



Article Methanol Production in the Brayton Cycle

Janusz Kotowicz, Mateusz Brzęczek *¹⁰, Aleksandra Walewska and Kamila Szykowska *¹⁰

Institute of Power Engineering and Turbomachinery, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland; janusz.kotowicz@polsl.pl (J.K.); aleksandra.walewska@polsl.pl (A.W.) * Correspondence: mateusz.brzeczek@polsl.pl (M.B.); kamila.szykowska@polsl.pl (K.S.); Tel.: +48-32-400-3080 (M.B.)

Abstract: This article presents the concept of renewable methanol production in the gas turbine cycle. As part of the work, an analysis was performed, including the impact of changing the parameters in the methanol reactor on the obtained values of power, yield and efficiency of the reactor, and chemical conversion. The aim of this research was to investigate the possibility of integrating the system for the production of renewable methanol and additional production of electricity in the system. The efficiency of the chemical conversion process and the efficiency of the methanol reactor increases with increasing pressure and decreasing temperature. The highest efficiency values, respectively $\eta = 0.4388$ and $\eta_R = 0.3649$, are obtained for parameters in the reactor equal to 160 °C and 14 MPa. The amount of heat exchanged in all exchangers reached the highest value for 14 MPa and 160 °C and amounted to $\dot{Q} = 2.28$ kW. Additionally, it has been calculated that if an additional exchanger is used before the expander (heating the medium to 560 °C), the expander's power will cover the compressor's electricity demand.

Keywords: methanol; gas turbine; hydrogen; carbon dioxide; renewable fuel



Citation: Kotowicz, J.; Brzęczek, M.; Walewska, A.; Szykowska, K. Methanol Production in the Brayton Cycle. *Energies* **2022**, *15*, 1480. https://doi.org/10.3390/en15041480

Academic Editors: Attilio Converti and Dmitri A. Bulushev

Received: 24 January 2022 Accepted: 15 February 2022 Published: 17 February 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).

1. Introduction

Methanol currently plays a very important role in the chemical industry and is a promising energy fuel, mainly produced from fossil fuels. Some of the alternatives under investigation use biogas, shale gas or captured CO_2 , and hydrogen. The CO_2 hydrogenation pathway, which contributes to the switch to renewable fuels, gives rise to a set of alternative pathways differing in CO_2 and hydrogen sources [1].

Carbon dioxide used in the methanol production process can be captured from fossil fuel power plants or directly from the air, where the latest is the only route fully compatible with the principles of the circular economy. In addition, electrolysis of water as a source of hydrogen can be powered by any form of renewable energy, such as solar or wind energy. There are also other interesting methods of obtaining hydrogen, including the use of ammonia borane as its source [2,3].

The overall concept of (green) methanol production is presented in Figure 1 [4]. It includes the supply of energy from renewable sources to the grid, where the excess energy from them is transferred to the hydrogen generator. The obtained hydrogen and carbon dioxide captured from the flue gases of a conventional power plant are supplied as substrates for the production of methanol.

Global methanol consumption reached 98.3 million tonnes in 2019 and is expected to exceed 120 million tonnes by 2025 and 500 million tonnes by 2050. China, as the world's largest producer and methanol consumer that accounts for more than half of the total global demand, consumed about 55 Mt of methanol in 2018, wherein 25% of it was used in the fuel industry. Over the next ten years, China is projected to see the greatest increase in demand in the future, because applications, such as transport and heating fuels expand. However, mainly for economic reasons, methanol is still almost exclusively produced from fossil fuels. About 65% of methanol production is based on natural gas reforming (gray



methanol), while the rest (35%) is largely based on coal gasification (brown methanol). Currently, only about 0.2% comes from renewable sources (green methanol) [4–6].

Figure 1. General scheme of the renewable methanol production concept.

The production of "renewable" methanol is based on four basic sources: biomass, municipal waste, industrial waste, and carbon dioxide. The first three are based on gasification and catalytic conversion technology. The last variant, using carbon dioxide, water, and surplus electricity from RES, is the most ecological option for its production. Catalytic hydrogenation of carbon dioxide is currently the technology with the greatest development prospects and a relatively high probability of being introduced in the near future as a commercial technology on a large scale [7,8].

Liquid methanol is synthesized via the exothermic reaction between hydrogen and carbon dioxide (or carbon monoxide) according to the following reactions [9]:

$$CO_{(g)} + 2H_{2(g)} \leftrightarrow CH_3OH_{(l)} \Delta H = -128 \text{ kJ/mol} (298 \text{ K})$$
(1)

$$CO_{2(g)} + 3H_{2(g)} \leftrightarrow CH_3OH_{(l)} + H_2O_{(g)} \Delta H = -87 \text{ kJ/mol} (298 \text{ K})$$
 (2)

In parallel, there is also a reverse endothermic reaction of the conversion to water vapor.

$$CO_{2(g)} + H_{2(g)} \leftrightarrow CO_{(g)} + H_2O_{(g)} \Delta H = +41 \text{ kJ/mol} (298 \text{ K})$$
 (3)

7.277 kg
$$CO_{2(g)} + 1$$
 kg $H_{2(g)} \leftrightarrow 5.298$ kg $CH_3OH_{(1)} + 2.979$ $H_2O_{(g)}$ (4)

The need to mitigate climate change and the elimination of carbon dioxide emissions from all types of energy consumption has increased global interest in renewable methanol. This type of production may increase the use of methanol as a chemical raw material and support industry and transport sectors in neutralizing carbon dioxide emissions, which is at a high level in these sectors of the economy. Moreover, renewable methanol can contribute to the improvement of the functioning of the energy system by storing energy in liquid form, which undoubtedly has advantages in the ease of transport compared to other forms of energy storage in gaseous forms. Currently, the cost of producing methanol from renewable sources is high and the production volume is low. With the right policies and falling renewable energy prices, green methanol could be cost-competitive until 2050 or even earlier. Methanol, for energy purposes, is mainly used in fuel cells, reciprocating engines, and gas turbines [10,11].

In the conventional methanol industry, typical reactor operating conditions are 50–100 bar and 200–300 °C. The authors' research shows that an increase in temperature leads to an increase in methanol production to some extent, and then a decrease in it. The authors obtained the best performance at a temperature of 270 °C and a pressure of 50 bar,

which is in line with those commonly used on an industrial scale in low-pressure methanol production processes [12,13]. In [14] it was found that the temperature of the maximum methanol yield moves up with the increase in pressure from about 235 °C to 250 °C for 40 to 100 bar, respectively. According to the researchers, methanol efficiency will increase with increasing pressure.

The influence of the working pressure on the yield of methanol at a fixed ratio of hydrogen to carbon dioxide equal to three and reaction temperatures ranging from 200 °C to 300 °C was investigated in [15]. In all tested cases, better menthol recovery was observed at higher working pressure and this effect was slight at low temperatures (200 °C) and dominant at higher temperatures. It has been found that the optimal process temperature (the one where the maximum yield has decreased with increasing operating pressure) for which the maximum yield is obtained is 240 °C at 50–60 bar, 230 °C at 70–90 bar, and 220 °C at 100 bar. The presented results may prove helpful in the selection of appropriate operational conditions for increasing the efficiency of the methanol synthesis process.

The gas turbine plays an increasingly important role in the petrochemical industry. In the industry, open-circuit gas power plants are widely used. Typically, a gas turbine works on the principle of internal combustion. Air passes through the compressor and then enters the combustion chamber. The products of combustion are expanded in a turbine, then drive an electric generator. The gas turbine is one of the most widely used devices to support the energy consumption of offshore platforms due to the multiple uses of fuel. However, the main negative effect of such engines is lower efficiency and large energy losses from the exhaust gas. The efficiency of the gas turbine is about 40% [16,17].

In order to improve the energy efficiency of the gas turbine and reduce the waste of resources, several methods are proposed to recover the thermal energy contained in the exhaust gas, such as heat exchangers installed in the exhaust path. The heat recovered from the flue gas can be used internally or externally. Conventional techniques for internal waste heat recovery include steam regeneration and injection, which are always integrated into gas turbine assemblies. A gas turbine with a steam injection into the combustion chamber is called a STIG turbine (Steam Injection Gas Turbine) [18]. In [19], the authors proposed the selection of a steam injection cooling scheme for a CHP plant and analyzed the operation of a gas turbine in a steam injection configuration. Steam injection by heat recovery steam generators improved the exergy efficiency of the system and reduced carbon dioxide emissions. In turn, other researchers [20] focused on the thermo-environmental and economic operation of the steam injection method with heat recovery, based on a power plant in northeastern Iran. The authors present a comprehensive model based on energy, exergy, environmental, and economic analyzes. The final model introduced the optimal conditions for the injection of steam into the combustion chamber. The optimum steam temperature of 318.5 °C was found at an ambient temperature of 38 °C and a relative humidity of 10%. The introduced heat recovery at the optimal steam temperature increased the power and net thermal efficiency by 56 MW and 4.6%, and also reduced the costs of energy production by 25.5%. Multivariate analyses of the operation of modern gas turbines operating in a wide range of pressures and with various methods of cooling are presented by authors in [21–23].

Gas turbines are widely used for energy generation due to their efficiency and low carbon dioxide emissions. Gas turbine plants are constantly evolving to meet the electricity demand of developing societies and economies. The gas turbine system consists of a compressor, combustion chamber, and expander. Each open and closed cycle gas turbine works in four processes, such as compression, combustion, expansion, and heat dissipation. Air is used as a refrigerant that is compressed in the compressor, combustion takes place in the combustion chamber, and the resulting exhaust gases are fed to the expander to produce energy. The gas turbine cycle is based on the Brayton cycle. The ideal Brayton cycle is characterized as a thermodynamic cycle that consists of isentropic and adiabatic gas compression followed by the addition of heat at constant pressure, and the extraction of energy by expanding the gas, as shown in Figure 2a–c [24,25].



Figure 2. (a). Brayton's cycle in the p-V plot. (b). Brayton cycle in a T-s plot. (c). General scheme of a gas turbine (A: air; C: compressor; CC: combustion chamber; F: fuel; T: expander; G: generator; EG: exhaust gas).

The concept of combining a gas turbine system with methanol production was presented in [17]. The authors' concept combines a gas turbine and a low-pressure installation for the production of methanol using the Lurgi method. Methanol is produced by catalytic hydrogenation of carbon monoxide and/or carbon dioxide in a methanol synthesis reactor. In the system behind the reactor there is a gas turbine in which high operating pressure generated electricity [17,26].

In [27], the integration between a power-to-methanol energy storage system and a chemically recuperated gas turbine (CRGT) power plant was investigated. The selected configuration leads to an efficiency of the power-to-methanol process of around 60%. The obtained methanol flow rate enables the supply of a small (several kW) gas turbine equipped with a methanol reforming section in order to increase the efficiency of the installation. CRGT power plants can be an interesting low-carbon technology for the use of renewable methanol, enabling efficient storage of surplus renewable energy, and then producing electricity with low CO_2 emissions.

In [28], a new method of fuel conversion was applied, consisting of combustion in a chemical loop in a gas turbine cycle powered with methanol with an intercooler. The methanol-fueled chemical loop gas turbine cycle represents a breakthrough in both the efficient use of alternative fuels and the mitigation of greenhouse gas emissions. The results obtained by the authors indicate that the gas turbine cycle with combustion in a chemical loop driven by methanol can provide a promising approach to both the efficient use of alternative fuel and the recovery of low-temperature waste heat.

The research of [29] has been proposed as an integrated system that includes an externally fired gas turbine (EFGT), a fuel cell (MCFC), an Organic Rankine Cycle (ORC), methane and/or methanol production, and a proton exchange membrane electrolyser (PEME). Three different production scenarios covering methane only, methanol only, and dual production, are investigated, considering the different operational loads of the electrolyser. If 10% of the energy produced is used by the electrolysis process to produce hydrogen used in the synthesis of methanol, the overall energy efficiency is 41%. In this case, the system uses 1012 tonnes/year of CO_2 to produce 393 tons of methanol per year.

The authors present a unique analysis of alternative fuel production systems in conjunction with a gas turbine cycle. The originality of the presented analyses is emphasized by the fact that they are performed in a wide range of pressure and temperature. The analyses available in the literature on the subject focus mainly on the analysis of the chemical side of the processes and operation of the reactor [9,30]. The complexity of the analyses carried out in this article covers the entire process of producing "green" methanol, from the use of renewable energy to the production of hydrogen, using CO_2 and also electricity production in the gas turbine cycle. This research expands and shows other modern possibilities of using a gas turbine for the production of methanol [27,28].

One should also not overlook the fact that the production of methanol uses carbon dioxide, which is largely responsible for the aggravation of climate change and global warming. Its use, for example, captured from the exhaust of a conventional power plant, may contribute to global climate change mitigation. According to the circular economy in which the consumption of raw materials and the amount of waste, as well as emission and loss of energy, are minimized by creating a closed loop of processes, in our case, CO₂ is used as raw material for production of methanol, which minimizes the amount of production waste [31,32].

2. A System for the Methanol Production in the Gas Turbine Cycle

The proposed installation for the methanol production is shown in Figure 3. In the initial phase, carbon dioxide is compressed to an appropriate pressure, then mixed with hydrogen, and the entire mixture is compressed again to the pressure required in the system. The mixture, prepared in this way, is directed to the heat exchanger HX1, where the heat is collected in order to adjust the temperature to the synthesis in the reactor, R. The methanol reactor operates in the temperature range from 160 °C to 220 °C and in the high pressure range from 8 MPa to 14 MPa. After passing through the reactor, the mixture is directed to the expander T, where electricity is produced.



Figure 3. Installation of methanol production in the gas turbine cycle (C: compressor; HX-heat exchanger; T: gas turbine; R: methanol synthesis reactor; S: separator; MR: separation membrane; G: generator; M: motor; Q: heat; CO₂: carbon dioxide; H₂: hydrogen; H₂O: water; CH₃OH: methanol).

The mixture is then directed to the heat exchanger HX2, where the heat is collected and the moisture condenses, simultaneously. Subsequently, the mixture is directed to separator S. In separator S, liquid methanol is collected while the remaining stream is directed to the membrane MR. After passing through the membrane, the separated hydrogen and carbon dioxide are recycled back into recompression and go through the process. Assumed parameters in the installation at characteristic points of circulation are presented in Table 1.

Parameter, Unit	Symbol	Value
Hydrogen pressure at the inlet system inlet, MPa	p_1	2.5
Carbon dioxide pressure at the system inlet, MPa	<i>p</i> ₂	0.15
Hydrogen temperature at the inlet to the installation, $^\circ C$	t_1	25
Temperature of carbon dioxide at the inlet to the installation, $^\circ C$	t_2	25
Pressure at the outlet of the gas turbine, -	p_{10}	150
Isentropic efficiency of a gas turbine, -	η_{iT}	0.9
Mechanical efficiency of a gas turbine, -	η_{mT}	0.99
Isentropic efficiency of compressors, -	η_{iC}	0.88
Mechanical efficiency of compressors, -	η_{mC}	0.995
Electric efficiency of the engine, -	η_{mel}	0.95
Mechanical efficiency of the engine, -	η_{mm}	0.998
Generator nominal efficiency, -	η_{ng}	0.9856

Table 1. Assumptions for the installation of methanol production in the gas turbine cycle.

3. Methodology of Calculations

The calculation methodology was taken from the authors' previous research on methanol production presented in [26,27].

The balance of components present in the reaction of methanol formation is carried out in accordance with the relationship (4). The efficiency of the methanol reactor is defined as the ratio of the amount of methanol obtained in the process to the theoretical amount of methanol determined from Equation (4), in accordance with:

$$\eta_R = \frac{u_{CH3OH}}{u_{CH3OH,stec}} \tag{5}$$

*u*_{CH3OH}—pure methanol yield, kg_{CH3OH}/kg_{H2}

 $u_{CH3OH,stec}$ —pure methanol yield calculated from Equation (4), kg_{CH3OH}/kg_{H2}

The efficiency of the chemical conversion process is the ratio of the chemical energy of the methanol formed to the amount of chemical energy supplied to the hydrogen process, according to the relationship:

$$\eta = \frac{HHV_{CH3OH} \cdot \dot{m}_{CH3OH}}{HHV_{H2} \cdot \dot{m}_{H2}} \tag{6}$$

HHV_{CH3OH}—22,341.21 kJ/kg

HHV_{H2}—142,327 kJ/kg

The amount of heat exchanged in the process is the sum of heat exchanged in all three exchangers:

$$\dot{Q} = \dot{Q}_{HX1} + \dot{Q}_{HX2} + \dot{Q}_{HX3}$$
 (7)

Q—amount of heat exchanged in all exchangers, kW

 Q_{HX} —amount of heat exchanged in the exchanger, kW

The amount of heat exchanged in individual exchangers is the product of the mass flow of a given factor and its enthalpy difference:

$$Q_{HX1} = \dot{m} \cdot (i_{in} - i_{out}) \tag{8}$$

 \dot{m} —the flow of the medium that exchanges heat in the exchanger, kg/s

 i_{in} —enthalpy of the medium at the inlet to the exchanger, kJ/kg

 i_{out} —enthalpy of the medium at the outlet of the exchanger, kJ/kg

4. The Results of the Analyses

The results of the obtained values at characteristic points of the installation are presented in Table 2.

Table 2. Examples of the analysis results obtained for the pressure of 14 MPa and the temperature of 160 $^{\circ}$ C at the inlet to the reactor in point 8.

Lp	m [kg/h]	p [MPa]	t [°C]	i [kJ/kg]	X [-]	CH ₃ OH	H ₂	CO ₂	СО	H ₂ O
1	0.45	2.5	25	356.9	1	0	1	0	0	0
2	3.34	0.15	25	20.8	1	0	0	1	0	0
3	0.55	2.5	25	356.9	1	0	1	0	0	0
4	1.00	2.5	25	356.9	1	0	1	0	0	0
5	7.28	2.5	272.9	257.0	1	0	0	1	0	0
6	8.28	2.5	107.5	269.0	1	0	0.12	0.88	0	0
7	8.28	14	342.6	890.5	1	0	0.12	0.88	0	0
8	8.28	14	160	404.6	1	0	0.12	0.88	0	0
9	8.28	14	290.6	649.4	1	0.28	0.07	0.48	0	0.01
10	8.28	0.15	43.7	-158.5	0.9	0.28	0.07	0.48	0	0.01
11	8.28	0.15	15	-349.0	0.8	0.28	0.07	0.48	0	0.01
12	1.28	0.15	15.0	63.1	0	0	0	0	0	0
13	7.00	0.15	15	31.9	1	0.34	0.08	0.56	0	0.01
14	7.00	0.15	15	12.4	1	0	0	1	0	0
15	0.55	0.15	15	213.9	1	0	1	0	0	0
16	0.55	2.5	126.6	1821.4	1	0	1	0	0	0
17	2.32	0.15	15	22.6	1	0	0	0	0	0

As part of the analysis of the results, graphs were drawn showing the effect of pressure and temperature changes (in point 8 in Figure 3) at the reactor inlet on:

- total amount of heat from heat exchangers HX1, HX2, HX3 (Q_{HX1}, Q_{HX2}, Q_{HX3});
- gas turbine power (*N*_{*T*});
- total power of compressors C (ΣN_c);
- yield (*u*_{CH3OH});
- efficiency of the chemical conversion (η);
- reactor efficiency (η_R) .

Figure 4 presents the results of calculating the power of the N_T gas turbine depending on the parameters in the reactor (pressure and temperature). The value of the power increases with the increase of these parameters. The highest power is obtained for 220 °C and 14 MPa, and amounts to $N_T = 1.96$ kW, and the lowest for 160 °C and 8 MPa ($N_T = 1.62$ kW). By changing the temperature t_8 by 10 °C, the power increase by 0.024 kW is noticeable. By changing the pressure p_8 by 1 MPa, the power increase is 0.032 kW. Increasing the pressure p_8 by 1 MPa allows for a greater increase in power than increasing the temperature t_8 by 10 °C.

Calculation results of the power of all three compressors in the system depending on the pressure p_8 and the temperature t_8 in the methanol reactor are presented in Figure 5. The value of the total power ΣN_c increases with increasing the assumed parameters. For the conditions prevailing in the reactor of 220 °C and 14 MPa, the highest power of compressors is obtained, equal to $\Sigma N_c = 2.97$ kW, and the lowest value for 160 °C and 8 MPa ($\Sigma N_c = 2.35$ kW). A 10 °C change in t_8 temperature causes a noticeable power increase of about 0.026 kW. The change in pressure p_8 by 1 MPa causes the power increase of 0.078 kW. Increasing the pressure p_8 by 1 MPa allows for a greater increase in power than increasing the temperature t_8 by 10 °C. As the reaction (2) is exothermic, and the assumed temperature in the reactor t_8 amounts to a maximum of 220 °C, it is not possible to obtain a higher turbine power, N_T , than the total power of the compressors, ΣN_c . It was checked that adding an additional heat source downstream of the reactor and heating the medium to 560 °C would increase the power of the N_T turbine and exceed the total power of the compressors, ΣN_c .



Figure 4. Influence of changes in pressure p_8 and temperature t_8 at the reactor inlet (Figure 3) on the power of the gas turbine N_T in kW.



Figure 5. Influence of changes in pressure p_8 and temperature t_8 at the reactor inlet (Figure 3) on the total power of compressors ΣN_c in kW.

Figure 6 shows the results of analysis of all three heat exchangers in relation to changes in pressure p_8 and temperature t_8 in the methanol reactor. With the decrease in temperature t_8 and the increase in pressure p_8 , the value of heat exchanged (Q) in the system increases. The amount of heat obtained for 160 °C and 14 MPa in the system reaches the highest value and amounts to Q = 2.28 kW. A change in temperature t_8 by 10 °C causes a noticeable decrease in the amount of heat exchanged by 0.065 kW, and a change in pressure p_8 by 1 MPa causes an increase in the amount of heat equal to 0.083 kW.

Reducing the temperature, t_8 , by 10 °C allows for a smaller increase in heat exchanged than increasing the pressure, p_8 , by 1 MPa.



Figure 6. Influence of changes in pressure, p_8 , and temperature, t_8 , at the reactor inlet (Figure 3) on the total amount of heat from the exchangers HX1, HX2, and HX3 (Q_{HX1} , Q_{HX2} , Q_{HX3}), in kW.

Figure 7 shows the results of the analysis of changes in the parameters to the chemical conversion efficiency η . The efficiency of the installation increases with the decrease in temperature, t_8 , and the increase in pressure, p_8 . The highest efficiency of the installation is achieved for 160 °C and 14 MPa ($\eta = 0.3649$), and the lowest for 220 °C and 8 MPa ($\eta = 0.2037$). The efficiency drop of 0.017 is due to a 10 °C change in temperature, t_8 . Increasing the pressure, p_8 , by 1 MPa causes an increase in the chemical conversion efficiency, η , equal to 0.01. A change in pressure, p_8 , by 1 MPa has a smaller effect on the efficiency, η , than a change in temperature, t_8 , by 10 °C.



Figure 7. Influence of changes in pressure p_8 and temperature t_8 at the reactor inlet (Figure 3) on the chemical conversion efficiency η .

The results of the η_R reactor efficiency analysis, depending on the pressure, p_8 , and the temperature, t_8 , in the reactor are shown in Figure 8. The reactor efficiency, η_R , in the analyzed installation increases with the increase of pressure, p_8 , and the decrease of the temperature, t_8 . The highest efficiency of the installation is achieved for 160 °C

and 14 MPa ($\eta_R = 0.4388$), and the lowest for 220 °C and 8 MPa ($\eta_R = 0.2449$). An increase in temperature, t_8 , by 10 °C causes a degradation of efficiency by 0.021, while an increase in pressure, p_8 , by 1 MPa causes a jump in efficiency by 0.012. A 10 °C change in temperature, t_8 , has a greater effect on efficiency than a 1 MPa change in pressure, p_8 .



Figure 8. Influence of changes in pressure, p_8 , and temperature, t_8 , at the reactor inlet (Figure 3) on the reactor efficiency, η_R .

The amount of obtained methanol, u_{CH3OH} , from the analyzed installation in relation to the change of parameters in the methanol reactor is shown in Figure 9. The value of the yield from the analyzed installation increases with increasing pressure, p_8 , and decreasing temperature, t_8 . The highest yield of 2.32 kg/h was achieved for 160 °C and 14 MPa. The smallest amount of methanol obtained from the system was 1.30 kg/h (at 220 °C and 8 MPa in point 8 in Figure 3). An increase in temperature, t_8 , by 10 °C causes a decrease in the amount of obtained product by 0.011 kg/h. Increasing the pressure, p_8 , by 1 MPa results in the amount of product obtained by 0.06 kg/h. A 10 °C change in temperature, t_8 , has a greater effect on the yield than a 1 MPa change in pressure, p_8 . Compared to the classic methanol production plant, the yield obtained in the analysis is lower by approximately 2 kg_{CH3OH}/kg_{H2}, which is due to the lack of an internal purification loop of the product.



Figure 9. Influence of changes in pressure, p_8 , and temperature, t_8 , at the reactor inlet (Figure 3) on the yield of methanol, u_{CH3OH} , in kg_{CH3OH}/kg_{H2}.

11 of 14

5. Summary

The article presents the concept of methanol production in the form of the gas turbine cycle. The production process uses hydrogen from the electrolysis process and carbon dioxide captured from the exhaust gases of a conventional power plant. As part of the research, the analysis of pressure and temperature changes at the inlet of the methanol synthesis reactor was performed. Replacement in the gas turbine cycle of the combustion chamber with a reactor (in which the exothermic reaction takes place) results in a number of benefits. The produced methanol not only contributes to reducing the amount of CO_2 in the atmosphere, but also to increasing the consumption of renewable energy. Additionally, it is possible to use methanol in a gas turbine as a fuel, as it allows for the production of electricity at the time of greater demand. Methanol is therefore an excellent energy carrier. The methanol produced in the installation (pipeline 17 in Figure 3) is in a liquid form, which makes it much easier and more profitable to transport.

The issues related to the development of effective and economically justified systems for the conversion of carbon dioxide into useful materials seem to be very promising in an era of continuously increasing fuel prices and the need to reduce CO_2 emissions. The produced methanol may constitute a competitive marine or automotive fuel or chemical feedstock for its potential consumers. Renewable methanol enables a rapidly growing part of the global economy to become carbon neutral using existing processes and infrastructures, enabling cooperation between different sectors to reduce overall CO_2 emissions and increase the importance of the circular economy. "Green" methanol is able to technically, economically, and practically reduce the greenhouse gas emissions of significant sections of the global economy [33].

As part of the analysis of the resulting charts, in order to open a wider discussion, the authors posed several research questions relating to the current work. This can trigger more broad interest in the future.

How did the change of parameters affect the value of the compressor and turbine power?

• The power values of the compressor, ΣN_c , and the N_T turbine increase with the increase of temperature, t_8 , and pressure, p_8 , prevailing in the reactor, reaching the highest value of 14 MPa and 220 °C and are, respectively, $\Sigma N_c = 2.97$ kW and $N_T = 1.96$ kW.

For which operating parameters of the reactor were the highest value of heat exchanged achieved?

 The amount of heat exchanged in all exchangers reached the highest value for 14 MPa and 160 °C, and equal 2.28 kW.

How do changes in pressure and temperature at reactor inlet effect methanol production efficiency and methanol reactor efficiency?

• The efficiency of the methanol production process, η , and the efficiency of the methanol reactor increase with increasing pressure, p_8 , and decreasing temperature, t_8 . This represents the expected development towards higher reactor pressures.

Are there any options for retrofitting the system to meet the compressor's energy demands?

 Inserting an additional heat exchanger preceding the expander, which heats the medium to 560 °C, will increase the expander's power so much that it will cover the compressor's electricity demand.

Author Contributions: Conceptualization: J.K. and M.B.; formal analysis: M.B.; funding acquisition: M.B. and K.S.; investigation: J.K., M.B. and A.W.; methodology: J.K. and M.B.; resources: J.K. and M.B.; writing—original draft: K.S. and A.W. All authors have read and agreed to the published version of the manuscript.

Funding: Scientific work supported by the National Science Center as part of the research project: "Research on various structures of systems for the energetic use of methanol and its production based on H₂ from the electrolysis process and CO₂ from CCS installation" (project no 2018/29/B/ST8/02244). The presented work was financed by the Silesian University of Technology with means from statutory research funds.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

.

Q	amount of heat, kW;
η_R	reactor efficiency, -;
HHV _{CH3OH}	22,341.21 kJ/kg;
HHV_{H2}	142,327 kJ/kg;
N_T	gas turbine power, kW;
р	pressure, MPa;
t	temperature, °C;
иснзон	pure methanol yield, kg _{CH3OH} /kg _{H2} ;
u _{CH3OH,stec}	pure methanol yield kg _{CH3OH} /kg _{H2} ;
ΣN_c	total power of compressors, kW;
i	enthalpy of the medium, kJ/kg;
η	efficiency of the chemical conversion, -;
m	the flow of the medium, kg/s.

Subscripts

•	separator of subscripts;
$1 \div 17$	numbers in characteristic points of installations;
CH ₃ OH	methanol;
H ₂	hydrogen;
CO ₂	carbon dioxide;
CO	carbon monoxide;
H_2O	water.

Abbreviations

А	air;
С	compressor;
CC	combustion chamber;
F	fuel;
Т	gas turbine;
G	generator;
EG	exhaust gas;
HX	heat exchanger;
R	methanol synthesis reactor;
S	separator;
MR	separation membrane;
G	generator;
М	motor;
CO ₂	carbon dioxide;
H ₂	hydrogen;
H ₂ O	water;
CH ₃ OH	methanol.

References

- 1. Vazquez, D.; Guillén-Gosálbez, G. Process design within planetary boundaries: Application to CO₂ based methanol production. *Chem. Eng. Sci.* **2021**, 246, 116891. [CrossRef]
- Eghbali, P.; Nişancı, B.; Metin, Ö. Graphene hydrogel supported palladium nanoparticles as an efficient and reusable heterogeneous catalysts in the transfer hydrogenation of nitroarenes using ammonia borane as a hydrogen source. *Pure Appl. Chem.* 2018, 90, 327–335. [CrossRef]
- Eghbali, P.; Gurbuzm, M.; Erturk, A.; Metin, Ö. In situ synthesis of dendrimer-encapsulated palladium(0) nanoparticles as catalysts for hydrogen production from the methanolysis of ammonia borane. *Int. J. Hydrogen Energy* 2020, 45, 26274–26285. [CrossRef]
- 4. Coskun Avci, A.; Toklu, E. A new analysis of two phase flow on hydrogen production from water electrolysis. *Int. J. Hydrogen Energy* **2022**, *47*, 6986–6995. [CrossRef]
- 5. Ravikumar, D.; Keoleian, G.; Miller, S. The environmental opportunity cost of using renewable energy for carbon capture and utilization for methanol production. *Appl. Energy* **2020**, *279*, 115770. [CrossRef]
- Berggren, M. Global methanol—State of the industry. In Proceedings of the 22nd IMPCA Asian Methanol Conference, Singapore, 5–7 November 2019.
- 7. Osman, M.; Zaabout, A.; Cloete, S.; Amini, S. Pressurized chemical looping methane reforming to syngas for efficient methanol production: Experimental and process simulation study. *Adv. Appl. Energy* **2021**, *4*, 100069. [CrossRef]
- 8. Schorn, F.; Breuer, J.; Samsun, R.; Schnorbus, T.; Heuser, B.; Peters, R.; Stolten, D. Methanol as a renewable energy carrier: An assessment of production and transportation costs for selected global locations. *Adv. Appl. Energy* **2021**, *3*, 100050. [CrossRef]
- Kotowicz, J.; Węcel, D.; Brzęczek, M. Analysis of the work of a "renewable" methanol production installation based ON H₂ from electrolysis and CO₂ from power plants. *Energy* 2021, 221, 119538. [CrossRef]
- 10. Chen, C.; Yang, A. Power-to-methanol: The role of process flexibility in the integration of variable renewable energy into chemical production. *Energy Convers. Manag.* **2021**, 228, 113673. [CrossRef]
- 11. Bos, M.; Kersten, S.; Brilman, D. Wind power to methanol: Renewable methanol production using electricity, electrolysis of water and CO₂ air capture. *Appl. Energy* **2020**, *264*, 114672. [CrossRef]
- 12. Cui, X.; Kær, S.; Nielsen, M. Energy analysis and surrogate modeling for the green methanol production under dynamic operating conditions. *Fuel* **2022**, *307*, 121924. [CrossRef]
- 13. Iwakiri, I.; Miguel, C.; Madeira, L. Modeling and simulation of a steam-selective membrane reactor for power-to-methanol. *Comput. Chem. Eng.* **2022**, *156*, 107555. [CrossRef]
- 14. Kiss, A.; Pragt, J.; Vos, H.; Bargeman, G.; de Groot, M. Novel efficient process for methanol synthesis by CO₂ hydrogenation. *Chem. Eng. J.* **2016**, *284*, 260–269. [CrossRef]
- 15. Lee, B.; Lee, H.; Lim, D.; Brigljević, B.; Cho, W.; Cho, H.-S.; Kim, C.-H.; Lim, H. Renewable methanol synthesis from renewable H₂ and captured CO₂: How can power-to-liquid technology be economically feasible? *Appl. Energy* **2020**, *279*, 115827. [CrossRef]
- 16. Gou, X.; Zhang, H.; Li, G.; Cao, Y.; Zhang, Q. Dynamic simulation of a gas turbine for heat recovery at varying load and environment conditions. *Appl. Therm. Eng.* **2021**, *195*, 117014. [CrossRef]
- 17. Kralj, A.; Glavic, P. Optimization of a gas turbine in the methanol process, using the NLP model. *Appl. Therm. Eng.* **2007**, *27*, 1799–1805. [CrossRef]
- Carapellucci, R.; Milazzo, A. Repowering combined cycle power plants by a modified STIG configuration. *Energy Convers. Manag.* 2007, 48, 1590–1600. [CrossRef]
- 19. Vadlamudi, T.; Kommineni, R.; Katuru, B. Exploration of turbine blade cooling strategies for performance boosting and CO₂ emissions reduction of combined cycle with steam injection based gas turbine. *Int. J. Ambient Energy* **2020**. [CrossRef]
- 20. Rad, E.; Kazemiani-Najafabadi, P. Thermo-environmental and economic analyses of an integrated heat recovery steam-injected gas turbine. *Energy* **2017**, *141*, 1940–1954. [CrossRef]
- 21. Kotowicz, J.; Brzęczek, M. Analysis of increasing efficiency of modern combined cycle power plant: A case study. *Energy* **2018**, 153, 90–99. [CrossRef]
- Kotowicz, J.; Brzęczek, M. Comprehensive multivariable analysis of the possibility of an increase in the electrical efficiency of a modern combined cycle power plant with and without a CO₂ capture and compression installations study. *Energy* 2019, 175, 1100–1120. [CrossRef]
- 23. Kotowicz, J.; Brzęczek, M.; Job, M. The thermodynamic and economic characteristics of the modern combined cycle power plant with gas turbine steam cooling. *Energy* **2018**, *164*, 359–376. [CrossRef]
- 24. Salilew, W.; Karim, Z.; Baheta, A. Review on gas turbine condition based diagnosis method. Mater. Today Proc. 2021. [CrossRef]
- Tahan, M.; Muhammad, M.; Karim, Z. A multi-nets ANN model for real-time performance-based automatic fault diagnosis of industrial gas turbine engines. J. Braz. Soc. Mech. Sci. Eng. 2017, 39, 2865–2876. [CrossRef]
- Greeff, I.; Visser, J.A.; Ptasiński, K.; Janssen, F. Utilisation of reactor heat in methanol synthesis to reduce compressor duty— Application of power cycle principles and simulation tools. *Appl. Therm. Eng.* 2002, 22, 1549–1558. [CrossRef]
- Tola, V.; Lonis, F. Low CO₂ emissions chemically recuperated gas turbines fed by renewable methanol. *Appl. Energy* 2021, 298, 117146.
 [CrossRef]
- Jin, H.; Zhang, X.; Hong, H.; Han, W. An innovative gas turbine cycle with methanol-fueled chemical-looping combustion. J. Eng. Gas Turbine Power 2009, 131, 061701. [CrossRef]

- 29. Eisavi, B.; Ranjbar, F.; Nami, H.; Chitsaz, A. Low-carbon biomass-fueled integrated system for power, methane and methanol production. *Energy Convers. Manag.* **2022**, 253, 115163. [CrossRef]
- Kotowicz, J.; Brzęczek, M. Methods to increase the efficiency of production and purification installations of renewable methanol. *Renew. Energy* 2021, 177, 568–583. [CrossRef]
- 31. Aydin, M.; Dincer, I. An assessment study on various clean hydrogen production methods. Energy 2022, 245, 123090. [CrossRef]
- 32. Dar, A.; Hameed, J.; Huo, C.; Sarfraz, M.; Albasher, G.; Wang, C.; Nawaz, A. Recent optimization and panelizing measures for green energy projects; insights into CO₂ emission influencing to circular economy. *Fuel* **2022**, *314*, 12094. [CrossRef]
- 33. Altayib, K.; Dincer, I. Development of an integrated hydropower system with hydrogen and methanol production. *Energy* **2022**, 240, 122780. [CrossRef]