

Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO₂ Capture Project

**Capture and Separation of Carbon Dioxide
from Combustion Sources**

Edited by

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Chapter 29

A COMPARISON OF THE EFFICIENCIES OF THE OXY-FUEL POWER CYCLES WATER-CYCLE, GRAZ-CYCLE AND MATIANT-CYCLE

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ABSTRACT

One of the technology areas targeted in the CO₂ Capture Project (CCP) has been oxy-fuel combustion. This process generates a flue gas consisting largely of carbon dioxide and water from which carbon dioxide is easily separated. The use of oxy-fuel combustion in gas turbine-based power generation will require new equipment, but also provides an opportunity to develop new cycles which may offer higher efficiencies than current air-based combined cycle systems, thus partially offsetting the additional cost of oxygen production.

Three oxy-fuel power generation concepts (Water-cycle, Graz-cycle and Matiant-cycle), based on direct stoichiometric combustion with oxygen, are evaluated in the present study. Considering cycle efficiency and given similar computational assumptions, the Graz-cycle and the latest versions of the Matiant-cycle seem to give rather similar net plant efficiencies (around 45%), while the Water-cycle is 3–5% points behind. When comparing the three cycles with the well-known *oxy-fuel gas turbine combined cycle* (similar to CC-Matiant-cycle), for which efficiencies in the range 44–48% have been reported, there is no obvious advantage for the three.

A challenge for all oxy-fuel cycles is the combustion. Both the fuel and the oxidant are supposed to be consumed simultaneously in the combustion process. This requires very good mixing and sufficient residence time. Incomplete combustion with CO formation may result, or a surplus of oxygen to the combustion process may need to be supplied. Another challenge is the development of turbo machinery capable of working with CO₂/H₂O mixtures at high temperatures and pressures.

In general, one can say that oxy-fuel cycles do not exhibit significantly better efficiency compared to post- and pre-combustion CO₂ capture methods. One can also question what other advantages oxy-fuel cycles offer compared to other options. A disadvantage with oxy-fuel cycles is that this technology only can be used in plants where CO₂ is to be captured. This means that equipment developed for this purpose may, as it seems today, have a limited market potential, and the motivation for technology development is not that evident.

The future for oxy-fuel cycles depends on: (1) Willingness to develop oxy-fuel turbo machinery and combustors, and (2) Future development of oxygen production technology. For the latter, the development of ion transport membranes is vital. In case of oxygen production other than cryogenic distillation, novel cycles like AZEP are very interesting.

INTRODUCTION

The basic idea behind oxy-fuel (implying a mixture of fuel and O₂)-based combustion processes and cycles is quite simple: use as pure an O₂ stream as possible as the fuel oxidiser in stoichiometric conditions in order

to generate mainly CO_2 and water (H_2O) from the combustion process. If either CO_2 and/or water generated from the combustion process are used as the working fluid in a thermodynamic cycle (e.g. in a Rankine or Brayton cycle), then CO_2 can be more readily separated from the exhausted working fluid of the power cycle. However, because fuel combustion in pure O_2 generates very high temperatures, the combustion or exhaust products are partly recycled back to the upstream combustion process in order to control the flame temperature and to meet temperature limitations of materials used in the construction of process equipment. Thus, in oxy-fuel combustion, fuel is burnt in a mixture of nearly pure O_2 and partially recycled flue gas. The recycled flue gas may either be CO_2 or H_2O .

It must be noted that high temperature burners for fuel combustion in pure oxygen have seen applications for several decades in the glass and steel melting industries. Although oxy-fuel combustion is commonly used, there is an established understanding that the current fleet of modern boilers, process heaters, gas and steam turbines cannot be used with a mixture of CO_2 and/or H_2O as the primary working fluid without redesign. Technical issues linked to the new working fluid composition impose a need for the adaptation of existing equipment or the development of new combustors, boilers, process heaters and turbines. Major benefits that could arise from the development of modified or new equipment for these applications include their reduced size or compactness (dependent on the level of dilution with flue gas recycling) as well as in the simplification and/or elimination of some balance of plant operations to remove trace concentrations of contaminants arising from fuel bound sources of NO_x , SO_2 , particulates and trace elements. An offsetting impact of these benefits, which often manifest as capital and operating cost savings in plants, is the need for the use of an oxygen production plant—the latter particularly in oxy-fuel based applications.

For both the H_2O and CO_2 recycle-based systems, a common feature is the requirement of an air separation unit (ASU) using cryogenic, membrane or adsorption-based techniques. For bulk O_2 production particularly at very high capacity and O_2 purity, cryogenic ASU is currently the most practical option for O_2 supply in oxy-fuel systems.

Several such cycles have been proposed in the literature and this theoretical study compares the thermodynamic performance of three of them, referred to here as the Water-cycle (H_2O recycle), the Graz-cycle (H_2O and CO_2 recycle) and the Matiant-cycle (CO_2 recycle). The well-known oxy-fuel concept *oxy-fuel gas turbine combined cycle* (see Figure 1) is not considered here, but is described elsewhere, for example, in Refs. [18–20].

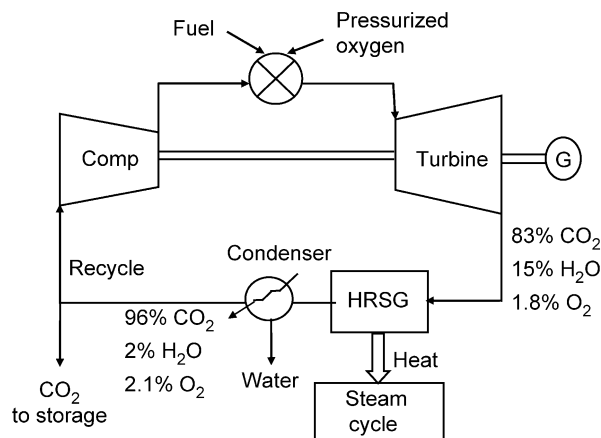


Figure 1: Principle of the oxy-fuel gas turbine combined cycle.

Evaluations of the three concepts are given in the following sections. The evaluations of the Water-cycle concept and the Graz-cycle concept are based on simulations performed by the simulation tool PRO/II (SIMSCI Inc.) while the evaluation of the Matiant-cycle is based on a literature review only.

Computational assumptions are given in Table 1. Production and intercooled gas-phase compression of oxygen is not shown in the flowsheet diagrams, but are taken into account in the energy balance. The compression of CO₂ from a pressure of 1 bar is not shown in the flowsheet diagrams, but is taken into account. The end-pressure of CO₂ is chosen to be 200 bar, and is reached by intercooled compression. The SRK (Soave-Redlich-Kwong) thermodynamic system including use of steam tables in PRO/II, was used for calculation of thermodynamic properties. The assumptions are, as far as possible, identical for the Water-cycle and the Graz-cycle. For these two cycles, a base case for each is defined using published data. A maximum turbine inlet temperature of 1328 °C was chosen, in order to resemble moderate F-type gas turbine technology. A model for taking into account the efficiency penalty of turbine cooling was applied. In addition to heat and mass balance calculations for the base cases, a number of parameter variations have been carried out. When not specified differently, the data in the sections on the Water-cycle and the Graz-cycle is as for the base case assumptions.

TABLE 1
COMPUTATIONAL ASSUMPTIONS

Fuel pressure	bar	50
Fuel temperature	°C	10
Fuel composition	%	CH ₄ 82; C ₂ H ₈ 9.4; C ₃ H ₈ 4.7; C ₄ H ₁₀ 1.6; C ₅ H ₁₂ 0.7; N ₂ 0.9; CO ₂ 0.7%
Oxygen purity	%	100
Heat exchanger pressure drop	%	3
Heat exchanger ΔT_{\min} gas/gas	K	30
Heat exchanger ΔT_{\min} gas/liquid	K	20
Combustor pressure drop	%	5
Turbine inlet temperature, max.	°C	1328
Polytropic efficiency compressor	%	91.4
Polytropic efficiency turbine, uncooled	%	91
Exhaust pressure drop (after turbine exit)	mbar	40
Steam turbine adiabatic efficiency (HP, IP, LP)	%	92, 92, 89
Max steam temperature	°C	560
Deaerator pressure	bar	1.2
Condenser pressure	bar	0.1
Cooling water inlet/outlet temperature	°C	8/18
Efficiency pumps (total, including motor drive)	%	75
CO ₂ compression adiabatic efficiency (1st, 2nd, and 3rd stages)	%	85, 80, 75
CO ₂ compression intercooling temperature	°C	20
CO ₂ compression intercooler pressure drop in coolers	bar	0.5
CO ₂ compression work calculated, 1–200 bar	kWh/kg	0.115
Generator mechanical efficiency	%	98.0
Oxygen production power requirement (1 bar)	kWh/kg	0.27
Mechanical drive efficiency (oxygen and CO ₂ compressors)	%	95
Auxiliary power requirements (of net plant output)	%	1

RESULTS AND DISCUSSION

Water-cycle

The evaluation of the Water-cycle, or CES (Clean Energy Systems Inc.) cycle, concept is, to a large extent, based on publications [1–4]. The Water-cycle can be categorised as a Rankine type power cycle. The working fluid (approximately 90–93% water, molecular basis) is compressed in the liquid phase, and hot gases are expanded to provide work. In the publications [1–4], there are various schemes for the cycle configuration with respect to the reheat arrangement; both single and double reheat are applied.

A flowsheet diagram of the process applied in the present study is shown in Figure 2. The fuel is compressed and preheated (not shown in the diagram) before the high-pressure combustion takes place in the HP combustor. Oxygen, from a cryogenic ASU, is fed in a stoichiometric ratio with the fuel in the combustor. Adding liquid hot water controls the combustor exit temperature. The combustor exit flow is expanded in a turbine (HPT). The turbine exit stream flows to a secondary, or reheat, combustor. By adding fuel and oxygen in a stoichiometric ratio to the reheater, the exit temperature of this unit is controlled. The HPT inlet temperature is 900 °C, which represents a very advanced steam turbine technology based on an uncooled, high-pressure turbine (HPT) while the LPT, in which the inlet temperature is 1328 °C, represents typical gas turbine technology based on a cooled, medium pressure turbine. The temperature of the LPT exit stream is 450 °C. The exhaust is cooled down by fuel preheating and water heating (recuperator). The exhaust condenses partly in the Condenser. Liquid water and CO₂ are split in the condenser. The CO₂ (in gaseous phase) is compressed to 1 bar. The water from the condenser is recycled back to the HP combustor, after compression and heating in the recuperator. However, a fraction of the water (H₂O), equal to the amount of water formed in the combustion, is bled off from the process.

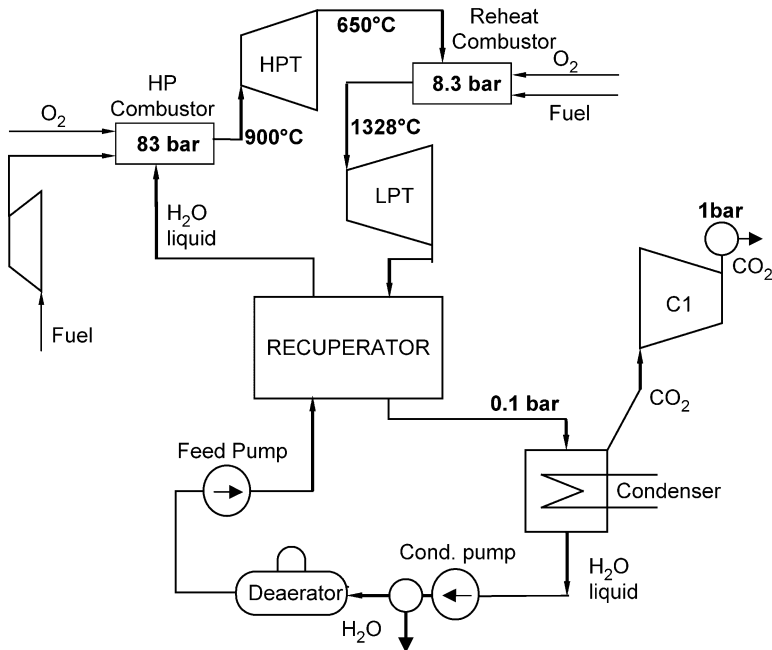


Figure 2: Flowsheet diagram of the Water-cycle.

A base case was defined with the assumptions given in Table 1. This base case is meant to resemble the CES “near-term” cycle, as published in [1], using a single reheat cycle. A heat and mass balance was calculated for this base case. Results are presented in Table 2. Additionally, calculations were carried out for a variation of some parameters:

- (1) High-pressure combustor (HP Combustor) exit temperature (600–1450 °C, base case is 900 °C)
- (2) High-pressure combustor (HP Combustor) pressure (83–200 bar, base case is 83 bar). The reheat pressure was set to 8.3 bar in the base case and varied assuming constant HPT/LPT pressure ratios.
- (3) Condenser pressure (0.1–1.0 bar, base case is 0.1 bar).

The results from the three-parameter variations are presented in Figures 3–5, respectively. The upper line in the figures represents the gross efficiency (for the power cycle itself; shaft power minus compression work). The other lines show the efficiency when including auxiliaries, pumps and (a) the energy penalty for producing atmospheric gaseous oxygen, (b) the energy penalty for compressing oxygen to the combustor pressure, and (c) the energy penalty for compressing CO₂ from atmospheric pressure to 200 bar. The energy penalty, in terms of efficiency reduction, can be seen as the difference between the curves.

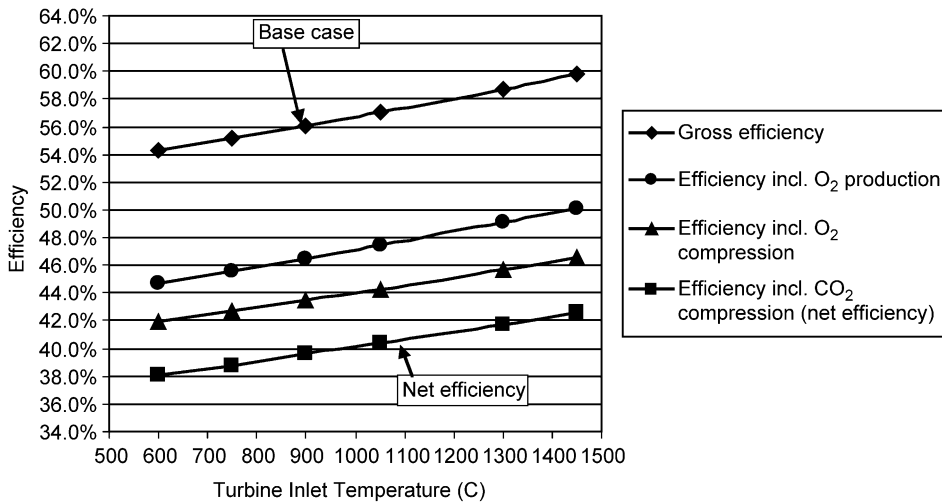


Figure 3: Efficiency for the Water-cycle. High-pressure combustor (HP combustor) exit temperature varied in the range 600–1450 °C, base case temperature is 900 °C.

The gross plant efficiency (shaft work = turbin – compressor power related to fuel lower heating value) was calculated to be 56.1% for the base case. The net plant efficiency, including fuel compression (very small), oxygen production, oxygen compression, compression of CO₂ and plant auxiliaries, was calculated to be 39.6% for the base case. This result is significantly lower than the claimed efficiency in [1–5]. It is not easy to extract the exact computational assumptions used in the publications [1–4]. It is unclear whether the energy penalty for oxygen production and compression is included.

The effect of varying the high-pressure combustor (HP Combustor) exit temperature is shown in Figure 3. The net plant efficiency increases by about 0.5% point for every 100 °C of increased temperature. At 1328 °C

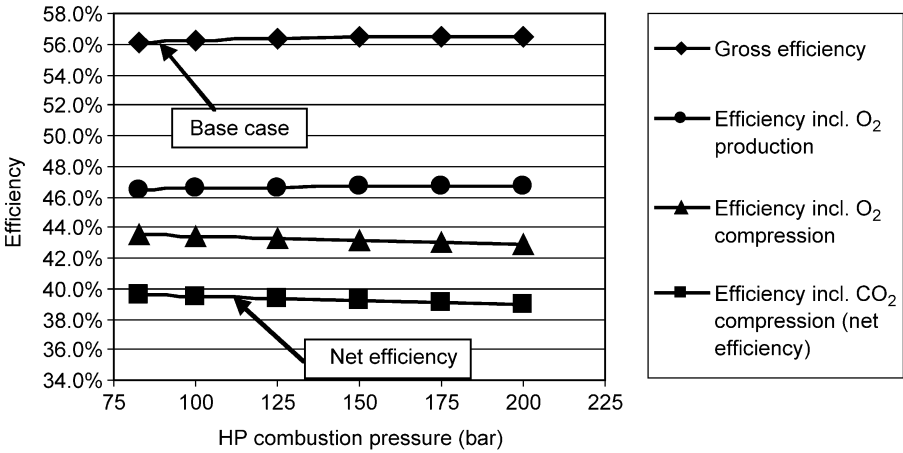


Figure 4: Efficiency for the Water-cycle. High-pressure combustor (HP combustor) pressure varied in the range 83–200 bar, base case pressure is 83 bar.

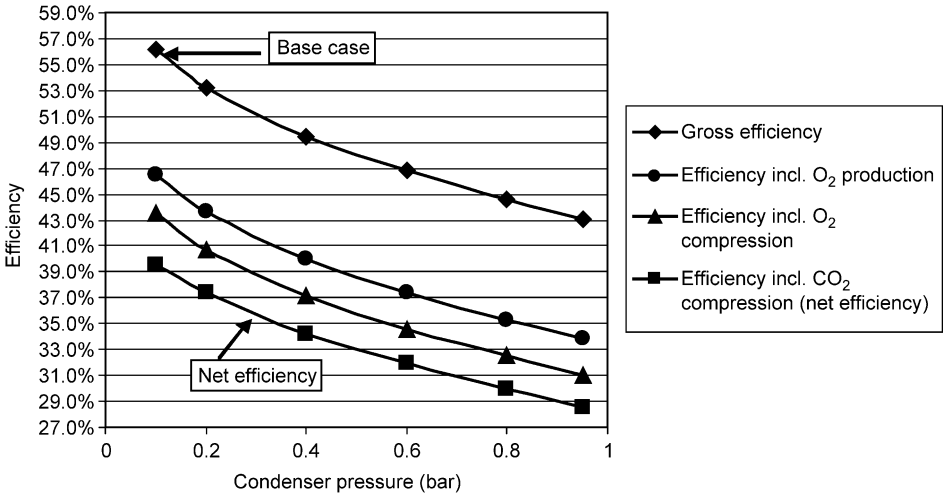


Figure 5: Efficiency for the Water-cycle. Condenser pressure varied from 0.1 bar (base case) to 1 bar.

exit temperature, the net plant efficiency is increased about 2.5% points (to 42%) compared to the base case (900 °C). Note that in this parameter variation, the exit temperature of the reheat combustor is kept constant at 1328 °C.

The effect of varying the high-pressure combustor (HP Combustor) pressure is shown in Figure 4. The change in net plant efficiency is not significant, when varying the pressure in the range 83–200 bar.

The effect of varying the condenser pressure is shown in Figure 5. The net plant efficiency increases by 0.5–1.2% points for every 100 mbar (0.1 bar) change in efficiency.

Graz-cycle

The evaluation of the Graz-cycle in the present study, including most parameter values, is based on publications [6–8]. A flowsheet diagram of the process is shown in Figure 6. The high-temperature section of the Graz-cycle consists of a combustor, which is fed with natural gas, oxygen, CO₂ and a stream of pure steam. The combustor pressure is 40 bar. The combustor exit stream, at 1328 °C, is expanded in the HPT. The turbine exit stream is cooled in a heat recovery steam generator (HRSG), where high-pressure steam is produced (174 bar, 560 °C). The steam is then expanded (HPT) to the combustor pressure of 40 bar. The hot gas from the HRSG is further expanded (LPT) to a condenser. The condensed water and CO₂ are separated in the condenser. The CO₂ stream is compressed (in C1–C3), with intercooling, before it is mixed into the combustor, as an inert gas for the control of the combustor exit temperature. The water collected from the condenser is preheated in the CO₂ compression intercoolers, before it is pressurised for steam generation. Excess water, as well as CO₂, formed in the combustion is removed from the cycle.

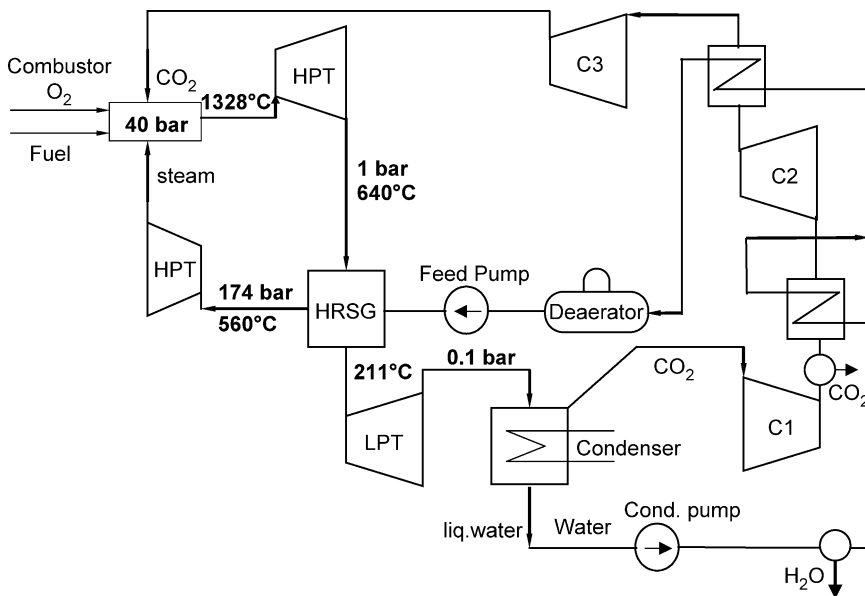


Figure 6: Flowsheet diagram of the Graz-cycle.

Simulations were carried out for a given set of computational assumptions, as well as with a variation in the condenser pressure. Results are given in Table 2. Further, Figure 7 shows net plant efficiency depending upon condenser pressure. As seen from Figure 7, the net efficiency decreases with increasing condenser pressure. The reason is that the LPT expansion work is higher than the CO₂ compression work such that the reduced expansion work only partly counteracts the decreased CO₂ compression work.

The net plant efficiency for the base case was calculated as 45.1% (condenser pressure 0.1 bar). The efficiency reported by Jericha and Fesharaki [6] is 63.1%, without any energy penalty for the oxygen production and compression. In the present study, the energy penalty for the oxygen production and compression was calculated to about 11%-points, and the CO₂ compression to about 14%-points.

TABLE 2
RESULTS FROM THE CALCULATION OF THE WATER-CYCLE AND THE
GRAZ-CYCLE (BASE CASES)

	Water-cycle	Graz-cycle
Chemical energy in fuel (LHV) (MW)	143.30	143.14
Turbines (MW)	80.51	130.83
Compressors (MW)	0.10	27.68
Gross power (MW)	80.41	103.15
Generator and mechanical efficiency	0.98	0.98
Net shaft power (MW)	78.80	101.09
Auxiliaries (MW)	0.79	1.01
Pumps (MW)	0.26	0.58
Oxygen production (MW)	11.13	11.05
Oxygen compression (MW)	4.29	4.70
Compression work, CO ₂ (MW)	5.62	19.25
Total consumers (MW)	22.09	36.59
Net electric output (MW)	56.71	64.50
Net efficiency (%)	39.6	45.1
Chemical energy in fuel (LHV) (%-points)	100.0	100.0
Turbines (%-points)	56.2	91.4
Compressors (%-points)	0.1	19.3
Gross power (%-points)	56.1	72.1
Generator and mechanical efficiency (%-points)	1.1	1.4
Net shaft power (%-points)	55.0	70.6
Auxiliaries (%-points)	0.5	0.7
Pumps (%-points)	0.2	0.4
Oxygen production (%-points)	7.8	7.7
Oxygen compression (%-points)	3.0	3.3
Compression work, CO ₂ (%-points)	3.9	13.5
Total consumers (%-points)	15.4	25.6
Net efficiency (%-points)	39.6	45.1

Matiant-cycle

The Matiant-cycle originated in a Russian patent [9], which Professor Yantovski of the Moscow Institute of Energy Research [10] presented in 1992. Later, both Yantovski and Mathieu have worked on research and concept development of the Matiant-cycle [11–15].

The basic Matiant-cycle is shown in a TS-diagram in Figure 8. This cycle is a recuperative Brayton-like cycle. The working fluid is compressed in the gaseous phase with intercooling (1–2). Then it is cooled such that a dense phase (as a liquid) can be pumped from point 3–4. At point 4, excess CO₂ is taken out of the process at the highest pressure (about 300 bar according to Mathieu and Nihart [12]). Then the working fluid is heated in a heat exchanger from point 4 to 5 and expanded to about 40 bar prior to reheating in a heat exchanger (6–7) and fed to a combustor (7–8). Then there is an expansion (8–9), a reheat combustor (9–10), and an expansion (10–11). The exhaust temperature after the last expansion is between 900 and 1000 °C. The heat of the exhaust is utilised for preheating of the compressed fluid 4–5 and 6–7. The Matiant-cycle involves a large amount of internal heat exchange between streams. The exhaust stream to be cooled (11–12) is at atmospheric pressure and at high temperature (900–1000 °C), and thus implies several potential problems related to heat exchanger technology. The net plant efficiency is calculated in Ref. [12]

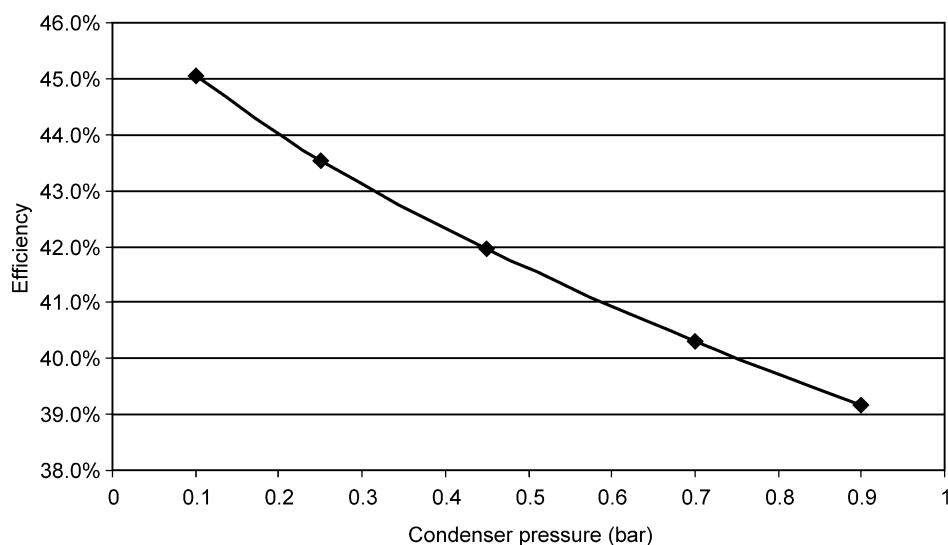


Figure 7: Net efficiency for the Graz-cycle. The condenser pressure was varied in the range 0.1–0.9 bar. Base case pressure is 0.1 bar.

to be about 44–45%. The turbine inlet temperature (points 8 and 10) is set to 1300 °C, and penalties for turbine cooling and oxygen production (energy requirement: 0.28 kWh/kg O₂) are included.

The basic Matiant-cycle does not exhibit any thermodynamic advantage when taking into account parasitic losses (as in Ref. [12]). This is mainly due to the HP expander, however, further development of the basic Matiant-cycle has resulted in two different concepts called the E-Matiant-cycle and the CC-Matiant-cycle. The E-Matiant-cycle is a full Brayton-type cycle, with the whole cycle in the gas phase. It highly resembles an intercooled recuperative gas turbine cycle.

The CC-Matiant-cycle (see Figure 9) resembles several previous cycle proposals involving a CO₂/O₂ gas turbine (stoichiometric combustion with oxygen from an ASU) combined with a steam bottoming cycle. In this cycle, the compression is adiabatic instead of intercooled, as in the basic Matiant-cycle. The only difference between the CC-Matiant-cycle and the combined cycle with a CO₂/O₂ gas turbine and a steam bottoming cycle, is a recuperator between the hottest exhaust and the compressor discharge stream. The exhaust temperature of a CO₂/O₂ gas turbine is higher, compared to an air gas turbine, for a given pressure ratio. This is because of different gas properties between the two cases. The combustion is stoichiometric. The oxidising agent is O₂ rather than air. The turbine inlet temperature is 1300 °C. The novel idea of the CC-Matiant-cycle is to utilise the exhaust gas temperature between 600 and 700 °C for preheating of the compressor discharge flow, and thereby avoid a large temperature difference in the superheating of steam in the heat recovery steam boiler. It is difficult to see that this recuperator could give any advantage. The reason is that the compressor discharge temperature is around 500 °C (for a given pressure ratio in this case), and the compressor discharge stream is preheated to about 600 °C. This is not very different from the temperatures of the high-pressure steam superheater in the heat recovery boiler. When taking into account the parasitic losses (mainly pressure losses) of the recuperator, the ducting and the valves, it is questionable whether the recuperator contributes anything in respect to efficiency. The net plant efficiency is calculated in Ref. [14] to about 47–49%. This is comparable to other publications [3,16,17] and [19,20] for this specific cycle configuration.

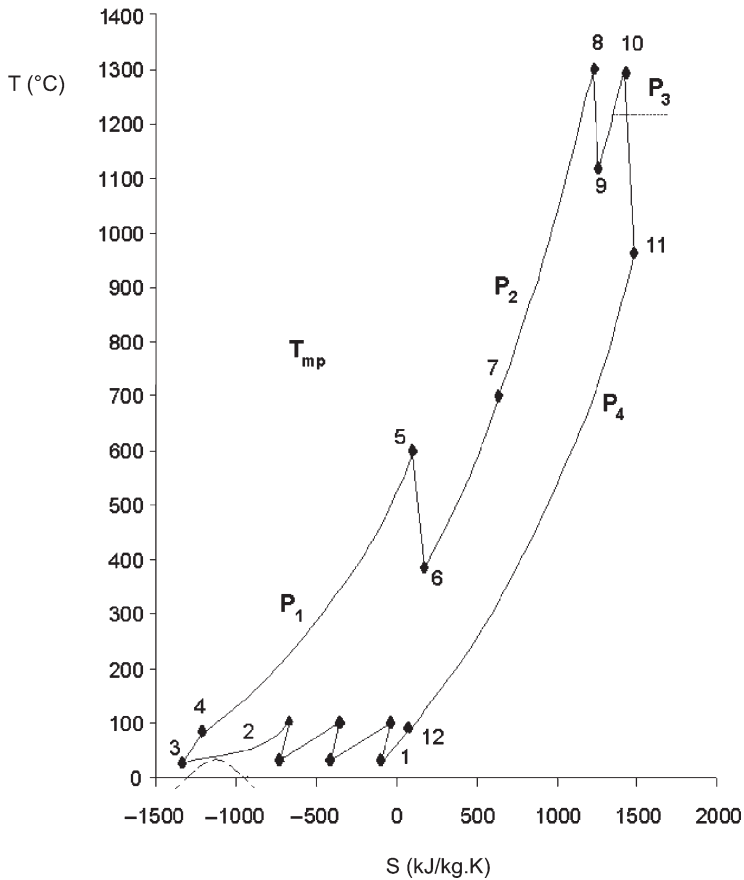


Figure 8: TS diagram for the basic Matiant-cycle [14]. Supercritical part (2–6), with reheat (6–8–11–12–2), sequential combustion (7–8 and 9–10), staged expansion (8–9 and 10–11), recuperator (hot side: 11–12, cold side 4–5 and 6–7), water cooler/separator (12): 6% H₂O + 0.02% of CO₂ recycled, staged compression with intercooling (1–3), CO₂ purge (4) = 8% of CO₂ recycled.

CONCLUSIONS

Three oxy-fuel power generation concepts (Water-cycle, Graz-cycle and Matiant-cycle), based on direct stoichiometric combustion with oxygen, are evaluated in the present study. Considering cycle efficiency and given similar computational assumptions, the Graz-cycle and the latest versions of the Matiant-cycle seem to give rather similar efficiencies, while the Water-cycle is 3–5% points behind. The Water-cycle is a Rankine-type cycle, while the Graz-cycle is a mixed Brayton/Rankine cycle, and the more recent Matiant-cycle is a combined topping/bottoming Brayton/Rankine cycle. It is commonly accepted, in general, that Brayton cycles, in combination with Rankine cycles, exhibit higher efficiencies than Rankine cycles alone. The thermodynamic explanation for this is that Brayton cycles combined with Rankine cycles have a higher ratio of the temperatures at which heat is supplied to, and rejected from, the cycle, compared to that of a Rankine cycle. According to the Carnot cycle efficiency definition, the efficiency is improved when this temperature ratio increases.

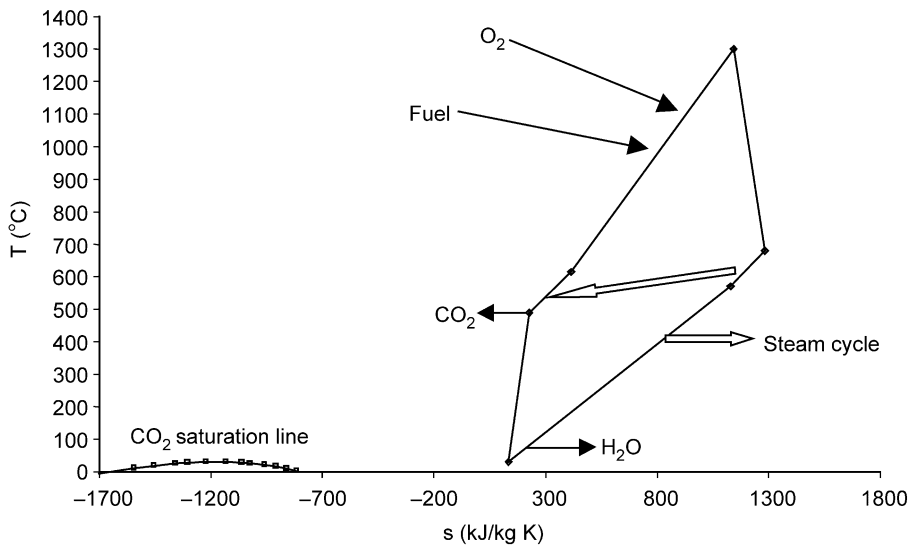


Figure 9: TS diagram for the CC-Matiant-cycle [14]. Characterised by: Brayton like gas cycle, adiabatic compression and expansion, sub-critical steam cycle (not shown), recuperator for hot exhaust \rightarrow 600 °C.

When comparing the three cycles with the well-known *oxy-fuel gas turbine combined cycle* (similar to CC-Matiant-cycle), for which efficiencies in the range 44–48% have been reported in Refs. [18,19,20] there is no obvious advantage for the three.

The Graz-cycle is an interesting option as an oxy-fuel concept. The high-temperature/pressure loop closely resembles an oxy-fuel gas turbine, with the same challenges related to compressor, combustor and turbine. Adding steam to the combustor may also help to reduce CO concentration for the stoichiometric combustion.

It should be noted that CO₂ is not completely recovered in power cycles with H₂O condensers due to solubility of CO₂ in water. However, the solubility of CO₂ in the specific systems investigated here is maximum 1% at 1 bar, which corresponds to about 4 g CO₂/kWh. This value is acceptable compared to a conventional combined cycles, which emits about 350–400 g CO₂/kWh. As the solubility is even lower at lower pressures, the Graz-cycle and Water-cycle seems more favourable regarding this issue.

A challenge for all oxy-fuel cycles is the combustion. Both the fuel and the oxidant are supposed to be consumed simultaneously in the combustion process. This requires very good mixing and sufficient residence time. Incomplete combustion with CO formation may result, or it may be required, to supply a surplus of oxygen to the combustion process. CES Inc. (Water-cycle) has developed a pressurised oxy-fuel combustor for the purpose of power generation. Another challenge is the development of turbo machinery capable of working with CO₂/H₂O mixtures at high temperatures and pressures. Existing turbo machinery components (air-based gas turbines) cannot be used, and a complete new design is required. For the Water-cycle and the Graz-cycle, steam turbine technology can be applied to some extent.

In general, one can say that oxy-fuel cycles do not exhibit significantly better efficiency compared to post- and pre-combustion CO₂ capture methods. One can also question what other advantage oxy-fuel cycles offer compared to other options. A disadvantage with oxy-fuel cycles is that this technology only can be used in plants where CO₂ is to be captured. This means that equipment developed for this purpose may, as it seems today, have a limited market potential, and the motivation for technology development is not that evident.

The future for oxy-fuel cycles depends on: (1) Willingness to develop oxy-fuel turbo machinery and combustors, and (2) Future development of oxygen production technology. For the latter, the development of ion transport membranes is vital. In case of oxygen production other than cryogenic distillation, novel cycles like AZEP are very interesting [21].

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