a moving beds system, a parallel packed beds system, a rotating disc system and an oxygen permeating membrane separation system.

### Drawings

- Fig. 1 depicts a schematic process flowsheet of a natural gas fuelled Allam power cycle.

Fig. 2 depicts a schematic of the chemical looping air separation (CLAS) process.

- Fig. 3 depicts the equilibrium partial pressure of  $O_2$  as a function of temperature for four different redox couples operating at 30 bar. The line  $OR_{in}$  indicates  $p_{O_2}$  at the inlet to OR (i.e. 6.3 bar) and the line  $RR_{out}$  indicates  $p_{O_2}$  of at the outlet of RR (i.e. 1.23 bar).

- Fig. 4 depicts a schematic process flowsheet of the Allam-CLAS cycle using (a) Mn-OCs and (b) Co-OCs.

- Fig. 5 depicts the effect of air flow rate and solids circulation on oxidation reactor exit temperatures for (a) Mn-OCs and (b) Co-OCs, respectively, and reduction reactor exit temperatures for (c) Mn-OCs and (d) Co-OCs, respectively.

- Fig. 6 depicts the effect of air flow rate and solids circulation on net electrical efficiency for the Allam-CLAS cycle running on (a) Mn-OCs and (b) Co-OCs.

- Fig. 7 depicts the effect of inert support mass fraction and solids circulation rate on oxidation reactor exit temperatures for (a) Mn-OCs and (b) Co-OCs, respectively, and reduction reactor exit temperatures for (c) Mn-OCs and (d) Co-OCs, respectively.

Fig. 8 depicts the effect of inert support mass fraction and solids circulation rate on the net energy efficiency of the Allam-CLAS cycle with Mn-OCs.

- Fig. 9 depicts the Sankey diagrams for Allam-CLAS cycles using (a) Mn-OCs and (c) Co-OCs, supplemented by the breakdowns of the sources of exergy destruction by component for Allam-CLAS cycles using (b) Mn-OCs and (d) Co-OCs.

**Fig. 10** depicts the Sankey diagram showing the flow of exergy through the various components of the Mn-OC based Allam-CLAS cycle.

- 5 **Fig. 11** depicts the Sankey diagram showing the flow of exergy through the various components of the Co-OC based Allam-CLAS cycle.

**Fig. 12** depicts the effect of isentropic efficiency of turbomachinery on overall performance of (a) Mn-OCs and (b) Co-OCs.

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**Fig. 13** depicts a schematic process flowsheet of the Co based Allam-CLAS cycle with the addition of reactor and turbine cooling.

- 15 **Fig. 14** depicts the effect of coolant flow on combustion temperature ( $T_{comb}$ ), turbine outlet temperature ( $TOT$ ), oxidant mixture temperature ( $T_{oxid}$ ), and net electrical efficiency ( $\eta_{net}$ ) of the Allam-CLAS system.

20 **Fig. 15** depicts a schematic illustration of the proposed next-generation ultra-efficient power cycle with inherent air separation and CO<sub>2</sub> capture, employing a generic high temperature air separation module (190), a generic heat recuperation scheme (24b) and natural gas (1b) as the fuel.

**Fig. 16** depicts a schematic illustration of the combined cycle gas turbine process (CCGT) fitted with post-combustion carbon capture (by amine scrubbing).

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**Fig. 17** depicts a schematic illustration of the triple pressure heat recovery steam generator.

**Fig. 18** depicts a schematic illustration of the amine CO<sub>2</sub> capture process using monoethanolamine (MEA) solvent.

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**Fig. 19** depicts a schematic illustration of high temperature air separation (HTAS) realised using a chemical looping concept with two interconnected reactors with solid (oxygen carrier) circulation between them.

- 35 **Fig. 20** depicts a schematic illustration of the oxyfuel combustion CCGT process. Oxygen is supplied by a cryogenic ASU.

Fig. 21 depicts a schematic illustration of the cryogenic ASU.

Fig. 22 depicts a schematic illustration of the pre-combustion capture of natural gas with amine scrubbing.

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Fig. 23 depicts a schematic illustration of the Allam cycle using ASU.

#### Description

10 As noted above, it has been surprisingly found that an Allam cycle system can be used in conjunction with a high temperature air separation system (e.g. a chemical looping air separation (CLAS) system) that enables the use of high-temperature oxygen instead of using cryogenic sources of oxygen to achieve a 56.04% net electrical efficiency with a 100% CO<sub>2</sub> capture rate (e.g. when a Co<sub>3</sub>O<sub>4</sub>-based oxygen carrier material is used). This disclosed Allam-CLAS power cycle presents a highly efficient and cost-competitive solution to generate zero-carbon electricity from natural gas. Thus, in a first aspect of the invention, there is provided a power production system, comprising:

- 15 a combustor configured to combust a fuel stream and an oxygen-enriched supercritical CO<sub>2</sub> stream to produce a combustion stream;
- 20 a supercritical CO<sub>2</sub> turbine configured to expand the combustion stream to provide a first discharge stream;
- a condenser configured to receive the first discharge stream and provide a recycled CO<sub>2</sub> stream;
- a high-temperature air separation system comprising:
  - 25 an oxidation reactor configured to house an oxygen carrier material in a reduced state, the oxidation reactor configured to receive compressed air and in use produce a depleted air stream and the oxygen carrier material in an oxidised state;
  - a hot air turbine configured to expand the depleted air stream to provide a second discharge stream;
  - 30 a reduction reactor configured to house the oxygen carrier material in an oxidised state, the reduction reactor configured to receive the recycled CO<sub>2</sub> stream and in use produce an oxygen-enriched CO<sub>2</sub> stream and the oxygen carrier material in a reduced state;
  - 35 a means or apparatus to transfer the oxygen carrier material from the oxidation reactor to the reduction reactor and vice versa when housed therein;

a compressor configured to receive the oxygen-enriched CO<sub>2</sub> stream to produce an oxygen-enriched supercritical CO<sub>2</sub> stream; and

a recuperator configured to interact with:

5 the first discharge stream from the supercritical CO<sub>2</sub> turbine and reduce its temperature;

the recycled CO<sub>2</sub> stream and increase its temperature;

the oxygen-enriched CO<sub>2</sub> stream and reduce its temperature; and

the oxygen-enriched supercritical CO<sub>2</sub> stream and increase its temperature.

10 In embodiments herein, the word “comprising” may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word “comprising” may also relate to the situation where only the components/features listed are intended to be present (e.g. the word “comprising” may be replaced by the phrases “consists of” or “consists essentially of”). It is explicitly contemplated that both the broader and narrower interpretations  
15 can be applied to all aspects and embodiments of the present invention. In other words, the word “comprising” and synonyms thereof may be replaced by the phrase “consisting of” or the phrase “consists essentially of” or synonyms thereof and *vice versa*.

The phrase, “consists essentially of” and its pseudonyms may be interpreted herein to refer to  
20 a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than 97% pure, such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

25 The combustor may be configured to receive two separate streams of gas – one being a fuel stream and one being an oxygen-enriched supercritical CO<sub>2</sub> stream or, more particularly, it may be configured to receive a combined gas stream formed from these two separate streams. In the latter case, the system may further comprise a suitable means or apparatus to effect mixing of the fuel (e.g. natural gas) and oxygen-enriched supercritical CO<sub>2</sub> streams before  
30 they are fed into the combustor. The combustor may be any suitable combustor and should be capable of operating at pressures of up to 30,000 kPa in a safe manner.

The term “recuperator” when used herein is intended to take its ordinary meaning in the art. As such, recuperator is a type of heat exchanger that has separate flow paths for each fluid  
35 that flows through its passages and heat is transferred through the separating walls.

As will be appreciated, the above aspect describes the system with reference to the components and how they interact together to provide the advantageous effects disclosed herein. With that in mind, it will be appreciated that the system described above does not include any of the chemical components. However, in an initial state for the chemical and energy processes discussed herein, an oxygen carrier material may be loaded into one or both of:

- (i) the oxidation reactor in a reduced state; and
- (ii) the reduction reactor in an oxidised state.

As will be appreciated, the oxygen carrier material may be loaded into only one of the oxidation and reduction reactors, or both (in the desired forms). The oxygen carrier material may be any suitable material that is capable of cyclically taking up and releasing gaseous oxygen in substantially concentrated CO<sub>2</sub> at a temperature of from 500 to 700 °C and a pressure of from 100 kPa to 10,000 kPa. When used herein, the term "substantially concentrated CO<sub>2</sub>" refers to a CO<sub>2</sub> gas stream that is >90 mol%, such as >95 mol%, such as from 98 to ≥99 mol% of CO<sub>2</sub>. Any material that has the properties required above may be used as an oxygen carrier material. Suitable oxygen carrier materials include, but are not limited to a material selected from one or more of MnO<sub>2</sub>, Co<sub>2</sub>O<sub>3</sub>, CuO, mixed-metal oxides (e.g. CaMnO<sub>3</sub> and SrFeO<sub>3</sub>), composites thereof, and solid solutions thereof.

The oxygen carrier material may conveniently be provided in a solid form (and is capable of remaining in solid form at the operating temperatures mentioned above). Particular solid forms of the oxygen carrier material that may be mentioned herein include, but are not limited to, particulate form.

The oxygen carrier material may also, in some embodiments, further comprise one or more catalysts and promoters (e.g. selected from one or more of the group consisting of Au, Ag, CeO<sub>2</sub> and ZrO<sub>2</sub>) to enhance the rates of the uptake and release of oxygen.

In embodiments of the invention that may be mentioned herein, the high-temperature air separation system may be a chemical looping apparatus.

In embodiments of the invention that may be mentioned herein, the means or apparatus to transfer the oxygen carrier material from the oxidation reactor to the reduction reactor and vice versa may be selected from one or more of the group consisting of a circulating fluidised beds system, a moving beds system, a parallel packed beds system, a rotating disc system and an oxygen permeating membrane separation system.

In embodiments of the invention, one or more of the following may apply:

- (a) the system may further comprise a fuel compressor to compress a fuel and provide the compressed fuel to the combustor;
  - 5 (b) the system may further comprise an air compressor to compress air and provide the compressed air to the oxidation reactor of the high-temperature air separation system; and
  - (c) the system may further comprise a means or apparatus to remove a portion of the recycled CO<sub>2</sub> stream, optionally wherein the means or apparatus is a valve.
- 10 In a second aspect of the invention, there is provided a method of power generation. This aspect (and its associated apparatus) will be described by reference to Figs. 15 and 19. Thus, there is provided a method of power generation (using a power production system) comprising:
- mixing a fuel stream (3) and an oxygen-enriched supercritical CO<sub>2</sub> stream (27) together and introducing the mixed stream into a combustor (4) operating at a pressure of up to 30,000
  - 15 kPa;
  - combusting the fuel to provide a combustion stream (5) comprising CO<sub>2</sub> and one or more secondary components;
  - expanding the combustion stream (5) across a supercritical CO<sub>2</sub> turbine (6) to generate power and provide a first discharge stream (7) comprising CO<sub>2</sub> and one or more secondary
  - 20 components, the supercritical CO<sub>2</sub> turbine (6) having an inlet for receiving the combustion stream and an outlet for release of the first discharge stream, where the combustion stream (5) is provided to the supercritical CO<sub>2</sub> turbine inlet at a temperature of from 1,000 to 1,500 °C;
  - withdrawing heat from the first discharge stream (7) by passing the first discharge
  - 25 stream through a recuperator (23) to provide a cooled first discharge stream (8);
  - passing the cooled first discharge stream through a condenser (9) to remove one or more secondary components (10) that are present in the cooled first discharge stream to provide a recycled CO<sub>2</sub> stream (11);
  - heating the recycled CO<sub>2</sub> stream (11/13) by passing the recycled CO<sub>2</sub> stream through
  - 30 the recuperator (23) to provide a heated recycled CO<sub>2</sub> stream (14) having a temperature of from 500 to 900 °C;
  - passing the heated recycled CO<sub>2</sub> stream (14) through a high-temperature air separation system (18) that is operating at a temperature of from 500 to 900 °C and a pressure of up to 10,000 kPa, to provide an oxygen-enriched CO<sub>2</sub> stream (22);
  - 35 withdrawing heat from the oxygen-enriched CO<sub>2</sub> stream (22) by passing the oxygen-enriched CO<sub>2</sub> stream through the recuperator (23) to provide a cooled oxygen-enriched CO<sub>2</sub> stream (24);

compressing the cooled oxygen-enriched CO<sub>2</sub> stream (24) to provide an oxygen-enriched supercritical CO<sub>2</sub> stream (26); and

heating the oxygen-enriched supercritical CO<sub>2</sub> stream (26) for introduction to the combustor, wherein

5 the high-temperature air separation (18) system operates by:

introducing a compressed air stream (17) into an oxidation reactor (18aa) comprising an oxygen carrier material in a reduced state to provide a depleted air stream (19) and the oxygen carrier material in an oxidised state;

10 expanding the depleted air stream (19) across a hot air turbine (20) to generate power and provide a second discharge stream (21); and

transporting the oxygen carrier material in an oxidised state (18a) to a reduction reactor (18bb) operating at a pressure of from 100 kPa to 10,000 kPa where it meets the heated recycled CO<sub>2</sub> stream (14) to provide the oxygen-enriched CO<sub>2</sub> stream (22) and the oxygen carrier material in a reduced state (18b), which is transported back to the oxidation reactor for re-oxidation, and wherein

15 the one or more secondary components (10) comprise water.

In certain embodiments of the invention, a product CO<sub>2</sub> stream (12) is withdrawn from the recycled CO<sub>2</sub> stream (11) prior to passing through the recuperator. As will be appreciated, any  
20 suitable means or apparatus may be used to draw off the product CO<sub>2</sub> stream. This may be any suitable valve and the valve may be a metered valve (or a valve controlled by a flow controlling means or apparatus) to ensure that only a fixed amount of CO<sub>2</sub> is removed from the system and process. The remaining recycled CO<sub>2</sub> stream (13) may be used in the rest of the process as described above. In embodiments of the invention, the product CO<sub>2</sub> stream  
25 may comprise substantially all of the CO<sub>2</sub> formed by combustion of the fuel, thereby retaining the level of CO<sub>2</sub> gas that started in the process cycle at approximately the same amount.

The combustion that occurs in the combustor (4) may be conducted at any suitable temperature. For example, the combustion may be carried out at a temperature of from about  
30 1,200° C. to about 5,000° C. As will be appreciated, any temperature in this range may be used, but it will be understood that, for energy efficiency, the system and process will be designed to operate at an approximately constant temperature when in use. Said temperature may be selected at any point from the temperature range provided above.

35 The fuel may be any suitable fuel that can be provided in gaseous form. For example, the fuel may comprise (or consist essentially of) one or more of hydrogen, a hydrocarbon gas, and carbon monoxide. That is, the fuel can be any hydrocarbon gas, be it natural gas, petroleum

gas, or gas derived from solid fuels (including biomass). In addition to hydrocarbon fuels, CO and hydrogen in their pure form or as a mixture will also work. As will be appreciated, the fuel may also contain a small fraction of CO<sub>2</sub> and H<sub>2</sub>O, with which the system could still operate. For example, a small fraction of CO<sub>2</sub> and H<sub>2</sub>O may refer to up to a total of 40% CO<sub>2</sub> and H<sub>2</sub>O content in the fuel, such as a total CO<sub>2</sub> and H<sub>2</sub>O content in the fuel of up to 20%, or, more particularly, a total CO<sub>2</sub> and H<sub>2</sub>O content in the fuel of up to 10%, such as up to 2 %. The fuel could also contain trace amount of inert gases, such as N<sub>2</sub> and Ar, which will not significantly affect the overall operation of the system. For example, a trace amount of inert gases may be up to a total of 5% in the fuel, such as a total inert gas content in the fuel of from 1 to 2%.

Thus, the fuel may be mixed with one or more diluents, such as H<sub>2</sub>O and an inert gas. Oxygen may be present as a diluent gas and may be present in an amount of from 0.01 to 5 %. In embodiments where oxygen and inert gases are present, then the total amount of the oxygen and inert gases may be up to 5% in the fuel, such as a total oxygen and inert gas content in the fuel of from 1 to 2%.

The oxygen carrier material is as defined hereinbefore.

In embodiments of the invention, the recycled CO<sub>2</sub> stream (11/13) may be a substantially pure CO<sub>2</sub> stream. For example, the recycled CO<sub>2</sub> stream may be from 98 to 99 mol% CO<sub>2</sub>.

In certain embodiments of the invention, one or both of the first discharge stream (7) and the recycled CO<sub>2</sub> stream (11/13) may be maintained at a pressure of from 2,500 to 5,000 kPa, such as about 3,000 kPa.

As mentioned above, the high-temperature air separation system may be a chemical looping apparatus. Also, as mentioned above, the means or apparatus to transfer the oxygen carrier material from the oxidation reactor to the reduction reactor and *vice versa* may be selected from one or more of the group consisting of a circulating fluidised beds system, a moving beds system, a parallel packed beds system, a rotating disc system and an oxygen permeating membrane separation system.

The currently disclosed system and method has a number of advantages over conventional systems and methods. Some of said advantages are discussed below.

Current oxyfuel combustion processes (including the Allam cycle) use standalone cryogenic air separation units (ASUs) to supply pure oxygen by distilling liquefied air (21% oxygen). The energy consumption for air separation is high and results in a significant deduction in the net

LHV efficiency of oxy-fuel combustion power plants, including ones that utilise supercritical CO<sub>2</sub> cycles. The currently disclosed design eliminates the need for ASU by incorporating a high temperature air separation technology into the process. The efficient heat integration between the high temperature air separation technology and the oxy-combustion thermal power cycle result in a close-to-zero energy penalty associated with oxygen supply.

When a conventional oxy-fuel combustion power plant (that is coupled to cryogenic ASU) is deployed at large scales (e.g. 200 – 600 MWe), the increased demand for pure oxygen will generate a large surplus of nitrogen and argon by-products, the value of which cannot be fully recovered due to the limited market demand for nitrogen and argon. In comparison, the only by-product of our system is oxygen-lean hot air, which is expanded through a gas turbine to generate more electricity. The residual heat carried by the depleted air stream can be further recovered by using it to pre-heat the incoming air or by using an adsorption chiller to generate process chill water for compressor cooling. Therefore, the invention presents a highly efficient carbon capture technology that is relevant to regions with high reliance on natural gas power plants, such as Singapore.

The current invention provides a suitable design for natural gas power (and other suitable feedstock fuels) plants with the following unique benefits:

- (1) simultaneous power generation with near 100% carbon capture;
- (2) a high overall net energy efficiency (59.0%) comparable to that of a natural gas combined cycle (NGCC) without carbon capture;
- (3) an economically competitive solution to completely decarbonise a grid primarily fuelled by natural gas (e.g. Singapore's national grid);
- (4) cheap zero-carbon electricity supply to consumers at prices lower than business-as-usual electricity produced by existing NGCC power plants in Singapore (with an emission factor of 0.41 kgCO<sub>2</sub>/kWh electricity) after carbon tax of \$5/tCO<sub>2</sub>.

Further aspects and embodiments of the current invention are summarised in the following numbered clauses.

1. This invention is concerned with a highly efficient natural gas-based power generation process utilising supercritical CO<sub>2</sub> cycles and a metal-oxide-based high temperature air separation system.
2. In one embodiment, the invention can be used for achieving simultaneous carbon capture and power generation using natural gas with ultra-high LHV to electricity efficiency (e.g. 59.3%, such as 59.03%).

3. In another embodiment, the invention can be used to supply cheaper and greener electricity with zero CO<sub>2</sub> emission. It can therefore be deployed as a decarbonisation solution to replace the existing largescale natural gas plants, which do not capture carbon.

5 Further aspects and embodiments of the current invention will now be described by reference to the following non-limiting examples.

Examples

10 Example 1

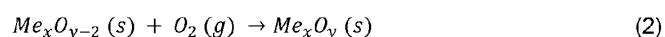
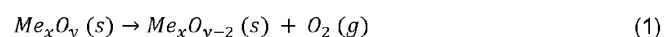
While past studies have focused on modelling the Allam cycle with ASU as the default means to supply oxygen, this study aims to integrate a novel high temperature air separation method, namely chemical looping air separation (CLAS), with the Allam cycle to improve the thermodynamic performance of the overall scCO<sub>2</sub>-based power generation scheme with inherent CO<sub>2</sub> capture.

Table 1. Nomenclature.

| Nomenclature                |                                      |                  |                                    |
|-----------------------------|--------------------------------------|------------------|------------------------------------|
| $T$                         | Temperature [°C]                     | CCS              | Carbon capture and storage         |
| $\dot{m}$                   | Mass flow rate [kg s <sup>-1</sup> ] | CLAS             | Chemical looping air separation    |
| $p$                         | Partial pressure [bar]               | CLOU             | Chemical looping oxygen uncoupling |
| $\dot{E}$                   | Exergy [kW]                          | CPU              | CO <sub>2</sub> processing unit    |
| $W$                         | Mechanical power [kW]                | EPP              | Equilibrium partial pressure       |
| Greek symbols               |                                      | HE               | Heat exchanger                     |
| $\eta$                      | Efficiency [%]                       | LHV              | Lower heating value                |
| $\omega$                    | Specific work [kJ/kg]                | LNG              | Liquefied natural gas              |
| Subscripts and superscripts |                                      | MSHE             | Multi stream heat exchanger        |
| th                          | Thermal                              | NGCC             | Natural gas combined cycle         |
| e                           | Electric                             | OC               | Oxygen carrier                     |
| w                           | Cooling water                        | OR               | Oxidation reactor                  |
| comb                        | Combustion                           | ORC              | Organic Rankine cycle              |
| oxid                        | Oxidant                              | RR               | Reduction reactor                  |
| ex                          | Exergetic                            | sCO <sub>2</sub> | Supercritical carbon dioxide       |
| Abbreviations               |                                      | SCWG             | Supercritical water gasification   |

|      |                     |     |                            |
|------|---------------------|-----|----------------------------|
| ASU  | Air separation unit | TIT | Turbine inlet temperature  |
| CASU | Cryogenic ASU       | TOT | Turbine outlet temperature |

Chemical looping air separation (CLAS) is an oxygen extraction process consisting of a chemical loop, wherein an oxygen carrier (OC) material is circulated between two reactors, viz. the oxidation and reduction reactor (Moghtaderi, B., *Energy Fuels* **2010**, *24*, 190-198), as shown in Fig. 2. The solid OC material (usually reducible oxides of transition metals) thermally decomposes in the reduction reactor (see Equation 11 below), releasing gaseous oxygen to the recycled CO<sub>2</sub> or steam. The decomposed and reduced OCs are oxidised (see Equation 11 below) in the OR to restore their original oxidation state. The oxygen-depleted air leaving the OR is then used to either preheat the incoming air or, in the case of pressurised operation, generate additional power through an expander. The regenerated OCs are circulated back to the reduction reactor, thus completing a loop. With suitable operating parameters and heat integration, the CLAS process could achieve air separation with low energy penalty. When CLAS is deployed in the form of interconnected reactors with solid circulation between them, the OCs will also serve as heat carriers to transport heat from the exothermic reaction (2) to the endothermic reaction (1), as described in the equations below.



By synergistically coupling Allam cycle with CLAS, we introduce a novel supercritical CO<sub>2</sub> based power cycle with superior energy efficiency. Specifically, the energy penalties associated with extracting oxygen from air can be minimised by the integration between CLAS and the Allam cycle, thereby achieving highly efficient generation of low-carbon electricity from natural gas with inherent capture of CO<sub>2</sub>.

## Example 2

While there are several materials which can serve as an oxygen carrier in chemical looping applications, the ones suitable for CLAS must be capable of releasing gaseous O<sub>2</sub> in the reduction reactor and taking up O<sub>2</sub> in the oxidation reactor. In addition, a good oxygen carrier should also possess high mechanical strength, cyclic durability, sintering resistance, high oxygen transfer capacity, and fast reaction rates. Amongst the 3d transition metals, the redox couples that are most suitable for CLAS include MnO<sub>2</sub>/Mn<sub>2</sub>O<sub>3</sub>, Mn<sub>2</sub>O<sub>3</sub>/Mn<sub>3</sub>O<sub>4</sub>, CoO/Co<sub>3</sub>O<sub>4</sub>, and CuO/Cu<sub>2</sub>O. In addition, mixed oxide phases (e.g. SrFeO<sub>3</sub>) have also shown promising CLAS

performance. It should, however, be noted that the oxygen release behaviour of the mixed oxide phases varies dynamically with the degree of lattice oxygen depletion; such complication makes it challenging to accurately compute the thermodynamic properties of these ternary oxide phases in process models. Therefore, the present disclosure focuses on the use of binary oxide phases (i.e. monometallic oxides) as the active components of oxygen carriers for CLAS applications.

Fig. 3 plots the equilibrium partial pressure of  $O_2$ ,  $p_{O_2,eq}$ , as a function of temperature for four monometallic oxides to illustrate the thermodynamics of oxygen release and uptake. The data used in creating Fig. 3 were taken from reference (Binnewies, M. & Milke, E., 2002. Thermochemical Data of Elements and Compounds, 168. Wiley Online Library). The heat capacities of the solid compounds and gases at constant pressure are also based on the same database and used to perform thermodynamic calculations, such as the enthalpy and Gibbs free energy of the redox reactions. The ideal range for high pressure operation of the Allam cycle was reported to be 200 – 400 bar while the optimum pressure ratio across the  $CO_2$  turbine was reported to be 6 – 12. In the present disclosure, the combustor was operated at 300 bar while the CLAS system was operated at 30 bar, assuming a pressure ratio of 10. Therefore, the  $p_{O_2}$  of the gas stream entering OR ( $OR_{in}$ ) is 6.3 bar (i.e. air with 21 vol%  $O_2$  compressed to 30 bar). Similarly, assuming the composition of the stream exiting RR ( $RR_{out}$ ) is 4.1%  $O_2$ , the  $p_{O_2}$  at  $RR_{out}$  is fixed at 1.23 bar. These operation points are denoted in the phase diagram shown in Fig. 3.

The intersection of the equilibrium curves of the metal oxides with the horizontal  $OR_{in}$  line identifies the highest operating temperature of the OR for the respective metal oxide couple. For  $CoO/Co_3O_4$ , this occurs at 1000 °C, implying that beyond this temperature, CoO cannot be oxidised to  $Co_3O_4$  in air at 30 bar. For the  $MnO_2/ Mn_2O_3$  redox couple, this upper limit is 594 °C. The  $Mn_2O_3/Mn_3O_4$  and  $CuO/Cu_2O$  equilibria do not intersect the  $OR_{in}$  line for  $T < 1200$  °C and are deemed unsuitable to be used in CLAS at 30 bar. Similarly, the intersection of the equilibria with the horizontal  $RR_{out}$  line represents the temperature below which the oxygen carriers would not spontaneously release gaseous oxygen. This lower temperature limit for RR is 537 °C for Mn-OCs and 948 °C for Co-OCs. Therefore, the present disclosure focuses on the use of the  $CoO/Co_3O_4$  and  $MnO_2/ Mn_2O_3$  redox couples for pressurised CLAS. For simplicity, the  $CoO/Co_3O_4$  and  $MnO_2/ Mn_2O_3$  redox couples are referred to as Co-OCs and Mn-OCs, respectively, from this point onwards.

### Example 3

The novel Allam-CLAS process using Mn-OCs is schematically illustrated in Fig. 4a. The model assumes the use of liquefied natural gas (1) as the feedstock. Following Fig. 4a, the fuel (natural gas) is stored in liquid form at a temperature of  $-163\text{ }^{\circ}\text{C}$  and atmospheric pressure. A pump (2) is used to pressurise the liquefied natural gas to 309 bar, in excess of 300 bar to compensate for pressure losses. The LNG, now pressurised (3), is discharged at a temperature of  $-155\text{ }^{\circ}\text{C}$  and enters the regasification heat exchanger (4). Within this heat exchanger, the LNG is heated by the exhaust gases (31) exiting the air turbine. This heat integration between the products of the CLAS cycle and the incoming fuel adds to the overall thermal efficiency of the process.

The compressed natural gas (5) at 303 bar and  $90\text{ }^{\circ}\text{C}$  is blended with a mixture of supercritical  $\text{CO}_2$  and  $\text{O}_2$ , both incoming at 303 bar and  $754\text{ }^{\circ}\text{C}$ . This mixture is co-fed to the combustion chamber (6) operating at 300 bar. The combustion exhaust products, at a temperature of  $1221\text{ }^{\circ}\text{C}$ , primarily consist of  $\text{CO}_2$  and water vapour. The expansion in the supercritical  $\text{CO}_2$  turbine (8) produces 36 MW power. The combustion exhaust (7), primarily consisting of  $\text{CO}_2$  and water vapour, is expanded in a supercritical  $\text{CO}_2$  turbine (8) with turbine inlet temperature of  $1221\text{ }^{\circ}\text{C}$ .

The turbine exhaust (9) exiting at a temperature of  $838\text{ }^{\circ}\text{C}$  is sent to a heat-exchanging recuperator (10) where it is used to heat the incoming supercritical  $\text{CO}_2$  and  $\text{O}_2$  mixture before it enters the combustion chamber. The cooled flue gas (11) is further cooled in a condenser (12) maintained at 31 bar. The condenser (12) separates the condensate water (13) from the  $\text{CO}_2$  (14). After water removal, an almost pure (99 mol%) stream of  $\text{CO}_2$  (14) is obtained.

A fraction (4%) of the pure  $\text{CO}_2$  (15) is sent to storage for sequestration or further utilisation, while the rest is recycled (16) to the high temperature air separation process. The recycled  $\text{CO}_2$  serves as a carrier gas (18) to the reduction reactor (19). Another novelty of the Allam-CLAS process lies in the use of the CLAS process, in which several reducible oxides which could be utilised as oxygen carriers. The reheated and recycled  $\text{CO}_2$  at a temperature of  $575\text{ }^{\circ}\text{C}$  is used to extract  $\text{O}_2$  from the oxidised carriers (33) in the reduction reactor and exits with a final  $\text{O}_2$  concentration of 4.1 vol%. The hot mixture of  $\text{CO}_2$  and  $\text{O}_2$  (20) passes through a cross-flow heat exchanger (17) to facilitate heat exchange and to feed the combustor (6). The circulation of  $\text{CO}_2$  in the system also facilitates heat supply from the combustion process to the CLAS unit.

Oxygen is supplied to the CLAS unit by air (25) fed through the air compressor (26). The CLAS operates at elevated pressure of up to 30 bar and  $500\text{--}600\text{ }^{\circ}\text{C}$ . After the oxidation reactor (28),

the depleted air (29, 5.5 vol% O<sub>2</sub>) is expanded in an air turbine (30). The heat of the exhaust (31) leaving the air turbine is further utilised to regasify the compressed LNG (3) in the regasification heater (4). The CO<sub>2</sub> + O<sub>2</sub> mixture (20) exiting the CLAS unit is cooled (21), compressed to supercritical pressure of 312 bar (23) in a supercritical compressor (22) and reheated (24) before entering the combustion chamber (6). The reduced carriers (34) are oxidised in the oxidation reactor (29).

The process flowsheet for Co-OCs is schematically illustrated in Fig. 4b. The CLAS sub-system employing Co-OCs differs from that using Mn-OCs due to the different operating temperature ranges that are required for CLAS, as stated in Example 2. Specifically, CLAS with Co-OCs includes additional heat recovery at the outlet and pre-heating for the inlet of oxidation reactor (29). Compressed air (27) is heated in a multi-stream heat exchanger (17) to 950 °C (28) prior to being sent to the oxidation reactor. Furthermore, heat is recovered from the oxygen-deficient stream leaving the oxidation reactor (30) before being expanded (31) in the air turbine (32). The reduced carriers (36) are oxidised in the oxidation reactor (29).

Example 4

The performance of the Allam-CLAS cycle was assessed by means of process modelling at steady state. The Allam cycle sub-system and the CLAS sub-system were modelled using Aspen Plus v10.0 software and MATLAB, respectively. Thermodynamic analysis and optimisation of the integrated system was also performed in MATLAB. The natural gas composition and thermodynamic properties used in this study (adopted from Scaccabarozzi, R. *et al.*, *Appl. Energy* **2016**, 178, 505-526) are summarised in Table 2. The process was simulated with a basis of 1 kg/s of fuel, unless specified otherwise. Peng-Robinson (PR) equation of state (EoS) was used to model the supercritical CO<sub>2</sub> power cycle as it has been reported to be the most suitable to accurately compute the thermo-physical properties and binary interactions of the relevant components involved (Li, H. & Yan, J., *Appl. Energy* **2009**, 86, 2760-2770). To verify the validity of our modelling approach, the basic Allam cycle - ASU system was simulated with similar design decisions and compared with other results of process modelling studies of Allam cycle in the literature (Scaccabarozzi, R. *et al.*, *Appl. Energy* **2016**, 178, 505-526; Chan, W. *et al.*, *Energy Convers. Manag.* **2020**, 224, 113382; and Li, B. *et al.*, *Energy Convers. Manag.* **2021**, 246, 114660).

Table 2. Natural gas composition and thermodynamic properties.

| Natural gas analysis, vol% | Value |
|----------------------------|-------|
|----------------------------|-------|

|                                   |       |
|-----------------------------------|-------|
| Methane                           | 89.00 |
| Ethane                            | 7.00  |
| Propane                           | 1.00  |
| Butane                            | 0.10  |
| Pentane                           | 0.01  |
| CO <sub>2</sub>                   | 2.00  |
| N <sub>2</sub>                    | 0.89  |
| Lower heating value (LHV) [MJ/kg] | 46.50 |

#### *Design of main components and assumptions*

The thermodynamic models and key assumptions used in the modelling of the Allam-CLAS cycle are listed in Table 3. All the components of the Allam cycle are modelled using blocks available in Aspen Plus. A RGIBBS block simulates the combustor, i.e. an equilibrium reactor solved by Gibbs free energy minimization. The temperature at the combustor outlet (i.e. turbine inlet temperature) is controlled by varying the flow rates of the recycled CO<sub>2</sub>, oxidant and the coolant. Unlike previous studies which use two heat exchangers in series, the Allam-CLAS recuperator is a single multi-flow heat exchanger. The outlet of the flue gas stream from the recuperator is set at 45 °C. The choice of using a minimum approach temperature of 5 °C and 10 °C for the cold and hot ends, respectively, is based on widely accepted values in literature, particularly in industrial settings (Zhu, Z. *et al.*, *Energy* **2019**, 174, 478–487; Zhu, Z. *et al.*, *Energy Convers. Manag.* **2019**, 199, 112058; and Rogalev, A. *et al.*, *J. Clean. Prod.* **2019**, 236, 117592). These values provide a reasonable balance between heat transfer efficiency or recovery potential and practical considerations in power plants and process industries. A stricter value of 5 °C was chosen for heat exchangers that require higher performance requirement such as cryogenic and refrigeration systems.

The material and energy flows in and out of the ASU take reference from the literature (Mancuso, L. *et al.*, *Oxy-combustion turbine power plants. IEAGHG report*, **2015**, 2015/05, 5) and are shown in Table 3, such that the performance of the ASU would be comparable to those modelled in previous studies. Table 3 also tabulates the assumed efficiencies of the turbomachinery. MCOMPR, a multistage compressor block with 5 stages of adiabatic compression and intercooling, is used to model the gas compressor. The composition of air is approximated to be 78.1 vol% N<sub>2</sub>, 21.0 vol% O<sub>2</sub> and 0.9 vol% Ar. Heat loss throughout the entire system is assumed to be negligible, unless otherwise stated. The chemical looping reactors were assumed to be perfectly mixed.

**Table 3.** Key design parameters and assumptions used in the model.

| Unit                                   | Operating condition/assumption                                                                                                                                                                                                           |
|----------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Combustion chamber                     | Operating pressure: 300 bar<br>Operation mode: Adiabatic<br>Calculation option: Phase and chemical equilibrium<br>Gibbs free energy minimization model                                                                                   |
| Chemical looping air separation (CLAS) | Operating pressure: 30 bar<br>Operation mode: Adiabatic<br>Oxygen carriers used:<br>- 60 wt% MnO <sub>2</sub> , 40 wt% Al <sub>2</sub> O <sub>3</sub><br>- 60 wt% Co <sub>3</sub> O <sub>4</sub> , 40 wt% Al <sub>2</sub> O <sub>3</sub> |
| Turbomachinery                         | Isentropic efficiency (%)<br>- Turbine – 93<br>- Compressors – 90<br>- Pump – 90<br><br>Mechanical efficiency (%)<br>- Turbine – 98<br>- Compressors – 99                                                                                |
| Pressure drops                         | Combustor, oxidation and reduction reactor – 1%<br>Recuperator high pressure flow – 1%<br>Recuperator low pressure flow - 3%<br>Condensers and intercoolers – 2%                                                                         |
| Air separation unit                    | Power consumption – 1391 kJ/kg <sub>O2</sub><br>Delivery conditions – 99.5% purity and 120 bar                                                                                                                                           |
| Recuperator and other heat exchangers  | $\Delta T_{hot} = 10\text{ }^{\circ}\text{C}$<br>$\Delta T_{cold} = 5\text{ }^{\circ}\text{C}$                                                                                                                                           |

*Thermodynamic analysis*

- 5 The gross power output of the whole cycle is computed by:

$$W_{gross} = W_{GT} \quad (3)$$

where  $W_{GT}$  is the power output by the Allam gas turbine.

The net power output of the whole cycle is computed by:

$$W_{net} = W_{GT} - W_{CLAS} \text{ (or } W_{ASU}) - W_{LNG} - W_{REC} \quad (4)$$

$$W_{CLAS} = W_{AT} - W_{AC} \quad (5)$$

where  $W_{net}$  is the net power output by Allam-CLAS;  $W_{CLAS}$  is the net power consumption by CLAS;  $W_{LNG}$  is the pumping duty of the LNG pump;  $W_{REC}$  is the compressor duty of the recycled CO<sub>2</sub> and O<sub>2</sub> mixture;  $W_{AT}$  is the air turbine output by CLAS;  $W_{AC}$  is the air compressor duty of the CLAS subsystem;  $W_{NG}$  is the power consumption associated with natural gas fuel compression.

The net specific work of the cycle is an important metric determining the system performance, defined as:

$$\omega = \frac{W_{net} (kJ/s)}{\dot{m}_{GT} (kg/s)} \quad (6)$$

where  $\dot{m}_{GT}$  is the mass flow rate of the stream entering the Allam gas turbine.

The gross electrical efficiency is defined as:

$$\eta_{gross} = \frac{W_{gross} (MW_e)}{LHV \text{ of fuel } (MJ/kg) \times \dot{m}_{fuel} (kg/s)} \times 100\% \quad (7)$$

The net electrical efficiency is defined as:

$$\eta_{net} = \frac{W_{net} (MW_e)}{LHV \text{ of fuel } (MJ/kg) \times \dot{m}_{fuel} (kg/s)} \times 100\% \quad (8)$$

A detailed exergy analysis was carried out for the Allam-CLAS system according to Tsatsaronis, G., *Energy* **2007**, 32, 249-253. The total exergy of a stream is the sum of its physical and chemical exergies:

$$\dot{E}_{t,i} = \dot{E}_{phy,i} + \dot{E}_{ch,i} \quad (9)$$

where  $\dot{E}_{t,i}$ ,  $\dot{E}_{phy,i}$  and  $\dot{E}_{ch,i}$  are the total exergy, physical exergy and chemical exergy of the  $i^{th}$  stream, respectively.

The methodology for exergy calculations were adapted from ref (Kotas, T. J., **2012**. The Exergy Method of Thermal Plant Analysis. Paragon Publishing). The physical exergy can be calculated by using:

$$\dot{E}_{phy,i} = (H - H_0) - T_0 \times (S - S_0) \quad (10)$$

where  $H$  and  $S$  are the specific molar enthalpy (kJ/kmol) and specific molar entropy (kJ/kmol-K) of the steam at the specified conditions, respectively. The subscript '0' denotes standard conditions (e.g.  $T_0$  and  $P_0$ ).

The chemical exergy is calculated by:

$$\dot{E}_{ch,i} = \dot{n} \left[ \sum_{j=1}^n x_j e_j^0 + RT_0 \sum_{j=1}^n x_j \ln(x_j) \right]$$

(11)

where  $x_j$  and  $e_j^0$  are the molar fraction and standard chemical exergy (kJ/mol) of the  $j^{th}$  component in the  $i^{th}$  stream.  $R$  is the universal gas constant.

The exergy destruction is simply the difference between the exergy entering and leaving the unit:

$$\dot{E}_d = \sum \dot{E}_{t,in} - \sum \dot{E}_{t,out}$$

(12)

The overall exergy efficiency is defined as the ratio of the net power produced and the chemical exergy of the natural gas fuel, according to Mukherjee, S. *et al.*, *J. Environ. Chem. Eng.* **2015**, 3, 2104-2114:

$$\eta_{ex} = \frac{W_{net} (MW_e)}{Chemical\ exergy\ of\ fuel (MW)} \times 100\%$$

(13)

**Example 5**

To the best of our knowledge, the Allam-CLAS cycle has not been previously studied by experiment or simulation. As a means of comparison and model validation, we simulate the conventional Allam cycle (with oxygen supplied by an air separation unit, ASU). The Allam-ASU model in the present disclosure was simulated with similar stream conditions, fuel input and operational variables as done in previously published articles. Table 4 summarises the key performance metrics of the Allam-ASU cycle modelled in this work and prior studies. The MAPE (mean absolute percentage error) values indicate that there is close agreement between the performance of the Allam-ASU model evaluated in this work and those in the literature. Therefore, the modelling approach and design assumptions used in the present disclosure are deemed acceptable and sufficiently accurate for further analysing of the performance of the Allam-CLAS system.

**Table 4.** Comparison of the modelling results of conventional Allam-ASU cycle in the present disclosure against those reported in the literature.

|  |       |                        |                                                                                  |                                                      |                                                        |                                |
|--|-------|------------------------|----------------------------------------------------------------------------------|------------------------------------------------------|--------------------------------------------------------|--------------------------------|
|  | Units | The present disclosure | Scaccabarozzi, R. <i>et al.</i> , <i>Appl. Energy</i> <b>2016</b> , 178, 505-526 | Li, B. <i>et al.</i> , <i>Energy Convers. Manag.</i> | Chan, W. <i>et al.</i> , <i>Energy Convers. Manag.</i> | Mean absolute percentage error |
|--|-------|------------------------|----------------------------------------------------------------------------------|------------------------------------------------------|--------------------------------------------------------|--------------------------------|

|                                   |                  |        |        | 2021, 246,<br>114660 | 2020,<br>224,<br>113382 | (MAPE)<br>[%] |
|-----------------------------------|------------------|--------|--------|----------------------|-------------------------|---------------|
| Thermal energy of feedstock (LHV) | MW <sub>th</sub> | 768.31 | 768.31 | 768.31               | 768.31                  | 0.00          |
| Turbine power output              | MW <sub>e</sub>  | 618.23 | 622.42 | 606.20               | 610.72                  | 1.28          |
| Recycle flow compression          | MW <sub>e</sub>  | 121.09 | 111.15 | 107.13               | 109.83                  | 9.68          |
| NG compressor                     | MW <sub>e</sub>  | 4.19   | 4.18   | 4.16                 | 4.16                    | 0.56          |
| Air separation unit               | MW <sub>e</sub>  | 85.55  | 85.54  | 85.20                | 85.55                   | 0.14          |
| Net electric power output         | MW <sub>e</sub>  | 407.40 | 419.31 | 409.13               | 409.13                  | 1.26          |
| Net specific work ( $\omega$ )    | kJ/kg            | 320.51 | 329.91 | 320.74               | 321.45                  | 1.10          |
| Net electric efficiency (LHV)     | %                | 53.03  | 54.58  | 53.06                | 53.25                   | 1.13          |
| Turbine outlet temperature        | °C               | 757.48 | 741.20 | 738.54               | 741.8                   | 2.24          |
| Recycle flow final temperature    | °C               | 741.3  | 721.20 | 718.54               | 721.8                   | 2.80          |
| Cooling flow final temperature    | °C               | 194.00 | 183.00 | 183.00               | 184.60                  | 5.40          |

|                                       |      |         |         |         |         |       |
|---------------------------------------|------|---------|---------|---------|---------|-------|
| Flue gas to condenser temperature     | °C   | 91.00   | 62.10   | 62.88   | 61.40   | 31.73 |
| Turbine inlet flow rate               | kg/s | 1271.10 | 1271.00 | 1270.99 | 1272.80 | 0.05  |
| Cooling flow rate                     | kg/s | 99.40   | 99.40   | 98.49   | 99.00   | 0.44  |
| Total recycle flow rate (with oxygen) | kg/s | 1353.90 | 1353.90 | 1352.95 | 1354.90 | 0.05  |

Example 6

In chemical looping systems, typical operating variables include solids circulation rate between the two CLAS reactors, mass flow rate of air into OR, and the mass fraction of the redox-active component in the oxygen carriers. In the present disclosure, alumina was modelled as the redox-inert component, which is expected to enhance cyclic durability of the Co-OC and Mn-OC oxygen carriers. The base design cases are modelled with oxygen carriers consisting of 40 wt% active redox component and 60 wt% alumina, as stated in Table 3. The desired operating conditions for the Allam-CLAS cycles with the specified oxygen carrier are first determined using a parametric analysis, i.e. the impact of the operating variables on the system performance, e.g. in terms of the net electrical efficiency ( $\eta_{net}$ ) was evaluated, discussed and optimized.

Effect of air flow rate and solid circulation

Fig. 5 summarizes the relationship between air flow rate and solid circulation, and the variation in outlet temperatures of the OR and RR with using Mn-OCs and Co-OCsError! Reference source not found.. Fig. 6 depicts the variation in net efficiency of the Allam-CLAS cycle with Mn-OCs and Co-OCs. The dashed lines in Fig. 6 represent the limits of operating temperatures, as discussed in Example 2.

In the case of Mn-OCs (Figs. 5a and 5c), it can be seen that increasing the solid circulation at a fixed air flow rate decreases  $T_{OR}$  and increases  $T_{RR}$ , because more heat is carried by the oxygen carrier particles from OR to RR, thereby narrowing the gap in operating temperature

between the two reactors. The decrease in  $T_{OR}$  would diminish the power produced from the depleted air turbine, rendering a lower net system output, as shown in Fig. 6a.

For the system employing Co-OCs (Figs. 5b and 5d), both  $T_{OR}$  and  $T_{RR}$  decrease with increased solids circulation. This can be explained by the design and the control strategy of the Co-OC-driven CLAS system, as shown in Fig. 4b. High solid circulation rate would remove heat from OR and cause a decline in  $T_{OR}$ , which would consequently decrease  $T_{28}$ , the temperature of the hot compressed air entering OR, owing to the control constraint imposed on the system:  $T_{28} = T_{OR} - 25$ . This decrease would inevitably disrupt the heat transfer within the MSHE, causing the oxidised solids (35) to carry less heat to RR. In addition, the control strategy fixes  $T_{31}$  (i.e. temperature of the stream entering depleted air turbine). Therefore, the overall penalty remains constant at a specific air flow rate due to constant operating temperature and volumetric flow rates through the CLAS turbomachinery. Consequently, there is no variation in efficiency with solid circulation rate, as shown in Fig. 6b.

For both OCs, when the air flow is increased, more cold air enters the OR, thereby reducing  $T_{OR}$  and indirectly reducing  $T_{RR}$ . At the same time, higher air flows give rise to higher parasitic energy penalties due to compression. Based on this analysis, it can be concluded that there is no justifiable benefit, in terms of energy efficiency, to increase the solids circulation and air flow beyond the minimum requirements (i.e. 800 kg/s and 19.11 kg/s, respectively, for the Mn-OC-driven Allam-CLAS system and 1000 kg/s and 19.11 kg/s, respectively, for the Co-OC-driven Allam-CLAS system).

#### *Effect of the mass fraction of inert support*

In the formulations of oxygen carriers, it is common to add support materials, which are often chemically inert, to improve the resistance to sintering, attrition, particle breakage and cyclic deactivation. In the present disclosure,  $Al_2O_3$  was used as a representative support material, with a simplifying assumption that there is no chemical interaction between the support and the redox active materials (i.e.  $Co_3O_4/CoO$  and  $MnO_2/Mn_2O_3$ ). To assess the effect of the inert support materials on the thermodynamic performance of the Allam-CLAS system, the mass fraction of the alumina support was adjusted between 2 wt% and 70 wt%.

From the modelling results shown in Fig. 7, it can be seen that, for both OCs, increasing the mass fraction of inert support at a given solid circulation rate reduces the temperatures of both OR and RR. However, as shown in Fig. 8, the impact of such changes on net efficiency in the case of Mn-OCs is limited to 0.3% points when operating within the desired window of operation conditions. For Co-OCs, changing the mass

fraction of the inert support does not impact the net efficiency. From an economic point of view, it makes sense to keep the solid inventories in both reactors as well as the solid circulation rate to their minima, as determined above. In practice, the optimal composition of the oxygen carriers, e.g. the optimal loading of redox-active metal oxides, should be determined experimentally under realistic operating conditions for Allam-CLAS cycle. In the subsequent modelling analyses, we continue to assume that both Mn-OCs and Co-OCs consist of 40 wt% of alumina support and 60 wt% redox-active materials.

### Example 7

Based on the optimal operation conditions (i.e. design conditions) determined in Example 6, the Allam-CLAS cycles should run with an excess air ratio of 1.2, using oxygen carriers having 40 wt% inert support, as shown in Table 3. The circulation rates for Mn-OCs and Co-OCs were set at 800 kg/s and 1000 kg/s, respectively. The thermodynamic performance of the Allam-CLAS cycle under these design conditions, as listed in Table 3, was examined and is discussed below.

#### *Energy analysis of the Allam-CLAS cycle*

The key performance metrics of the system modelled are listed in Table 5. The power output from the s-CO<sub>2</sub> turbine of the Allam-CLAS cycle is rated at 36.00 MW, which translates to a gross energy efficiency of 77.42% for both oxygen carriers examined. The overall power consumption by the recycle flow compressors, LNG pumps and the oxygen production unit for the system using Mn-OCs is 10.03 MW, yielding a net electrical efficiency of 55.85%. Given the base efficiency of the Allam-ASU cycle of 53.03%, the Mn-OC based Allam-CLAS cycle improves efficiency by 2.8% points. It is also worth noting that the net specific work output of the Mn-OCs based Allam-CLAS cycle is ~1.2 times that of the Allam-ASU cycle. According to the literature, the energy penalty associated with oxygen production by a cryogenic ASU is ~1391 kJ/kg<sub>O<sub>2</sub></sub> (Mancuso, L. *et al.*, Oxy-combustion turbine power plants. IEAGHG report, 2015, 2015/05, 5), which is equivalent to 11.1% of the total LHV of the natural gas combusted, representing substantial energy penalties associated with air separation. In comparison, the energy penalty for operating the Allam-CLAS with Mn-OCs is as low as 744 kJ/kg<sub>O<sub>2</sub></sub>, i.e. 5.9% of the total LHV value of the fuel. Clearly, using CLAS to deliver oxygen to the Allam cycle substantially reduces the penalty associated with air separation by 49%, making it significantly more efficient than ASU. The main energy consuming equipment of the CLAS system is the air compressor. Under the specified design conditions of excess air flow ratio of 1.2, the air compressor in Mn-OC based CLAS consumes 10.69 MWe while the depleted air turbine generates 7.93 MWe.

**Table 5.** Key performance metrics of the Allam-CLAS cycle.

|                                       | Units            | Allam<br>ASU | Allam-CLAS |        |
|---------------------------------------|------------------|--------------|------------|--------|
|                                       |                  |              | Mn-OCs     | Co-OCs |
| Thermal energy of feedstock (LHV)     | MW <sub>th</sub> | 768.31       | 46.50      | 46.50  |
| Turbine power output                  | MW <sub>e</sub>  | 618.23       | 36.00      | 36.00  |
| Recycle flow compression              | MW <sub>e</sub>  | 121.09       | 7.22       | 7.22   |
| NG compressor                         | MW <sub>e</sub>  | 4.19         | 0.06       | 0.06   |
| Oxygen production unit                | MW <sub>e</sub>  | 85.55        | 2.75       | 2.66   |
| Net electric power output             | MW <sub>e</sub>  | 407.40       | 25.97      | 26.06  |
| Net specific work ( $\omega$ )        | kJ/kg            | 320.51       | 378.74     | 380.05 |
| Net electric efficiency (LHV)         | %                | 53.03        | 55.85      | 56.04  |
| Turbine outlet temperature            | °C               | 757.48       | 838.20     | 838.20 |
| Recycle flow final temperature        | °C               | 741.30       | 753.50     | 753.50 |
| Cooling flow final temperature        | °C               | 194.00       | -          | -      |
| Flue gas to condenser temperature     | °C               | 91.00        | 60.00      | 60.00  |
| Turbine inlet flow rate               | kg/s             | 1271.10      | 68.57      | 68.57  |
| Cooling flow rate                     | kg/s             | 99.40        | -          | -      |
| Total recycle flow rate (with oxygen) | kg/s             | 1353.9       | 67.57      | 67.57  |

For the Co-OCs based Allam-CLAS cycle, the parasitic energy penalty associated with pumps, compressors and expanders adds up to a total of 9.94 MW, affording a net electrical efficiency of 56.04%, which is marginally higher than the Mn-OCs based Allam-CLAS cycle and 3% higher than the Allam-ASU cycle. The net specific work output of the Co-OC based Allam-CLAS system is ~1.2 times that of the Allam-ASU cycle, similar to the Mn-OC based Allam-CLAS system. When Co-OCs are used, the energy penalty associated with oxygen generation is ~719 kJ/kg<sub>O<sub>2</sub></sub>, or 5.7% of the overall LHV value of the fuel. The CLAS air compressor in the Co-OC system has identical design parameters as the case of Mn-OCs. Therefore, it also consumes 10.69 MWe, while the depleted air turbine recovers 8.03 MWe.

The minor difference in the energy performance of the CLAS sub-system between Mn-OCs and Co-OCs arises from the fact that the depleted air in the Mn-OCs system exits the OR at lower temperatures ( $T_{29} = 567$  °C) than the Co-OCs case ( $T_{31} = 600$  °C), i.e. the latter produces more shaft work per kg of depleted air. In general, the reactions taking place in RR and OR are endothermic and exothermic, respectively. Therefore, the heat integration between RR and OR, by means of solid circulation (i.e., the oxygen carriers also serve as heat carriers) is

critical to the efficient operation of the CLAS cycle. In the case of the Co-OCs, the sensible heat of the gaseous stream leaving RR is utilised to (i) heat the compressed air in a multi-stream heat exchanger and (ii) heat the incoming recycle stream of CO<sub>2</sub> (as shown in Fig. 4b). In comparison, for the Mn-OCs Allam-CLAS system, the sensible heat of the RR outlet is used to only heat the inlet to the RR (as shown in Fig. 4a). In addition, the efficiencies of both Allam-CLAS systems can be further improved by adopting waste heat utilisation methods, such as recovering the waste heat from the air compressor in the CLAS, and adopting absorption refrigeration technologies.

#### 10 Exergy Analysis

The results of the exergy analysis of the Allam-CLAS systems using Mn-OCs and Co-OCs are illustrated by Sankey diagrams, as shown in Figs. 9a and 9c, respectively. The systems' exergy outputs include the captured CO<sub>2</sub> and the net electrical power output, while the breakdown of exergy destruction by individual process component are shown in Figs. 9b and 9d. Exergy is also lost in the form of exhausts from the depleted air turbine following the regasification heater.

The overall exergy efficiency,  $\eta_{ex}$ , of the process, as defined by Eqn **Error! Reference source not found.**, is 56.94% for Mn-OCs based Allam-CLAS system; this is greater than the Allam-ASU cycle's claimed exergy efficiency of 51.62% (Li, B. *et al.*, *Energy Convers. Manag.* **2021**, 246, 114660). Because extremely irreversible adiabatic processes occur during combustion, combustors are often found to be the most exergy-wasteful component in a powerplant. Accordingly, the combustor is the biggest contributor to exergy destruction, accounting for more than half of total exergy loss. The turbomachinery is the second significant source of exergy destruction, accounting for 23% of all the exergy loss. Due to the large temperature differentials between the hot and cold streams, the recuperator, which handles numerous hot and cold streams at different pressure levels, accounts for 14% of the exergy loss. The LNG pump appears to be the most efficient process equipment, which is responsible for 0.1% of the total exergy destruction. The exergy destruction is also visually represented in Figs. 10 and 11, which show the Sankey flow diagrams of the power plant detailing the losses occurring at each unit operation.

For the Co-OCs based Allam-CLAS system, the overall exergy efficiency,  $\eta_{ex}$  is 57.13%. Similar to the Mn-OCs based system, the combustor affords >50% exergy destruction, while the turbomachinery gives rise to about 23% destruction. Owing to the greater solids circulation rates of Co-OCs (1000 kg/s) than that of Mn-OCs (800 kg/s), as well as the need to pre-heat the compressed incoming air, the Co-OCs CLAS sub-system exhibits a minor increase in

exergy destruction compared to the Mn-OCs based CLAS sub-system. Nonetheless, the Co-OCs based Allam-CLAS system provides a higher total exergy efficiency due to increased power generation and improved exergetic performance of the regasification heater, partly because the  $\text{Co}_3\text{O}_4/\text{CoO}$  redox cycle operates at higher temperatures than the  $\text{MnO}_2/\text{Mn}_2\text{O}_3$  redox cycle.

### Example 8

We examined the sensitivity of the modelling results to design assumptions, such as isentropic efficiency of turbomachinery, the addition of coolant streams, and the conditions of the fuel feedstock.

#### *Effect of isentropic efficiency of turbomachinery*

As discussed in Example 7, turbomachinery represents a major source of exergy destruction in the Allam-CLAS cycle. Therefore, we performed a sensitivity analysis to evaluate the extent of such impact, by varying the isentropic efficiencies of turbines and compressors between 85% and 95%.

From the results shown in Figs. 12a and 12b, the isentropic efficiency of the turbomachinery varies almost linearly with the net energy efficiency of the system. At 85% isentropic efficiency, the net system efficiency is between 51 – 52%; this number increases to 57 – 58% at 95% turbomachinery efficiency. For both OC systems, an increase of 1% in compressor efficiency affords a 0.5% rise in the net efficiency, while a 1% increase in turbine efficiency increases the net efficiency of the system by 0.25%. Similar sensitivity is also observed for the Allam-ASU cycle. In comparison, the efficiencies of turbomachinery have greater impact on the net efficiency of conventional combined cycle gas turbine (CCGT) powerplants, in which a 1% increase in isentropic efficiency could lead to a 1% increase in net efficiency (Horlock, J. H., *Advanced gas turbine cycles: a brief review of power generation thermodynamics*. 2013). The observation that the Allam-CLAS cycle is less susceptible to changes in the design parameter can be attributed to the use of the recuperator, which buffers the impact of inefficiency in turbomachinery, i.e. a decrease in isentropic efficiency increases the temperature of the compressed streams, thereby enhancing the pre-heating of the cold streams and subsequently increasing the effectiveness of the heat integration (Scaccabarozzi, R. *et al.*, *Appl. Energy* 2016, 178, 505-526).

#### *Effect of turbine and reactor cooling*

Turbine and reactor cooling was not incorporated in the design case of the Allam-CLAS cycle as it would reduce the thermodynamic efficiency that the power cycles could potentially achieve. In practice, the temperature at which the combustor and the supercritical CO<sub>2</sub> turbine operate should be regulated by means of cooling. In the case of the Allam cycle turbine developed by NET Power and Toshiba Corporation (Sasaki, T. *et al.*, 2017. Development of turbine and combustor for a semi-closed recuperated Brayton cycle of supercritical carbon dioxide. In: ASME Power Conference. American Society of Mechanical Engineers), turbine cooling is achieved by flowing cold CO<sub>2</sub> through nozzles placed in the holes and passageways of the inner casing. In other research works, El-Masri's continuous expansion model has been used (Scaccabarozzi, R. *et al.*, *Appl. Energy* 2016, 178, 505-526). In the present disclosure, we investigated the consequence of cooling by incorporating the insertion of two low temperature streams directly into the turbine and combustor blocks in the process model to approximate similar temperature regulation effects and study the influence on the energy balance of the system. However, it should be noted that a detailed examination of the turbine cooling model is outside the purview of this investigation.

Fig. 13 depicts the Allam-CLAS scheme specifying combustor and turbine cooling using recycled and compressed CO<sub>2</sub>, for a Co-OC based system configuration. After flue gas condensation, the "captured CO<sub>2</sub>" stream (15) is compressed in a gas compressor (37). A portion of the compressed CO<sub>2</sub> is transferred to storage (39) [VL1][MCU2][VL3], whilst the remaining (40) is cooled and liquefied (42) before compression to 300 bar to achieve supercritical state (44). The compressed supercritical CO<sub>2</sub> is regasified at 500 °C in the recuperator before being split equally to serve as two coolant streams, i.e. (45) and (46) for cooling the combustion chamber and the supercritical CO<sub>2</sub> turbine, respectively.

Fig. 14 illustrates the impact of increasing the flow rate of coolant stream (42) on the temperatures of the combustion chamber (6) [ $T_{comb}$ ], turbine outlet (9) [ $TOT$ ], oxidant mixture (24) [ $T_{oxid}$ ], and the system's net electrical efficiency. As the coolant flow is increased from 0.1 kg-CO<sub>2</sub>/s to 2.3 kg-CO<sub>2</sub>/s, which corresponds to about 0.15 – 3.35 % of the total sCO<sub>2</sub> turbine outlet flow, the temperatures of all the above-mentioned streams and components drop linearly. In the range of coolant flow rates investigated,  $T_{comb}$  declines from 1225 °C to 1173 °C, i.e. with an average rate of 24 °C/kg-CO<sub>2</sub>/s. The impacts of coolant flows on  $TOT$  and  $T_{oxid}$  are 22 °C/kg-CO<sub>2</sub>/s and 21 °C/kg-CO<sub>2</sub>/s, respectively. The net electrical efficiency of the system diminishes from 55.75% at 0.1 kg-CO<sub>2</sub>/s of coolant flow to 54.61% at 2.3 kg-CO<sub>2</sub>/s of coolant flow. Therefore, recycling, pumping, compression and reheating more CO<sub>2</sub> as coolants results in considerable drop in the power output. However, this decrease is negligible in light

of the efficiency benefits brought about by the Allam-CLAS system. In addition, the proposed cooling strategy is simple to design, implement and control, at the cost of a small efficiency penalty. Therefore, the addition of a turbine cooling scheme does not change the conclusion of the present process modelling study.

5

Several practical challenges and technical considerations that may need to be addressed for the commercial deployment of the Allam-CLAS cycle are discussed below.

- 10 a) Ensuring that the system could operate stably under varying load and transient operating conditions. This will require the development of a detailed control scheme, taking into account system dynamics. One of the possible outcomes of the control study is further modification to the system configuration.
- 15 b) The projected capital costs and operational cost (beyond fuel consumption) will dictate the competitiveness of the new Allam-CLAS scheme. While an economic analysis is out of the scope of this paper, the estimated capital cost of the traditional Allam cycle is in the range of \$900/kW to \$1200/kW, which is more favourable than natural gas-fired combined cycle power plants without carbon capture (\$1172/kW - \$1370/kW) (Rubin, E. S. & Zhai, H., *Environ. Sci. Technol.* **2012**, *46*, 3076–3084). Therefore, there is potential for the Allam-CLAS scheme to become economically competitive in the
- 20 future.
- c) Finally, the regulatory framework and policies governing the incentives and carbon pricing of zero or low emission technologies will foster the trust and investment in such power cycles.

25 *Effect of changing the inlet conditions of the fuel feedstock*

Most of the published literature has focused on using natural gas (NG) as the fuel in the Allam cycle. However, the Allam cycle can also be driven by gasified coal. When coal is used, there are a few additions and changes required for the system, such as a) coal feed and preparation system, b) coal gasifier and syngas clean-up operation, and c) syngas-combustion turbine.

30 The system would also need further optimisation to account for the differences in fuel properties, combustion characteristics and emissions. In fact, the Allam cycle has been noted to be flexible with different gasifier systems and different ranks of coal while maintaining high efficiencies in the range of 46.8–48.2%. While the Allam-CLAS cycle reported here has not been modelled using coal as the feedstock, it is anticipated that a coal-fired Allam-CLAS cycle

35 would bring the same improvement in thermodynamic efficiency.

Furthermore, the availability of natural gas depends strongly on geological locations. Therefore, in many user cases, NG is supplied by shipping in its liquefied form (LNG). LNG has a high amount of cold energy due to its boiling point of  $-162\text{ }^{\circ}\text{C}$ , which can be exploited by oxy-combustion cycles. For instance, the cold energy carried by LNG can be utilised by i) 5 flue gas condenser, or ii) chillers to produce cold water as utility. In addition, the energy consumption due to fuel compression is drastically lower, because pumping LNG and regasifying compressed LNG are significantly less energy demanding processes than compressing natural gas. For example, at the base case design conditions, the simulation results suggest that it is 21 times more energy consuming to compress natural gas to a 10 pressure of 300 bar than to pump LNG to the same pressure. Additionally, the Allam-CLAS system also eliminates the need for gas-fired regasification through thermal recuperation with the exhaust depleted air from the air turbine outlet. This is perhaps the simplest way to utilise the heat surplus from the exhaust gas but perhaps not an ideal use of the LNG cold. Alternative process options such as organic Rankine cycle (ORC) or combined cooling and power 15 generation systems could be explored at the cost of increasing the footprint, capital investment and system complexity; these may be explored in future studies.

The present disclosure proposes a novel Allam-CLAS system for the efficient generation of electricity with inherent  $\text{CO}_2$  capture (i.e. with a capture rate of 100%). The performance of the 20 Allam-CLAS system relative to the basic Allam-ASU system is evaluated by means of process modelling & thermodynamic analysis, realised through ASPEN Plus simulations and the sensitivity analysis. Compared to the Allam-ASU system, the Allam-CLAS system achieves more efficient air separation at temperatures closer to temperatures at which natural gas is oxy-combusted in supercritical conditions. After optimizing the main operating parameters of the CLAS sub-system (e.g., air flow rate and oxygen circulation rate), from the results of the 25 modelling study, the following conclusive remarks were drawn:

- a. Allam-CLAS cycle offers simultaneous power generation with 100% carbon capture at a higher net overall fuel-to-electricity conversion efficiency (56.04%) and exergy efficiency (57.14%) than the Allam-ASU cycle (net energy conversion efficiency = 53.03%, exergy 30 efficiency = 53.4%) and natural gas combined cycle plants without carbon capture (net efficiency = 50 – 55%). This is due to the replacement of the air separation unit with a significantly better performing oxygen supply process (i.e. CLAS);
- b. a promising and economically competitive solution to decarbonise a grid primarily fuelled by natural gas is proposed via this unique power generation system. The problem of 35 production of surplus  $\text{N}_2$  by-product can be avoided by eliminating the ASU from the Allam cycle. The only products are water and oxygen-lean air, with pure  $\text{CO}_2$  readily available for transportation storage at pipeline specifications;

- c. the novel Allam-CLAS cycle is also exergetically favourable, providing a 57.13% efficiency compared to the 53.4% for the Allam-ASU cycle. More than half of the losses were encountered in the combustor chamber due to irreversible destruction of exergy. This loss could be reduced to some extent by reducing the temperature gradient across the combustor;
  - d. the air flow rate into the OR greatly affects the system efficiency. The effect of excess air ratio on the system performance has been studied. Regardless of the oxygen carriers used (i.e. Mn-OCs or Co-OCs), operating at lower excess air ratios (design case value = 1.2) yields the maximum electrical output. In comparison, the solid circulation rate plays a lesser role in determining the system performance. In general, the optimum solids circulation should be decided based on the operating temperature of the CLAS system and the desired solid inventory. The design case was based on the solid circulation rate closest to the thermodynamic boundaries of operation; and
  - e. with respect to the turbomachinery, it will require compact and durable components to sustain operation under conditions desired by this novel power cycle. The isentropic efficiencies of 0.93 and 0.90 for turbine and compressor are based on values used in the literature. Notwithstanding the need for cooling turbine blades and limiting the TIT, our modelling results show that the losses due to turbine cooling are marginal.
- Taken together, the proposed cycle offers an opportunity to make significant advancement in the development of oxy-combustion-driven power cycles utilising sCO<sub>2</sub>, to achieve high cycle efficiency and zero emissions. On the other hand, further research may be performed to address the mechanical design of key components in the Allam-CLAS cycle, such as recuperator, combustor and turbomachinery.

#### Example 9

Our novel process, in its most generic representation (i.e. not specifying the detailed designs of the heat recuperation scheme or the high temperature air separation system, using natural gas as the fuel), is schematically illustrated in Fig. 15. Natural gas (1b), after compression (3b) in a fuel compressor (2b), is blended with a mixture of supercritical CO<sub>2</sub> and O<sub>2</sub> (28b), and co-fed to the combustion chamber (4b) operating up to 300 bara. The exhaust (5b), primarily consisting of CO<sub>2</sub> and water vapour, is expanded in a supercritical CO<sub>2</sub> turbine (6b) (with turbine inlet temperature of 1300 °C). The turbine exhaust (7b) is sent to a heat-exchanging recuperator (24b). The cooled flue gas (8b) is further cooled in a condenser (9b) whilst being maintained at 30 bara. The condenser (9b) separates the condensate water (10b) from the CO<sub>2</sub> (11b). After water removal, an almost pure (98~99 mol%) stream of CO<sub>2</sub> (11b) is obtained.

A stream splitter (12b) splits the pure CO<sub>2</sub> into two streams (13b) and (14b). A fraction (~5%) of the pure CO<sub>2</sub> (14b) is sent to storage for sequestration or further utilisation, while the rest (~95%) is recycled (13b), reheated to 800 °C in the recuperator (24b), and used as the carrier gas (15b) in the high temperature air separation (HTAS) unit (19b) to extract ~5% O<sub>2</sub> (23b) to feed the combustor (4b). The circulation of CO<sub>2</sub> in the system also facilitates heat supply from the combustion process to the HTAS unit (19b). Oxygen is supplied to the HTAS unit (19b) by an air compressor (17b). The HTAS operates at elevated pressure of up to 100 bara and 500 – 700 °C. After the HTAS (19b), the depleted air (20b) (~85 vol% N<sub>2</sub>) is expanded in an air turbine (21b). The heat of the exhaust (22b) leaving the air turbine can be further utilised in an absorption cooler to produce chilled water as a process utility (not shown here). The CO<sub>2</sub> + O<sub>2</sub> mixture (23b) exiting the HTAS unit is cooled (25b), compressed in the compressor (26b) to supercritical pressures (27b) and reheated (28b) before entering the combustion chamber (4b). Here, the HTAS process can be any embodiment of technologies that facilitate oxygen extraction and release at high temperatures, including chemical looping systems achieved by a circulating fluidised beds system, a moving beds system, a parallel packed beds system, and a membrane separation system.

#### Example 10

A CCGT power plant, as schematically illustrated in Fig. 16, utilises two power cycles, viz. a Brayton cycle (generating energy using the gas turbine) and a Rankine cycle (generating energy using the steam turbine). The heat transfer between the two cycles is facilitated by a heat recovery steam generator (HRSG), which extract heat from the gas turbine exhaust to supply a triple pressure (with the high pressure, intermediate pressure and low pressure stages operating at 124, 30 and 6.5 bar, respectively) steam turbine system with double reheating (see Fig. 17). Compressed natural gas (3c) is combusted in compressed air (6c), which is supplied by an air compressor (5c). The combustion chamber (7c) operates at 30 bara and produces flue gas (8c) at ~1500 °C. The hot flue gas (8c) is expanded in a gas turbine (9c) with a pressure ratio of 30:1. The gas turbine exhaust (10c), at atmospheric pressure and ~ 646 °C, is sent to a HRSG (11c) which generates, reheats, and superheats steam for the Rankine cycle (see Fig. 17). The live steam temperatures are 525, 540 and 520 °C for the high, intermediate, and low-pressure stages, respectively. With the condenser (15d, see Fig. 17) operating at 0.05 bar, the maximum allowable temperature rise of the cooling water is 10 °C. The cooled exhaust (stream 12c, at 25 °C and ~ 7 mol% CO<sub>2</sub>) is sent to a CO<sub>2</sub> capture unit (13c), where CO<sub>2</sub> (15c) is removed by a post-combustion amine capture unit (13c) using a 40% (w/w) solution of monoethanolamine (MEA).

As illustrated in Fig. 17, in the HRSG, feed water (16d) from the Condenser (15d) is pumped to a low pressure of 6.5 bar (1d) in a LP feed pump (17d) and passed through a LP Economiser (2d), where the stream (3d) is split in a stream splitter (4d) into (6d) to the IP feed pump (18d), and (5d) to the LP Evaporator (7d). The LP steam (8d) is superheated (10d) in a LP Superheater (9d) and mixed in a stream mixer (11d) with the reheated reject steam mixture (33d) from the LP reheater (32d). This mixture is expanded (14d) in the LP turbine (13d). The split stream (6d) is pumped to 30 bar (19d) and heated (21d) in the IP Economiser (20d) to be split again into (23d) feeding to the IP Evaporator (24d) and (34d) feeding into the HP feed pump (35d). The IP steam (25d) is superheated (27d) in the IP Superheater (26d) and mixed in a stream mixer (28d) with the reheated reject steam (46d) from the IP reheater (45d). This mixture is expanded (31d) in the IP turbine (30d). The split water stream (34d) is pumped to 124 bar (36d), heated (38d) in the HP Economiser (37d), vaporised (40d) in the HP Evaporator (39d), and superheated (42d) in the HP Superheater (41d) before being sent to the HP turbine (43d) where it will be expanded (44d).

As illustrated in Fig. 18, in the CO<sub>2</sub> capture unit, the exhaust gas (1e) is fed counter-currently to the lean amine solvent flow (24e) in the absorber (3e) where ~90% of the CO<sub>2</sub> is removed from the flue gas and the clean gas (4e) leaves from the top of the absorber. The CO<sub>2</sub>-rich amine (5e) is depressurised (7e) through a valve (6e), heated (10e) in a heat exchanger (8e) against the hot regenerated amine (16e) and passed as feed to the stripper (14e) where CO<sub>2</sub> is stripped off the hot amine solution. The CO<sub>2</sub> rich gas (12e) exits from the top of the stripper (14e). The cold regenerated amine (9e) from the bottom of the stripper (14e) is cooled (9e) in the heat exchanger (8e), and mixed (20e) with the water make up stream (18e) and the MEA make up stream (17e) in a mixer (19e) before being cooled further (22e) in a cooler (21e). A pump (23e) is utilised to feed the lean amine (24e) solution to the absorber/ and is recycled to the absorber (3e). As illustrated in Fig. 18, there is also a condenser (13e), and a reboiler (15e).

By simulating the CCGT + amine scrubbing system using ASPEN Plus with a basis of 1 kg/s of natural gas feed, we can calculate the energy efficiency of the CCGT power plant coupled with post-combustion capture. Similarly, our invention, the ultra-efficient supercritical CO<sub>2</sub> power cycle (as depicted in Fig. 15) is also simulated using ASPEN Plus with the same basis of natural gas feed (1 kg/s). In all the simulations performed, we assume the steam turbines, the gas turbines and the scCO<sub>2</sub> turbines all have an isentropic efficiency and a mechanical efficiency of 90% and 98%, respectively.

- The HTAS sub-process (see Fig. 19) is represented by the embodiment of a chemical looping system using the  $MnO_2/M_2O_3$  redox couple (Streams 8f and 12f) to supply oxygen; the  $MnO_2$  oxygen carrier is circulated between the reduction reactor (9f) and the oxidation reactor (4f) at a rate of ~45 kg/s. Recycled  $CO_2$  (11f) is fed to the reduction reactor at 800 °C to generate the oxygenated feed (10f). Air (1f) is pressurised (3f) in an air compressor (2f) and fed to the oxidation reactor (4f). The depleted air (5f) is expanded (7f) in a hot air turbine (6f) and released. As illustrated in Fig. 19, there is also an oxidation reactor (4f), and a reduction reactor (9f).
- 10 The key results of the process simulations, together with the efficiency analysis of both CCS power plants, are summarised in Table 6. The gas turbine output of the CCGT system is 29.9 MW (33) cf. 39.3 MW achieved by the supercritical  $CO_2$  turbine (6). On the other hand, CCGT requires less compression duty than the supercritical  $CO_2$  system. Overall, the net electrical efficiency of the CCGT power plant fitted with post-combustion amine scrubbing is 47.2% cf.
- 15 59.0% of the present disclosure. Therefore, the present disclosure offers a substantial efficiency gain margin compared to the state-of-the-art CCS solution.

Table 6. Summary of modelling results and performance comparison.

| Source                                               | CCGT<br>with post<br>combustion<br>capture | Oxyfuel<br>CCGT | Pre-<br>combustion<br>gas capture<br>CCGT | ASU-<br>supercritical<br>$CO_2$ | HTAS-<br>supercritical<br>$CO_2$ |
|------------------------------------------------------|--------------------------------------------|-----------------|-------------------------------------------|---------------------------------|----------------------------------|
| Fuel input<br>(LHV) (MW)                             | 46.5                                       | 46.5            | 46.5                                      | 46.5                            | 46.5                             |
| Gas turbine<br>for<br>combustion<br>products<br>(MW) | 29.9                                       | 21.7            | 24.5                                      | 38.0                            | 39.3                             |
| Gas turbine<br>for depleted<br>air (MW)              | -                                          | -               | -                                         | -                               | 20.8                             |
| HRSG (MW)                                            | 7.72                                       | 11.0            | 7.47                                      | -                               | -                                |
| Fuel<br>Compressor<br>(MW)                           | 0.59                                       | 0.59            | 0.59                                      | 1.2                             | 1.2                              |

|                                                           |      |      |      |      |      |
|-----------------------------------------------------------|------|------|------|------|------|
| <b>Air Compressor (MW)</b>                                | 10.5 | -    | 7.70 | -    | 21.0 |
| <b>CO<sub>2</sub> Compressor and Capture Penalty (MW)</b> | 4.6  | 5.9  | 4.0  | 6.0  | 10.4 |
| <b>ASU Penalty + O<sub>2</sub> Compressor (MW)</b>        | -    | 3.33 | -    | 6.79 | -    |
| <b>Net electric power output (MW)</b>                     | 23.0 | 22.8 | 19.7 | 24.0 | 27.5 |
| <b>Net electrical efficiency (%)</b>                      | 47.2 | 49.1 | 42.3 | 51.6 | 59.0 |

**Example 11**

In this example, we compare our ultra-efficient supercritical CO<sub>2</sub> power cycle with a natural gas-based oxyfuel combustion power plant, i.e. a CCGT system with an oxyfuel combustion gas turbine, as schematically illustrated in Fig. 20. The oxyfuel combustion CCGT system utilises pure O<sub>2</sub> (21g) supplied by a cryogenic air separation unit (19g), where air (18g) is split into its components O<sub>2</sub> (21g) and N<sub>2</sub> (20g). After compression (23g) in an oxygen compressor (22g), the pure oxygen (~ 99.5 mol%) at ~ 130 °C and 30 bar (23g), is mixed with the recycled CO<sub>2</sub> (17g) incoming at ~ 120 °C and 30 bara. Natural gas (1g) is compressed (3g) in a fuel compressor (2g) and sent to the combustion chamber (4g) along with (23g) & (17g) are mixed with compressed natural gas (3g). The combustion chamber (4g) is operating at 30 bara. The high-pressure flue gas at ~1540 °C (5g) is expanded (7g) in a gas turbine (6g). The exhaust (7g), leaving the gas turbine (6g) at ~ 25 °C, 1 bara, is sent to a heat recovery steam generator (8g). The HRSG (8g) adopts the configuration depicted in Fig. 17. The flue gas (9g) exits the

HRS (8g) at atmospheric conditions ( $\sim 25^\circ\text{C}$ , 1 bara) and is sent to a condenser (10g), which separates water (11g) from the captured, high-purity  $\text{CO}_2$  (12g). A stream splitter (13g) splits the stream (12g) into two streams. A part of it is sent to storage (14g) for further utilisation, whereas the rest (15g) is recycled and compressed (17g) to 30 bara in a supercritical  $\text{CO}_2$  compressor (16g) to be used as the carrier gas as well as the flame temperature regulator for the oxyfuel combustion (4g). As illustrated in Fig. 20, there is also an air separation unit (19g), and a compressor (16g).

The detailed process flow diagram of the air separation unit (19g) supplying the oxyfuel combustion (4g) is shown in Fig. 21. For simplicity, we assume air inlet (1h) to be composed of 21%  $\text{O}_2$ , 78.1%  $\text{N}_2$  and 0.9% Ar with no other components. In brief, fresh air (1h) is compressed (3h) in an air compressor (2h) and split into two streams (5h & 6h) in a stream splitter (4h). One stream (6h) is further compressed (8h) in a second stage air compressor (7h). Both air streams (5h & 8h) are cooled in a heat exchanger (9h) by the cold gases (19h) and liquid  $\text{O}_2$  (26h) leaving the ASU. The double-compressed cold air (10h) is cooled (12h) through expansion (11h; expander). The partially liquefied air stream (13h) is fed to the high-pressure (HP) column (14h) where Ar and  $\text{N}_2$  (15h) are produced and leave from the top. The oxygen-rich liquid (16h) leaving the bottom of the HP column is depressurised using a Joule-Thomson (JT) valve (22h) and fed (23h) to the low-pressure column (24h). The gases (15h) leaving the top of the HP column (14h) is subcooled (18h) by the cold gas (25h) leaving the LP column (24h) and further cooled (21h) by a JT-valve (20h) before entering the LP column (24h) at the top. Liquid  $\text{O}_2$  (26h) leaves the bottom of the LP column (24h) and is further heated (28h) to vaporise it to gaseous  $\text{O}_2$ , whereas the gaseous products (25h), consisting of  $\text{N}_2$  and Ar leave from the top of LP column (24h) and are heated (19h) in a subcooler (17h) before being further heated (27h) in the multi stream heat exchanger (27h).

Based on the simulation results (see Table 6), it can be seen that the ASU-oxyfuel-CCGT system achieves a net electrical efficiency of 49.1%, marginally higher than the efficiency of CCGT-amine scrubbing system evaluated in Example 10. However, our invention, viz. the ultra-efficient  $\text{scCO}_2$  power cycle still compares favourably to the ASU-oxyfuel-CCGT system in terms of net electrical efficiency (59.0% vs 49.1%), while both systems are capable of capturing all the  $\text{CO}_2$  produced by the combustion of natural gas.

### Example 12

The pre-combustion capture process removes carbon prior to combustion by firstly converting the fuel to a mixture of  $\text{CO}_2$  and  $\text{H}_2$ . The schematic flow diagram of pre-combustion capture

implemented for a CCGT scheme is shown in Fig. 22. At the inlet, natural gas (1i) is compressed (3i) in a fuel compressor (2i) before being sent as feed to the reformer (4i). Air (23i) is compressed (25i) in an air compressor (24i) before being split into two streams (27i and 28i) in a stream splitter (26i). Stream 27i serves as feed to the reformer (4i) along with the compressed natural gas (3i). The syngas (5i) produced is cooled (7i) from 1000 °C to 250 °C in the HRSG (6i). The HRSG configuration the same as the one shown in Fig. 17). Steam (9i and 12i) is fed to both Water gas shift reactors (8i and 12i). The hydrogen concentration in the syngas is progressively increased by two water gas shift reactors connected in series (8i and 12i), operating at 352 °C and 183 °C, respectively.

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The syngas (13i) leaving the low temperature shift reactor (11i) contains primarily N<sub>2</sub>, H<sub>2</sub> and CO<sub>2</sub>. Thereafter, the CO<sub>2</sub> (16i) in the syngas (14i) is removed by amine scrubbing in the CO<sub>2</sub> capture unit (15i). The configuration of the amine scrubbing unit (15i) follows the one shown in Fig. 18. After scrubbing (15i), the CO<sub>2</sub> content in the syngas (17i) is reduced to 300 ppm, i.e. the syngas consists of primarily of N<sub>2</sub> and H<sub>2</sub>. The decarbonised syngas (17i) is combusted in the combustion chamber (18i) along with the other split compressed air stream (28i) and the combustion flue (19i) is expanded (21i) through a gas turbine (20i) for power generation. The heat of the turbine outlet (21i) is further recovered by the HRSG (6i) for additional power generation and the exhaust gas (22i) is released.

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As shown in Table 6, the pre-combustion capture - CCGT process has a net LHV to electricity efficiency of 42.3%. Therefore, the said invention, with a net electrical efficiency of 59.0%, is a significantly more efficient thermoelectric power plant scheme incorporating CO<sub>2</sub> capture. In addition, the absence of the Rankine cycle in the said invention eliminates the hardware and utility requirement associated with steam generation (for both the water-gas-shift reactors and the Rankine cycle), which is a major source of energy penalty for pre-combustion carbon capture system.

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### Example 13

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The state-of-the-art supercritical CO<sub>2</sub> power cycle, viz. the Allam cycle is schematically illustrated in Fig. 23. Natural gas (1j) is compressed (3j) in a fuel compressor (2j) and fed to the combustion chamber (5j), operating at 300 bara, along with the supercritical mixture of CO<sub>2</sub> and O<sub>2</sub> (4j). The system utilises pure O<sub>2</sub> (20j) supplied by a cryogenic air separation unit (18j), where air (17j) is split into its components O<sub>2</sub> (20j) and N<sub>2</sub> (19j). The working of the ASU is described in Example 11 (also see Fig. 21). The flue gas (6j) leaves the combustion chamber (5j) at ~1450 °C and is expanded in a supercritical turbine (7j) to 30 bara at a pressure ratio

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of 10. The turbine exhaust (8j) at ~987 °C is cooled (10j) in the recuperator (9j) before being sent to the condenser (11j) where water (12j) is removed and the dehydrated CO<sub>2</sub> (13j) is split in a stream splitter (14j). A fraction of the product CO<sub>2</sub> (15j) is exported for storage and further utilisation, whereas the rest (16j) is recycled, mixed with pure O<sub>2</sub> (20j) from the ASU (18j) and re-pressurised (22j; compressor) to 300 bara (23j). This supercritical mixture (23j) is pre-heated (4j) in the recuperator (9j) before entering the combustion chamber (5j).

Based on the results of the Aspen Plus simulation (Table 6), the ASU + Allam cycle power plant (Example 13) affords a net electrical efficiency of 51.6%, which is more efficient than a conventional CCGT power plant retrofitted with post-combustion amine scrubbing (Example 10), ASU + oxyfuel combustion in CCGT (Example 11) and pre-combustion capture CCGT (Example 12). The supercritical CO<sub>2</sub> turbine output by the said invention is similar to that of the ASU-supercritical CO<sub>2</sub> process (Example 13). On the other hand, our next-generation ultra-efficient power cycle incorporates a novel HTAS technology (such as the one shown in Fig. 19) to supply the oxygen required for combustion. The heat consumed by HTAS (18) is efficiently recovered by the air turbine (20). In comparison, the cryogenic ASU consumes substantial energy to separate oxygen from air. Therefore, the said invention is substantially more efficient than the ASU + Allam cycle process (by 7.4% efficiency points).

It is clear from Examples 10 to 13 that our next-generation ultra-efficient power cycle is by far the most energy-efficient carbon capture technology compared to all other large-scale carbon capture technologies in the literature.

## Claims

1. A power production system, comprising:

a combustor configured to combust a fuel stream and an oxygen-enriched supercritical CO<sub>2</sub> stream to produce a combustion stream;

a supercritical CO<sub>2</sub> turbine configured to expand the combustion stream to provide a first discharge stream;

a condenser configured to receive the first discharge stream and provide a recycled CO<sub>2</sub> stream;

a high-temperature air separation system comprising:

an oxidation reactor configured to house an oxygen carrier material in a reduced state, the oxidation reactor configured to receive compressed air and in use produce a depleted air stream and the oxygen carrier material in an oxidised state;

a hot air turbine configured to expand the depleted air stream to provide a second discharge stream;

a reduction reactor configured to house the oxygen carrier material in an oxidised state, the reduction reactor configured to receive the recycled CO<sub>2</sub> stream and in use produce an oxygen-enriched CO<sub>2</sub> stream and the oxygen carrier material in a reduced state;

a means or apparatus to transfer the oxygen carrier material from the oxidation reactor to the reduction reactor and *vice versa* when housed therein;

a compressor configured to receive the oxygen-enriched CO<sub>2</sub> stream to produce an oxygen-enriched supercritical CO<sub>2</sub> stream; and

a recuperator configured to interact with:

the first discharge stream from the supercritical CO<sub>2</sub> turbine and reduce its temperature;

the recycled CO<sub>2</sub> stream and increase its temperature;

the oxygen-enriched CO<sub>2</sub> stream and reduce its temperature; and

the oxygen-enriched supercritical CO<sub>2</sub> stream and increase its temperature.

2. The power production system according to Claim 1, wherein in an initial state, the oxygen carrier material is present in one or both of:

(i) the oxidation reactor in a reduced state; and

(ii) the reduction reactor in an oxidised state.

3. The power production system according to Claim 2, wherein the oxygen carrier material is a material capable of cyclically taking up and releasing gaseous oxygen in substantially concentrated CO<sub>2</sub> at a temperature of from 500 to 700 °C and a pressure of from 100 kPa to 10,000 kPa, optionally wherein the oxygen carrier material is selected from one or more of MnO<sub>2</sub>, Co<sub>2</sub>O<sub>3</sub>, CuO, mixed-metal oxides (e.g. CaMnO<sub>3</sub> and SrFeO<sub>3</sub>), composites thereof, and solid solutions thereof.

4. The power production system according to Claim 2 or Claim 3, wherein the oxygen carrier material is in a solid form, optionally wherein the oxygen carrier material is in particulate form, further optionally wherein the oxygen carrier material further comprises one or more catalysts and promoters (e.g. selected from one or more of the group consisting of Au, Ag, CeO<sub>2</sub> and ZrO<sub>2</sub>) to enhance the rates of the uptake and release of oxygen.

5. The power production system according to any one of the preceding claims, wherein the high-temperature air separation system is a chemical looping apparatus.

6. The power production system according to any one of the preceding claims, wherein the means or apparatus to transfer the oxygen carrier material from the oxidation reactor to the reduction reactor and *vice versa* is selected from one or more of the group consisting of a circulating fluidised beds system, a moving beds system, a parallel packed beds system, a rotating disc system and an oxygen permeating membrane separation system.

7. The power production system according to any one of the preceding claims, wherein one or more of the following apply:

- (a) the system further comprises a fuel compressor to compress a fuel and provide the compressed fuel to the combustor;
- (b) the system further comprises an air compressor to compress air and provide the compressed air to the oxidation reactor of the high-temperature air separation system; and
- (c) the system further comprises a means or apparatus to remove a portion of the recycled CO<sub>2</sub> stream, optionally wherein the means or apparatus is a valve.

8. A method of power generation comprising:  
mixing a fuel stream and an oxygen-enriched supercritical CO<sub>2</sub> stream together and introducing the mixed stream into a combustor operating at a pressure of up to 30,000 kPa;  
combusting the fuel to provide a combustion stream comprising CO<sub>2</sub> and one or more secondary components;

expanding the combustion stream across a supercritical CO<sub>2</sub> turbine to generate power and provide a first discharge stream comprising CO<sub>2</sub> and one or more secondary components, the supercritical CO<sub>2</sub> turbine having an inlet for receiving the combustion stream and an outlet for release of the first discharge stream, where the combustion stream is provided to the supercritical CO<sub>2</sub> turbine inlet at a temperature of from 1,000 to 1,500 °C;

withdrawing heat from the first discharge stream by passing the first discharge stream through a recuperator to provide a cooled first discharge stream;

passing the cooled first discharge stream through a condenser to remove one or more secondary components that are present in the cooled first discharge stream to provide a recycled CO<sub>2</sub> stream;

heating the recycled CO<sub>2</sub> stream by passing the recycled CO<sub>2</sub> stream through the recuperator to provide a heated recycled CO<sub>2</sub> stream having a temperature of from 500 to 900 °C;

passing the heated recycled CO<sub>2</sub> stream through a high-temperature air separation system that is operating at a temperature of from 500 to 900 °C and a pressure of up to 10,000 kPa, to provide an oxygen-enriched CO<sub>2</sub> stream;

withdrawing heat from the oxygen-enriched CO<sub>2</sub> stream by passing the oxygen-enriched CO<sub>2</sub> stream through the recuperator to provide a cooled oxygen-enriched CO<sub>2</sub> stream;

compressing the cooled oxygen-enriched CO<sub>2</sub> stream to provide an oxygen-enriched supercritical CO<sub>2</sub> stream; and

heating the oxygen-enriched supercritical CO<sub>2</sub> stream for introduction to the combustor, wherein

the high-temperature air separation system operates by:

introducing a compressed air stream into an oxidation reactor comprising an oxygen carrier material in a reduced state to provide a depleted air stream and the oxygen carrier material in an oxidised state;

expanding the depleted air stream across a hot air turbine to generate power and provide a second discharge stream; and

transporting the oxygen carrier material in an oxidised state to a reduction reactor operating at a pressure of from 100 kPa to 10,000 kPa where it meets the heated recycled CO<sub>2</sub> stream to provide the oxygen-enriched CO<sub>2</sub> stream and the oxygen carrier material in a reduced state, which is transported back to the oxidation reactor for re-oxidation, and wherein

the one or more secondary components comprise water.

9. The method according to Claim 8, wherein a product CO<sub>2</sub> stream is withdrawn from the recycled CO<sub>2</sub> stream prior to passing through the recuperator.
10. The method according to Claim 9, wherein the product CO<sub>2</sub> stream comprises substantially all of the CO<sub>2</sub> formed by combustion of the fuel.
11. The method according to any one of Claims 8 to 10, wherein the said combustion is carried out at a temperature of from about 1,200° C to about 5,000° C.
12. The method according to any one of Claims 8 to 11, wherein the fuel comprises one or more of hydrogen, a hydrocarbon gas, and carbon monoxide, optionally wherein the fuel is mixed with one or more diluents selected from H<sub>2</sub>O, and an inert gas (e.g. N<sub>2</sub> and Ar)
13. The method according to any one of Claims 8 to 12, wherein the oxygen carrier material is a material capable of cyclically taking up and releasing gaseous oxygen in substantially pure CO<sub>2</sub> at a temperature of from 500 to 700 °C and a pressure of from 100 kPa to 10,000 kPa.
14. The method according to Claim 13, wherein the oxygen carrier material is selected from one or more of MnO<sub>2</sub>, Co<sub>2</sub>O<sub>3</sub>, CuO, mixed-metal oxides (e.g. CaMnO<sub>3</sub> and SeFeO<sub>3</sub>), composites thereof, and solid solutions thereof.
15. The method according to Claim 13 or Claim 14, wherein the oxygen carrier material is in a solid form, optionally wherein the oxygen carrier material is in particulate form, further optionally wherein the oxygen carrier material further comprises one or more catalysts to facilitate the uptake and release of oxygen.
16. The method according to any one of Claims 8 to 15, wherein the recycled CO<sub>2</sub> stream is a substantially pure CO<sub>2</sub> stream, optionally wherein the recycled CO<sub>2</sub> stream is from 98 to 99 mol% CO<sub>2</sub>.
17. The method according to any one of Claims 8 to 16, wherein one or both of the first discharge stream and the recycled CO<sub>2</sub> stream are maintained at a pressure of from 2,500 to 5,000 kPa, such as about 3,000 kPa.
18. The method according to any one of Claims 8 to 17, wherein the high-temperature air separation system is a chemical looping apparatus.

19. The method according to any one of Claims 8 to 18, wherein the means or apparatus to transfer the oxygen carrier material from the oxidation reactor to the reduction reactor and *vice versa* is selected from one or more of the group consisting of a circulating fluidised beds system, a moving beds system, a parallel packed beds system, a rotating disc system and an oxygen permeating membrane separation system.