Semi-Closed Oxy–Fuel Combustion Power Cycles with CO2 Recirculation

Subjects: Energy & Fuels

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With the increases in organic fuel prices and growing legislative restrictions aimed at increasing environmental safety and reducing the carbon footprint, the task of increasing thermal power plant efficiency is becoming more and more topical. Transforming combusting fuel thermal energy into electric power more efficiently will allow the reduction of the fuel cost fraction in the cost structure and decrease harmful emissions, especially greenhouse gases, as less fuel will be consumed. There are traditional ways of improving thermal power plant energy efficiency: increasing turbine inlet temperature and utilizing exhaust heat. An alternative way to improve energy efficiency is the use of supercritical CO_2 power cycles, which have a number of advantages over traditional ones due to carbon dioxide's thermophysical properties. In particular, the use of carbon dioxide allows increasing efficiency by reducing compression and friction losses in the wheel spaces of the turbines; in addition, it is known that CO_2 turbomachinery has smaller dimensions compared to traditional steam and gas turbines of similar capacity.

supercritical carbon dioxide　　power cycle　　Brayton cycle　　Rankine cycle

1. Introduction

Unlike closed CO_2 cycles, where the working fluid heating is carried out from outside by means of a heat exchanger (boiler, heat recovery boiler, etc.), in semi-closed cycles, the working fluid heating occurs in the combustion chamber, where the fuel burns in a carbon dioxide environment with an oxidizer supplied. After that, additional carbon dioxide formed during fuel combustion is separated from the main stream; after expansion in the turbine, it is compressed and utilized. This approach allows two problems to be solved:

- Optimization of the structure of the metal consumption of the main equipment due to the absence of massive boiler units;

- Minimization of greenhouse gas emissions into the atmosphere through carbon dioxide capture and deposition.

Closed thermodynamic cycles with oxygen–fuel combustion are energy complexes consisting of the cycle itself, oxygen production plants and plants for carbon dioxide preparation for deposition. The following closed thermodynamic cycles have become widely known: a semi-closed cycle with oxygen–fuel combustion (SCOC-CC), MATIANT cycles, NET Power cycles (Allam cycle), Graz cycles, "water" (CES) cycles and membrane cycles (AZEP cycle, ZEITMOP) [1]. The first modifications of these cycles appeared at the end of the last century. Today, the USA,

Japan and European countries are actively developing these technologies. By grant making, the active financing of "green" electric power generation technologies, creating legislative bases to stimulate the reduction of carbon dioxide emissions and conducting scientific research, experimental installations are being built, and prerequisites are being created for the development of power units with "zero" emissions of harmful substances. Large energy corporations are joining forces to create demonstration plants capable of releasing up to 50 MW of electric power to the grid [2].

According to the technology of oxygen–fuel combustion, three streams enter the combustion chamber of the oxy–fuel energy complex: fuel (gaseous, including gas produced from coal), oxygen and a stream of carbon dioxide, limiting the maximum temperature in the combustion chamber. A mixture of carbon dioxide and water vapor is formed as a result of the burning reaction (3–4). Predominantly, a two-component fluid at a temperature from 1000 to 1700 °C is directed to the cooled turbine, the fluid expands in the turbine (4–5) and then enters a surface heat exchanger, which can be a heat recovery boiler or a regenerative heat exchanger (5–6). Having given away most of the heat energy, the flow is directed to the cooler–separator (CS). In the CS (6–1), the working fluid cooling is accompanied by the formation of a condensate of water vapor removed from the cycle. After that, the flow rich in carbon dioxide is sent to the compressor (1–2), increases its pressure and then is fed for recirculation into the combustion chamber. Thus, the thermodynamic cycle is closed [3]. To replenish the material balance, part of the working medium is removed for deposition. Carbon dioxide storage tanks can be both natural and artificial.

The above cycles can be classified according to their methods for obtaining oxygen and limiting combustion chamber temperature. The oxygen–fuel cycle using cryogenic air separation units (ASU) includes a semi-closed cycle with oxygen–fuel combustion, such as the Allam cycle and the Graz cycles. The AZEP and ZEITMOP cycles use high-temperature membrane ASUs integrated into the thermal circuit. Temperature limitation in the combustion chambers of oxygen–fuel cycles is achieved by recirculating part of the working fluid flow. In this, chemical composition of the recirculation flow may vary. So, in a semi-closed cycle with oxygen–fuel combustion (the MATIANT cycle and the Allam cycle), a stream of carbon dioxide, which, in these cases, is the main component of the working fluid, is supplied for recirculation, and, in the Graz cycles and the "water" cycle, a stream with a high content of water vapor is provided.

A common feature of these cycles is the almost complete absence of harmful gas emission into the atmosphere. Oxygen–fuel technology allows the sequestering of up to 99% of the CO_2 generated as a result of burning carbon fuel in oxygen. The remaining technical and economic parameters of prospective TPP cycles, according to available estimates, differ significantly.

2. SCOC-CC

The semi-closed cycle with oxygen–fuel combustion, which was proposed for the first time in 1992 by scientists Bolland and Saether [4], has a simple configuration and is essentially a combined Brayton–Rankine cycle with an oxygen–fuel oxidizer and dioxide recirculation. The main advantage of the CO-CC cycle among closed cycles with oxygen–fuel combustion is the ease of implementation.

The gaseous fuel and high-purity oxygen are supplied into the combustion chamber with a stoichiometric ratio (2–3). Since the torch temperature during the combustion of such a mixture can reach 3500 °C, a third stream is also fed into the combustion chamber—a mixture with a high CO_2 content, which is necessary to limit maximum temperature. The resulting gas flow, consisting of approximately 80% CO_2 at a temperature of 1300–1400 °C, is directed to a gas turbine (3–4), which causes rotation of the electric generator. After expansion in the GT, the working fluid enters the heat recovery boiler (4–1). Due to regeneration of the combustion product heat at the GT output, superheated steam is generated in the combustion chamber and feeds the steam turbine (ST), which is also used to generate electric power (6–7–8–9). Flue gases at the combustion chamber output are directed to the condenser, in which the separation of most water due to its condensation at a pressure close to atmospheric pressure takes place. Then, part of the carbon dioxide flow is removed from the cycle for subsequent sequestration. The rest of the flow, consisting mainly of carbon dioxide, is recirculated and enters the compressor input.

Unlike open gas turbine cycles, in which the main component of the working fluid is nitrogen, in a semi-closed cycle with oxygen–fuel combustion, the proportion of carbon dioxide in the working fluid composition varies from 80 to 96%. In this cycle, the chemical composition of the working fluid depends on many factors, including type of fuel used, oxidizer purity, the thermodynamic parameters of the recirculation flow and the amount of excess air required to achieve complete combustion.

Since the cycle is semi-closed, the minimum pressure does not necessarily have to be equal to atmospheric pressure. On the one hand, an increase in the minimum pressure leads to a decrease in the turbomachinery and combustion chamber dimensions; on the other hand, it increases the wall thicknesses of the power equipment. Studies of the effect of minimum pressure on the efficiency of a semi-closed cycle with oxygen–fuel combustion have shown that its increase from 1 to 10 bar leads to a change in efficiency of only 0.5% [5]. However, at increasing pressure, an important problem is the cooling of the gas turbine blades. On the one hand, increased operating pressure reduces volumetric flow rate and, consequently, surface area to be cooled. On the other hand, the heat transfer coefficients on both sides of the cooled channels increase, and, consequently, the total heat flow through the blade walls becomes greater. This, in turn, leads to an increase in the temperature difference along the blade thickness with reduction of the permissible increase in the cooler temperature in the internal cooling channels. As a result, more refrigerant is consumed to remove the same heat flow. These factors confirm the expediency of maintaining the exhaust pressure of the SCOC-CC cycle gas turbine at the atmospheric level.

Results of analysis of the recirculation flow temperature effect on energy efficiency and design features of a semi-closed cycle with oxygen–fuel combustion are given in [6]. On the one hand, a decrease in the temperature of the recirculation flow leads to a decrease in the amount of compressor work and, on the other hand, an increase in cold source losses, primarily due to the increase in the proportion of condensed moisture. It was shown that there is no clear optimum for this parameter; for gas temperature at the GT output equal to 620 °C, it is in the range from 40 to 70 °C. Accordingly, to achieve maximum cycle efficiency, the recirculation flow temperature should be slightly higher than the temperature of the cold source.

The working medium initial parameters at the gas turbine input have the greatest impact on energy efficiency of the SCOC-CC cycle. According to the research results given in [7], the net efficiency of the semi-closed cycle with oxygen–fuel combustion at gas inlet temperatures equal to 1300–1400 °C and degrees of pressure increase in the range of 30–45 varies in the range of 45–48%.

The optimal degrees of pressure increase for the initial temperatures of the working fluid at 1400 and 1600 °C are approximately equal to 60 and 90 bar, respectively, which is significantly more than for traditional gas turbine plants [8].

3. MATIANT Cycles

The concept of the MATIANT cycle was presented for the first time in 1997 by two inventors, Mathieu and Jantowski [9]. A distinctive feature of this technology is the expansion of a working mixture with a high content of carbon dioxide in three turbines: high-, middle- and low-pressure turbines (HPT, LPT1, LPT2).

Carbon dioxide is compressed in the multi-stage compressor with intermediate cooling to a pressure of 300 bar and enters the regenerator for heating. After taking part of the heat from the gases at the LPT output, the heated flow is directed to the HPT, where it expands to a pressure of 40 bar and returns to the regenerator for reheating. From the regenerator output, the flow is directed to the first cooled combustion chamber, where the temperature rises to 1300 °C due to the combustion reaction of the fuel supplied to the chamber in the oxygen contained in the working mixture. Then, the hot combustion products expand in the cooled LPT1, after which, they are sent to the second cooled combustion chamber, to which fuel and oxygen are also supplied. From the combustion chamber output, the heated working fluid is sent to the cooled LPT2, where it expands to approximately atmospheric pressure. A hot carbon dioxide stream at the LPT2 output serves as the hot fluid of the regenerator. From the regenerator output, the flow is directed to a condenser, in which, in addition to cooling the working fluid due to heat transfer to the environment, water condensation also occurs with subsequent separation.

The results of the thermodynamic studies given in [10] revealed a significant influence of the compressor internal relative efficiency on the MATIANT cycle efficiency; with an increase in internal relative efficiency from 75 to 90%, the energy complex net efficiency is increased by 5.5%. A decrease in maximum pressure (pressure at the HPT input) from 300 to 150 bar leads to a decrease in net efficiency of about 1%, and an increase in the MPT input pressure from 40 to 100 bar increases net efficiency by more than 3%.

The above estimates were obtained without a detailed calculation of the process of working fluid expansion in cooled LPT1 and LPT2. The decrease in net cycle efficiency due to turbine cooling losses was assumed to be 2.5%. However, taking into account the overheating of the working fluid at the LPT1 and LPT2 input, total consumption for cooling has a noticeable effect on the cycle efficiency at the high initial parameters, which causes a significant error in the authors' estimation of the technology efficiency. More accurate thermodynamic studies require the development of a methodology for determining consumption for cooling and losses at carbon dioxide

turbine cooling or adaptation of existing methods for traditional gas turbines operating with air as a working fluid and refrigerant.

In addition to developing an efficient turbine cooling system, when designing the MATIANT cycle, special attention should be paid to the regenerative heat exchanger. Creating this element may require large capital costs due to the significant heating surface area and high cost of materials (nickel alloys) necessary for its manufacture. Cold carbon dioxide flow at the compressor output with a pressure of 300 bar should be heated to 600–700 °C by the heat taken from the LPT output working fluid with a temperature and pressure at the regenerator input of 900–1000 °C and 1 bar. Currently, heat exchangers with such high temperatures and pressure differences are not used in the energy industry.

A modification of the technology under consideration called the "E-MATIANT" cycle was proposed in [11]. Advantages of this new cycle version consist of the reduction in the number of thermal circuit elements, reduction in the maximum cycle pressure and greater efficiency due to reducing the losses for compression in the compressor. The working fluid expansion takes place in two cooled turbines of high (10–11) and low (12–13) pressure. At the input of each turbine, its own cooled combustion chamber is installed, and fuel and oxygen are supplied into the chambers in addition to the working fluid. From the second turbine output, the working fluid is fed to the regenerator while heating the compressed carbon dioxide at the pump output.

The minimum pressure in the "E-MATIANT" cycle, similar to that in the prototype, is close to atmospheric pressure, and the input HPT pressure has an optimum: 60 bar. Optimization is carried out for a constant working fluid temperature at turbine inputs equal to 1300 °C and underheating in the regenerator equal to 20 °C. The isentropic efficiency of the compressor used in the calculations is in the range between 85% (three first stages) and 80% (last stage). Maximum efficiency of the "E-MATIANT" cycle achieved at an input pressure of 60 bar is 47%, excluding turbine cooling losses.

4. Allam Cycle

The concept of the Allam cycle was patented in 2010 by inventor Rodney John Allam [12]. The technology allows the achievement of a net efficiency of 48% with CO_2 emissions close to zero. In comparison, the net efficiency of natural gas combined cycle (NGCC) power units using sequestration technology does not exceed 48%, and that of steam-gas plants with coal gasification and sequestration is 39% [13].

In the Allam cycle, carbon dioxide is compressed in a multi-stage compressor with intermediate cooling up to 80 bar (2–8) and then it is fed to the pump (8–9), after which, it reaches maximum pressure in the cycle in the range from 200 to 400 bar. After the pump, the carbon dioxide is sent to the regenerator (9–10), where it is heated to 700–750 °C by the heat of the working fluid at the turbine output and the heated refrigerant used for the intermediate cooling of the oxygen in the plant for carbon dioxide preparation. Processing in the regenerator of WHR produced at intermediate oxygen cooling makes it possible to compensate the thermal balance between the hot and cold flows. After the regenerator, most of the carbon dioxide flow is directed into the combustion chamber

(10–11); in order to limit maximum temperature, a smaller part is used to cool the gas turbine. The remaining carbon dioxide is mixed with the compressed oxygen stream and is also sent to the combustion chamber. In the combustion chamber, the working fluid temperature increases to 1150 °C due to the combustion of fuel with oxygen. The use of carbon dioxide recirculation in order to limit temperature at the GT input causes the working fluid to consist of 90% carbon dioxide. Expansion in the GT wheel space (11–12) occurs to a pressure of 20–30 bar, which is less than the critical pressure of carbon dioxide. From the GT output, the working fluid is sent to the regenerator (12–1). The optimal pressure of the working fluid at the gas turbine input is in the range from 200 to 400 bar, and the degree of pressure reduction in the turbine is in the range from 6 to 12 [14].

An important advantage of this technology is the competitive unit cost of installed capacity. The specified indicator for the Allam cycle using natural gas is equal to 1400–1500 $/kW due to the compactness of the entire plant and power equipment caused by the high minimum pressure of the working fluid in the range of 20–40 bar and the absence of traditional steam-gas cycle elements (steam turbine, recovery boiler, steam pipelines, devices for reducing emissions of nitrogen oxide, carbon monoxide, sulfur, synthesis gas cooler, catalysts, etc.).

The creation of a gas turbine and combustion chamber using the Allam cycle is possible on the base of existing groundwork for the development of steam turbine and gas turbine technologies. The Allam cycle temperatures are lower than the temperatures in modern gas turbine and steam-gas cycles but significantly higher than temperatures in steam turbine cycles. In other words, the maximum pressure does not exceed the pressure in the latest steam turbines but exceeds the pressure in gas turbines at times.

The absence of the danger of nitrogen oxide formation makes it possible to concentrate efforts in the design of the Allam cycle combustion chamber to achieve high indicators of structural durability and efficiency of the burning process. Moreover, the main indicator of combustion chamber efficiency is the content of carbon monoxide in the combustion products, which can be minimized by optimizing the combustion chamber length.

An important difference between the Allam cycle combustion chamber and the combustion chamber for traditional GT is the presence of at least three supply streams: fuel (natural gas), oxidizer (oxygen) and maximum temperature limiter (carbon dioxide). The hot stream at such a combustion chamber's output consists mostly of carbon dioxide.

Advantages of the Allam cycle in comparison with other oxygen–fuel cycles are its high efficiency, compactness and, as a result, the relatively low cost of a kilowatt of installed capacity. The disadvantages include, first of all, the fact that the maximum temperature at the turbine input is limited by the maximum permissible temperature and the pressure of the working fluid in the regenerator, which, in turn, depends on the alloys used for their manufacture.

5. Modified Semi-Closed Oxy–Fuel Combustion Power Cycles with CO$_2$ Recirculation

For cycles with oxygen–fuel combustion, the working fluid temperature at the turbine input is limited only by the heat resistance of the combustion chamber materials but can be increased using cooled turbine blades; therefore, improving the gas turbine blade cooling efficiency is one of the areas of research required to improve the energy efficiency of the cycles under consideration. The second direction of research towards improving the oxygen–fuel energy cycles' efficiency relates to WHR sources, as well as decreasing the cooling temperature of the working fluid, that is, in general, this direction can be described as decreasing the "temperature of the cold source".

A separate direction for improving semi-closed CO_2 power cycle efficiency is creating energy technology complexes based on oxygen–fuel power plants, which generate electric power and produce hydrogen by electrolysis from water or in conversion reactors from natural gas. It is planned that the produced hydrogen or synthesis gas can serve as fuel for energy generation and storage and also as fuel for transport.

The following promising modifications of oxygen–fuel cycles using supercritical carbon dioxide are considered:

- SCOC-CC cycle with refrigerant cooling;

- SCOC-CC cycle with water injection;

- SCOC-CC cycle with WHR;

- Allam cycle using liquefied natural gas for cooling;

- Allam cycle with WHR;

- MATIANT cycle with production of electric power and methane in Sabatier reactors.

Paper [15] considered the cooling of turbine blades using the cooled condensate of the second circuit in the SCOC-CC cycle, as well as the cooling of turbine blades using water injection.

The difference between this cycle and the basic SCOC-CC cycle consists of the use of an additional heat exchanger for the cooled turbine blade refrigerant. In this heat exchanger, the refrigerant is cooled by the condensed water of the second circuit, and the water, in turn, is heated by the heat removed. Furthermore, reducing the refrigerant temperature allows the reduction of the flow, which increases the efficiency of the turbine. The use of this approach allows an increase in the cycle efficiency of 3.2%. The scheme disadvantages include the necessity of an additional heat exchanger, which increases the power unit metal consumption and, as a result, capital cost.

The second method considered in [11] to reduce the cooled blade refrigerant consumption of carbon dioxide turbines was water injection. Water injection reduces the temperature of the refrigerant due to evaporation. Water for injection can be taken from the cooler–separator, which eliminates the need for additional expensive water treatment. Water injection makes it possible to increase the cycle efficiency by 1.5% compared to the basic version,

which is less than in the case of cooling by a second circuit condensate. Advantages of this scheme include the simplicity and cheapness of the water injection implementation, which does not have a big impact on the power unit specific capital costs.

For the Allam cycle, the issue of WHR is also relevant. The Allam cycle provides for a large number of compressors which require cooling of the working fluid for more efficient compression. In particular, cooling is required for compressors used to compress the oxygen at the output of the ASU.

Paper [16] proposed a modification of the Allam cycle with WHR when cooling compressors at the output of the ASU using the Brayton cycle with recompression. In this cycle, in the process of multi-stage compression after leaving the ASU, oxygen is sequentially cooled after each compressor stage (line 1′–5′) while transferring heat to the Brayton cycle with recompression, after which, it is compressed in the last stage of the oxygen compressor and combined with the flow of compressed carbon dioxide. Further, the Allam cycle remains unchanged. This solution makes it possible to increase the cycle efficiency by 3.7% compared to the basic version of the Allam cycle with the same gas parameters at the turbine input (1083 °C and 30 MPa). The disadvantage of the cycle, similar to other schemes with WHR, is the significant increase in capital costs.

Efficient compression in a multi-stage CO_2 compressor also requires cooling after each stage. In [17], it was proposed to use liquefied natural gas for cooling. In addition, the paper also proposed the WHR of cooled carbon dioxide after a separator–cooler, using liquefied natural gas as a cold source. Despite the low temperature of carbon dioxide before the compressor, the use of liquefied natural gas with a temperature of −163 °C allows for a sufficient temperature difference for the energy cycle functioning.

In the considered cycle, when carbon dioxide is cooled after water separation, the working fluid is heated in the heat exchanger according to the organic Rankine cycle scheme and then is expanded in the turbine, cooled and condensed in the cooler and is compressed by the pump. At this point, the Rankine organic cycle cooler uses liquefied natural gas coming from a cooling natural gas storage facility. Further, the LNG successively enters heat exchangers designed to cool carbon dioxide after its compression in the compressor stages. Advantages of the considered cycle include the highest efficiency of the Allam cycles, considered equal to 53%, and the scheme disadvantages include high capital costs for the equipment for the Rankine organic cycle, as well as a limited scope of application; the cycle can be implemented only in the immediate vicinity of the liquefied natural gas regasification terminal.

One of the ways to increase economic indicators and energy generation efficiency is currently the production of hydrogen or other fuels, for example, synthesis gas or synthetic methane, as an additional product or during periods of low energy demand for energy for storage in the form of chemical fuel energy. The production of combustible gases at oxygen–fuel power units has a high attractiveness since carbon dioxide emissions into the atmosphere are minimal at these power units, which ensures the carbon neutrality of the product produced. A promising direction is the production of synthetic methane from carbon dioxide and hydrogen, which makes it possible to utilize carbon dioxide more efficiently from an economic point of view.

In [18], the MATIANT cycle using a part of carbon dioxide as a component for the production of synthetic methane was investigated. In this cycle, part of the carbon dioxide formed during burning is sent for deposition (34%), and most of it is mixed with hydrogen obtained by electrolysis from water, compressed in a compressor and then sent to a Sabatier reactor. During the Sabatier reaction, methane and water, as well as by-products hydrogen, carbon monoxide and carbon dioxide, are formed in the presence of a nickel catalyst.

The advantage of the described schematic diagram is the ability to deposit a lower volume of carbon dioxide, which reduces the requirements for CO_2 storage, while the system has a sufficiently high efficiency of 43% at a gas turbine inlet temperature of 1300 °C. The cycle disadvantages include the high energy costs for electrolysis and the high cost of additional equipment, i.e., the electrolyzer and Sabatier reactor. Since the cycle under consideration includes not only energy generation, but also production of an additional product, it cannot be compared with other cycles in terms of technical and economic parameters.

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