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Integrated Coproduction of Power and Syngas from Natural Gas to Abate Greenhouse Gas Emissions without Economic Penalties

Mikhail Granovskiy*



house gas (GHG) emitters because of their substantial CO_2 release. To avoid these emissions, precombustion and postcombustion CO_2 capture alongside oxy-fuel combustion were considered in the literature. However, because of additional energy requirements, these options generally induce an approximately 7–10% decrease in net heat-to-power efficiencies regarding regular NG-air-fired stations without CO_2 capture. To compensate for this declination, in this study, a simultaneous generation of power and syngas (CO and H₂) was proposed in an integrated NG-oxygen-fired gas turbine unit (GTU). Hence, the combustion chamber in the NG-oxygen-fired gas



turbine cycle was replaced by an NG partial oxidation reactor, which converts it into syngas. The syngas was separated from the working fluid of the cycle by the condensation of water vapor (steam), and a part of it was withdrawn from the GTU to be utilized as a chemical feedstock. A benchmark thermodynamic analysis at the same input–output conditions and requirements for carbon capture was conducted to compare the proposed unit with NG-air and NG-oxygen-fired power plants. The integration effect was shown by increasing the heat-to-power efficiency from 48 to 54%. With carbon monoxide (CO) as an intermediate, the author proposed capturing carbon in NG (methane) in liquid formic acid, which is a good commodity for transportation to a place where it can be reconverted into CO or H_2 to manufacture various industrial chemicals. Simple economic considerations show that because of a substantially higher cost of formic acid than an equivalent power, CO conversion into formic acid substantiates the integrated approach as economically attractive.

1. INTRODUCTION

Combustion of natural gas (NG) with a primary (70–90% vol.) component methane (CH_4) is characterized by the lowest (between other gaseous and liquid fossil fuels) GHG (greenhouse gas) emissions or CO_2 release per unit of its heating value because of the highest H:C = 4:1 ratio. The U.S. Energy Information Administration identified a tremendous increase in NG consumption in the 2000s to become presently the second energy provider after petroleum. In 2018, according to the U.S. Energy Information Administration, the U.S. electric power and industrial sectors account for about 35 and 34% of total NG utilized, respectively.¹ The production of chemicals is associated with about 40% of NG assigned to the industrial sector.² The chemical industry utilizes steam-methane reforming as a primary technology to manufacture syngas-a mixture of hydrogen (H_2) and carbon monoxide (CO). The components of interest (H₂ or CO, or both) are used to upgrade refinery products and manufacture high-tonnage commodities, such as ammonia (consumes H_2), methanol (H_2 and CO), plastics (H_2 and CO), and many other industrial chemicals. Based on the foregoing statistics, an economically reasonable reduction of GHG emissions from NG-fired power generation stations and steam-methane reforming furnaces will significantly impact the total release of GHGs in the United States.

This study aims at demonstrating that air replacement by oxygen in modern NG-fired power generation plants facilitates earlier impractical modifications of their thermal cycles and key devices (e.g., combustion chamber in the scheme proposed) to integrate them with syngas utilization technologies, thereby improving thermal efficiencies (heat to power), as well as environmental (GHG emissions) and economic impacts.

2. NG-AIR-FIRED GAS TURBINE AND COMBINED UNITS WITH A CO₂ CAPTURE PLANT

In contemporary NG-air-fired gas turbine units (GTUs) (Figure 1), air $[O_2:N_2 \approx 1:4(vol)]$ works as an oxidizer and working media. Heat is transmitted to the working media in the combustion chamber through methane combustion in excess of air (air:CH₄ \approx 20–30:1) as follows:

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Figure 1. Contemporary *NG*-air-fired power plant unit with a carbon capture plant. Flow rate values in parentheses (mol), works (W_C, W_T) , and heat (Q) values are given per 1 mol of incoming CH₄ (in parentheses).

$$CH_4 + 2O_2(8N_2) \rightarrow CO_2 + 2H_2O + (8N_2) + 802 \text{ kJ}$$
(1)

The gas expands in the turbine at higher temperatures compared to the temperatures of the gas in the compressor, resulting in mechanical work generated in the turbine (W_T) exceeding the work consumed by the compressor (W_C) . With a high efficiency (\approx 98%), this difference is converted using electric generators into electricity. When the sensible heat of air downstream of the turbine is utilized in the bottoming Rankine water-steam cycle, the overall conversion of the CH₄ heating value (LHV(CH₄) = 802 kJ/mol) into power is performed in the combined cycle.

Table 1 presents the typical parameters of GTUs³ used to conduct thermodynamic calculations.

Table 1. Parameters of GTU for Thermodynamic Analysis

maximum temperature of the working fluid at the combustion chamber outlet (turbine inlet), T_{\max}	1200 °C
minimum temperature of the working fluid in the unit (after cooling downstream of turbine), $T_{\rm min}$	25 °C
maximum pressure in the GTU cycle, P_{max}	15 bar
minimum pressure in the GTU cycle, P_{\min}	1 bar
isentropic efficiency of the compressor	0.85
isentropic efficiency of the turbine	0.90

Pressure losses in the combustion chamber and heat transfer equipment are neglected. When performing calculations per one mole of CH_4 , the volume of air entering the GTU is calculated based on the following conditions: (i) the oxygen content in the air should exceed its stoichiometric amount to combust CH_4 (reaction 1) and (ii) the temperature at the compressor inlet should be equal to T_{min} .

Thermodynamic calculations were performed using ASPEN Plus software with Redlich–Kwong–Soave (RKS) and Peng Robinson equations of states. Both are the modifications of their Redlich–Kwong predecessor and use cubic equations of states for all thermodynamic properties, except liquid molar volume. They are recommended (ASPEN Tech) for gas processing, refinery, and petrochemical applications to obtain reasonably valid results at all temperatures and pressures. Thermodynamic calculations were conducted with both methods to determine an insignificant difference (less than 1 percentage point) in energy-(heat, work) and mass- (component flow rates) related parameters. The results obtained using the RKS thermodynamic method are presented in Figure 1 and further in Figure 4.

The thermal efficiency of GTU η_{gt} shown in Figure 1 (assuming that methane comes from a pipeline at an elevated pressure) is calculated as follows:

$$\eta_{\rm gt} = \frac{W_{\rm T} - W_{\rm C}}{\rm LHV_{\rm CH4}} = \frac{638.5 - 330.4}{802} = 0.38(38\%) \tag{2}$$

Contemporary combined *NG*-air-fired power plants have thermal efficiencies between 50 and 60%.⁴ Assigning the value $\eta_{cc} = 0.55$ to the combined cycle in Figure 1, the efficiency of Rankine cycle η_{R} can be derived from eq 3 as follows:

$$\eta_{cc} = \frac{(W_{\rm T} - W_{\rm C}) + W_{\rm R}}{\rm LHV_{CH4}} = \eta_{\rm gt} + \frac{W_{\rm R}}{Q} \frac{Q}{\rm LHV_{CH4}}$$
$$= \eta_{\rm gt} + \eta_{\rm R} \frac{Q}{\rm LHV_{CH4}} = 0.55 \ (55\%)$$
(3)

where W_R is the work generated in the Rankine cycle, and Q is the sensible heat of air downstream of the turbine.

Therefore, $\eta_{\rm R} = 0.24$ supports the literature data reporting the ratio between the generated power in the gas turbine and Rankine cycles.⁵

Introducing the carbon capture CO₂ separation process into the *NG*-air-fired power plant shown in Figure 1 substantially impacts its efficiency and economics. According to estimations,^{6,7} its thermal efficiency decreases by about 7–8%, in the case considered, from $\eta_{cc} = 0.55$ to $\eta_{cc}^{ccs} = 0.47$.

3. NG-OXYGEN-FIRED COMBINED CYCLE TO AVOID CO₂ SEPARATION

Semiclosed (sometimes called closed) GTUs are associated with methane combustion in technically pure oxygen, allowing combustion products—carbon dioxide (CO₂) and H₂O (steam)—to be their working fluids. A principal diagram of the NG-oxygen-fired combined cycle is presented in Figure 2. The use of oxygen instead of air in GTUs eliminates the presence of N₂ and NO_x in combustion products, making flue gases comprise only CO₂ and water vapor H₂O. After the condensation of water vapors, CO₂ gas can be compressed and



Figure 2. Principle scheme of semiclosed NG-oxygen-fired gas turbine cycle. Flow rate values (mol) are given per 1 mol of incoming CH_4 (in parentheses).

pumped into a pipeline for subsequent utilization or storage as a final stage in its sequestration. A closed character of the thermodynamic cycle allows increasing minimum pressure (P_{\min}) of the cycle, making the unit more compact (less metal intensive) and reducing CO₂ compression work. There is no need for CO₂ separation from flue gases; only cooling, water vapor condensation, and drying are necessary.

Numerous configurations of NG-oxygen-fired semiclosed GTUs utilizing different sets of parameters are proposed.^{8–10} They show gross thermal efficiencies (without accounting for the electricity required for air separation) to be lower and higher than 55%. For this analysis and following the Carnot principle stating that the thermodynamic efficiency of a thermal cycle does not depend on its working fluid, the efficiency of the NG-oxygen-fired unit (Figure 2) is assigned to be equal to that of the NG-air-fired one (Figure 1).

The net efficiency of the NG-oxygen-fired cycle will be lower because of the power required for air separation. Based on data,^{11,12} contemporary cryogenic air separation plants consume power around 0.25 kWh/kg_O₂ that translates into 29 kJ/ mol_O₂. With this factor, the thermal efficiency of the NGoxygen-fired GTU decreases to $\eta_{cc}^{ox} = 0.48$. A comparison of the net thermal efficiencies of NG-air-fired with postcombustion CO₂ capturing $\eta_{cc}^{ccs} = 0.47$ and NG-oxygen-fired $\eta_{cc}^{ox} = 0.48$ combined cycles shows that an advantage of an NG-oxygen-fired cycle is not evident (within possible boundaries for an error).

4. STEAM-METHANE REFORMING FURNACE

An industrial method to convert the most abundant hydrocarbon gas, methane, into syngas (a mixture of H_2 and CO in the presence of CO_2 and H_2O (steam)) in methane-steam reforming furnaces (Figure 3) is typically represented by two reactions proceeding in catalytic tubes:

$$CH_4 + H_2O \xrightarrow{Catalyst} CO + 3H_2 - 206 \text{ kJ (endothermic)}$$
(4)

$$CO + H_2O \xrightarrow{\text{Catalyst}} CO_2 + H_2 + 41 \text{ kJ (exothermic)}$$
(5)

This process requires a catalyst, an excess of steam (a regular methane: steam volumetric ratio is 1:3–4), and external high-temperature (\approx 900 °C) heat supply. A significant portion of methane (1/3) is combusted in air to heat the catalyst within



Figure 3. Principal schematic of a steam—methane reforming furnace. Volumetric ratios are given in parentheses.

tubes where another methane fraction (2/3) is converted into syngas. This means that to obtain 4 moles of syngas (H₂ and CO), 1.5 mol of methane is consumed, following the proportion given below:

1.5 mol
$$CH_4 \rightarrow 4$$
 mol syngas (6)

$$0.37 \text{ mol } \text{CH}_4 \to 1 \text{ mol syngas} \tag{7}$$

There is also known catalytic "dry reforming", wherein, instead of steam, methane is mixed with excess carbon dioxide (CO_2) . Thermodynamically, the reaction system can be described with the same reversible reactions 4 and 5.

The case when methane is first converted into H_2 and CO in a steam—methane reformer, followed by CO conversion into H_2 and CO₂ in a separate water—gas shift reactor (reaction 5), and CO₂ capture and the removal of both from H_2 and flue gases was also considered. The obtained H_2 can fuel the air-fired GTU without the need for a carbon capture and storage (CCS) plant. The thermal efficiency here is substantially lower than that of the NG-air-fired GTU with postcombustion CO₂ separation (Figure 1) and NG-oxygen-fired GTU (Figure 2).⁶

5. INTEGRATED GTU FOR POWER AND SYNGAS COGENERATION

A coproduction of power and syngas (CO and H_2 are components of interest in syngas) has been considered as a promising option to improve the efficiency of NG-air-fired GTUs.¹³ Air is supplied to the combustion chamber in a substoichiometric amount to promote the partial oxidation of methane instead of its full combustion as follows:

$$CH_4 + O_2(4N_2) \rightarrow CO + H_2 + H_2O(4N_2) + 278 \text{ kJ/mol}$$
(8)

Instead of a combustion chamber, the GTU has a partial oxidation reactor to reflect the matter of reaction 8. H_2 and CO, as products of partial oxidation (8), are diluted in N_2 , which claims an application of cryogenic or other capital- and energy-intensive separation technologies to have them fit for the following utilization. Because of these separation costs and a low conversion rate of reaction 8 caused by the dilution of reactants CH_4 and O_2 in N_2 , this approach has not been widely adopted.

Replacing air with oxygen in GTUs with semiclosed cycles greatly alleviates the abovementioned cogeneration. Figure 4 shows a principal process flow diagram of the proposed semiclosed GTU cycle with the coproduction of power and syngas and the results of thermodynamic calculations.

A partial oxidation reactor is simulated using an adiabatic "Gibbs reactor" model, which assumes the thermodynamic equilibrium at the reactor outlet. All flow rates, work, and heat are calculated per 1 mol of incoming CH_4 . The detailed stream table is presented in the Supporting Information.

The GTU shown in Figure 4 has the following distinct features: (i) the ratio of $CH_4:O_2 = 1:1$ is not enough to completely burn CH_4 ; (ii) one part (2/3) of syngas is withdrawn from the cycle, and another part of syngas (1/3) comes into the partial oxidation reactor, which replaces the combustion chamber; (iii) only water separation is required to obtain syngas slightly diluted only in CO_2 ; and (iv) pumping water to the highest pressure in the cycle allows for a reducing compressor load.

Overall, a mass balance of the unit (mass in = mass out) is described by the partial oxidation of CH_4 as follows:



Figure 4. Principal process flow diagram of the NG-oxygen-fired GTU with the coproduction of power and syngas. All flow rates (mol), works, and heat are given per 1 mol of incoming CH₄.

$$CH_4 + O_2 \rightarrow 0.58CO + 1.42H_2 + 0.42CO_2 + 0.58H_2O$$
(9)

The "Gibbs reactor" model computes an equilibrium composition with H_2 and CO in the product gas. Emphatically, it may not be achieved, and instead of partial oxidation, an incomplete combustion of CH_4 occurs as follows:

$$CH_4 + O_2 \rightarrow 0.5CO_2 + H_2O + 0.5CH_4$$
 (10)

As shown in previous studies,^{14,15} the presence of the oxyhydrogen flame accelerates steam reforming and helps shift the interactions of a hydrocarbon and substoichiometric O_2 toward partial oxidation products H_2 and CO. As presented in a provisional patent,¹⁶ an injection of the oxy-hydrogen flame generated using the burner accommodated in a partial oxidation reactor of methane promotes its interactions with substoichiometric oxygen toward syngas:

$$CH_4 + 0.5O_2 + (Flame: {H_2 + 0.5O_2})$$

= Shifting to
→ CO + 2H₂ + H₂O (11)

A noncatalytic partial oxidation is fast, requires high temperatures, and accelerates by the most active species, radicals formed in the hot zones of the reactor. Also, because of the absence of a catalyst, the reactor exhibits a negligible pressure loss. Based on the foregoing, recycling a part of the syngas back into a partial oxidation reactor (Figure 4) promotes reaching equilibrium composition associated with the partial oxidation of methane (9).

Another option is to combine adiabatic combustion and reforming, called autothermal reforming (Figure 5). Here, endothermic reforming utilizes the sensible heat of combustion products and can be formally represented using one partial oxidation reactor, as shown in Figure 4. Compared to the staggered oxy-fuel combustion in some consecutive chambers where oxygen and fuel are distributed in a way to reach maximum admissible temperature in each chamber, followed by an interstage heat transfer "through the wall" to water¹⁷ or

A partial oxidation reactor as a combination of auto-thermal reformers



Figure 5. Representation of a partial oxidation reactor as a combination of combustors and catalytic reformers of methane.

supercritical CO_2 ,¹⁸ the staggered combustion shown in Figure 5 is controlled by the catalytic endothermic reaction accepting combustion products as its reactants. Both methods help in reducing the recirculation of exhaust gases (combustion products) per unit of released heat to control the maximum combustion temperature, resulting in a more compact unit without loss in efficiency.

Introducing the adiabatic catalytic methane reformer downstream of the combustor and turbine of NG-oxygen-fired GTU cycle¹⁹ results in a mass balance similar to that shown in eq 9. The drawback of conducting methane reforming downstream of the turbine is its slow reaction rate compared to methane partial oxidation proceeding at much higher temperatures and involving active short-living radicals. An adiabatic reactor will be associated with a large catalytic space and an increasing pressure drop. Consequently, increasing pressure losses induces a decrease in the power generation efficiency.

6. EFFICIENCY OF POWER AND SYNGAS COPRODUCTION

Mechanical work W_{int} generated in the integrated scheme (Figure 4) per one mole of CH_4 consumed is determined as follows:

$$W_{int} = W_{T} - W_{C} - W_{C_{-02}} - W_{p} - W_{02} = 168.0 - 14.4$$

- 11.8 - 0.3 - 29.0 = 112.5 kJ/mol, (12)

where W_T is the work generated by the turbine, W_C , $W_{C_{-02}}$ are the works consumed by compressors, W_p is the work to pump water, and W_{O2} is the work required to separate air.

Two moles of CO and H_2 in the syngas are withdrawn. To determine the effect of integration, the performance indicators of power and syngas coproduction shown in Figure 4 are compared with the same ones for two separate technologies: power generation in the NG-oxygen-fired GTU and syngas production by steam reforming obtained as described in the previous sections of this article. This comparison is presented in Figure 6. Figure 6 shows that at the same consumption rate of methane and production rate of syngas, the integrated technology allows for the generating more power. The thermal power generation efficiency for the integrated scheme η_{int} can be calculated as follows:

$$\eta_{\rm int} = \frac{112.5}{0.26 \times 802} = 0.54(54\%) \tag{13}$$

The gain in the power generation efficiency is about 6%. Remarkably, industrial steam reforming is accompanied by CO_2 production within catalytic tubes and in the furnace, meaning that syngas and flue gases have a substantial percentage of CO_2



Figure 6. Comparison of the integrated technology (Figure 4) to make power and syngas (a) with the separated manufacturing of the same products (b).

(Figure 3). The absence of flue gases is another advantage of the integrated scheme.

The abovementioned gain is achieved in an easy power generation unit without a capital-intensive steam turbine and negative pressure condenser as a part of the water—steam Rankine cycle. However, an evaluation of economics (levelized cost of electricity and syngas) in integrated schemes is out of the scope of this article.

7. SYNGAS UTILIZATION TO REDUCE GHG EMISSIONS WITHOUT ECONOMIC PENALTIES

From Figure 4, carbon-containing components CO and CO_2 are withdrawn from the power generation cycle. The presence of CO_2 in syngas can be eliminated by employing an industrial reverse water—gas shift reaction as follows:

$$CO_2 + H_2 \rightarrow CO + H_2O - 41 \text{ kJ} \text{ (endothermic)}$$
 (14)

This means that 0.42 mol of CO_2 can be converted to CO to obtain an equimolar mixture of H_2 and CO.

CO participates in numerous industrial chemical reactions referred to as carbonylation (e.g., acetic acid production through Monsanto technology), and it is required to manufacture isocyanates, polyurethane plastics, and many other chemicals. CO is a poisonous gas; therefore, its use is permitted only immediately after its generation. Manufacturers have to implement NG steam or dry reforming, following CO separation to obtain pure one. Therefore, a safe and economically viable option to transport CO will be attractive in many cases.

Formic acid HCOOH is a good fit for being a CO carrier. It is a transportable liquid that has its own several applications. Moreover, in the presence of concentrated sulfuric acid and at very moderate heating, formic acid is decomposed into CO(gas)and H_2O as follows:

HCOOH
$$\xrightarrow{\text{H2SO4 conc.}}$$
 CO + H₂O (15)

The content of CO in concentrated formic acid reaches 61% (wt), and an 85–98% solution of formic acid in water is a usual salable product. Syngas manufactured in the integrated scheme (Figure 4) can be utilized to produce formic acid (Figure 7).

A well-known BASF technology²⁰ allows the processing of pure CO into formic acid. The overall reaction looks easy (Figure 7), but it is a multistage process in which methanol (CH₃OH) is consumed and released. A few publications^{21,22}



Formic Acid Production reaction (overall): $CO+H_2O \rightarrow HCOOH$ Reaction requires a catalyst: sodium methoxide (CH_3ONa) diluted in an excess of methanol (CH_3OH). Technology was developed by BASF.

Figure 7. Schematic diagram of syngas utilization to manufacture formic acid.

demonstrate the modification of the process to accept syngas and separate H_2 and CO at the methyl formate synthesis stage (an intermediate in formic acid production).

Formic acid is a fuel for direct formic acid fuel cells, which may serve as a potential power source for portable devices.²³ The known catalysts can selectively convert formic acid into a mixture of H₂ and CO₂. At normal conditions, 1 L of formic acid carries 590 L of hydrogen and is considered as H₂ storage, following the catalytic reaction at elevated temperatures:²⁴

HCOOH
$$\xrightarrow{\text{Pt or Ru Catalyst}}$$
 CO₂ + H₂ (16)

Based on the foregoing, CO_2 sequestration by its pipeline transportation and storage in former NG or oil reservoirs and saline aquifers might be reconsidered to produce formic acid as a CO carrier.

A rough estimated revenue to produce formic acid from syngas is demonstrated in Figure 8. Figure 8 shows that the



Figure 8. Revenue to manufacture different products from syngas.

revenue to manufacture synthetic gasoline through Fischer– Tropsch synthesis is close to the same for power generation and significantly lower than that to produce formic acid because synthetic gasoline competes with the much cheaper gasoline extracted from crude oil in refineries. Industrially manufactured formic acid is only a synthetic product. At a generally accepted price for oxygen, that is, \$40/ton, the price of 1 mol of O₂ utilized in the integrated scheme (Figure 4) is around 0.14 cents, which is significantly lower than the potential revenue from formic acid production.

8. CONCLUSIONS

Thermodynamic analysis reveals that a proposed replacement of the combustion chamber in the NG-oxygen-fired GTU cycle by a partial oxidation reactor allows for generating power and syngas simultaneously. Syngas (CO, H_2 , and CO₂) can be easily

separated from the working fluid of the cycle by the condensation of water vapor (steam). The effect of an integrated coproduction of power and syngas is shown by increasing the heat-to-power efficiency from 48 to 54%.

To avoid GHG (CO_2) emissions, it is suggested (i) to use H₂ in syngas to convert CO₂ in the gas mixture to CO by a wellknown water—gas shift reaction and (ii) to convert CO into formic acid, for instance, by a well-known BASF technology. Here, through CO as an intermediate, carbon in natural gas (methane) is captured in liquid formic acid, which is a good commodity for transportation to a place where it can be reconverted into CO or H₂ to manufacture various industrial chemicals. Simple economic considerations show that, because of a substantially higher cost of formic acid than an equivalent power, CO conversion into formic acid substantiates the integrated approach as economically attractive.

There are needs to study the noncatalytic and catalytic reaction kinetics of the methane—syngas mixture with oxygen to find the best reactor configuration to introduce the partial oxidation of methane into an NG-oxygen-fired GTU power generation cycle.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00743.

Principal process flow diagram of a NG-oxygen-fired GTU with the coproduction of power and syngas. All flows are tagged with numbers. Work and heat produced or consumed, pressures, temperatures, and rates of flows (PDF)

AUTHOR INFORMATION

Corresponding Author

Mikhail Granovskiy – Southern Research, Laboratory of Sustainable Chemistry and Catalysis, Birmingham, Alabama 35205, United States; o orcid.org/0000-0002-5326-3686; Phone: +1 205 709 0233; Email: mgranovskiy@ southernresearch.org, mgranovskii@gmail.com

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c00743

Notes

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NOMENCLATURE

CCS, carbon capture and storage GHG, greenhouse gas GTU, gas turbine unit LHV, lower heating value NG, natural gas P_{max} , P_{min} , maximum and minimum pressures in thermodynamic cycles, bar Q_t sensible heat, kJ/mol CH₄ T_{max} , T_{min} , maximum and minimum temperatures in thermodynamic cycles, °C

 $W_{\rm D}$, $W_{\rm C}$, $W_{\rm C_{-O2}}$, $W_{\rm P,n}$ mechanical work of gas turbines, gas compressors, additional oxygen compressor, and water pumps, respectively, kJ/mol CH₄

 W_{O2} power (electricity) to separate air to manufacture oxygen, kJ/mol_CH₄

x, *y*, flow rates of components, mol/mol_CH₄

Greek Letters

 $\eta_{gv}\eta_R \eta_{cc} \eta_{cc}^{ccs}$, η_{cc}^{ox} tabthermal efficiencies of gas turbine, Rankine, combined, combined with carbon capture, and oxygen fired cycles, respectively

 η_{int} tabthermal efficiency of power generation in the integrated scheme for the coproduction of power and syngas

REFERENCES

(1) U.S. Energy Information Administration. Via https://www.eia. gov/todayinenergy/detail.php?id=40013, Accessed Jan 10, 2020

(2) U.S. Energy Information Administration. Via https://www.eia. gov/todayinenergy/detail.php?id=45196#:%7E:text= The%20chemicals%20industry%2C%20which%20consumes, also %20declined%20notably%20this%20spring, Accessed Jan 10, 2020

(3) Soares, C. Simple and Combined cycles. *The gas turbine handbook;* US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory. 2006 Via https://www.netl.doe.gov/coal/turbines/handbook, Accessed Jan 10, 2020

(4) Annual technology baseline; National renewable energy laboratory (NREL), 2018 Via https://atb.nrel.gov/electricity/2018/index. html?t=cg, Accessed Jan 10, 2020

(5) Ibrahim, T.; Rahman, M. Thermal Impact of Operating Conditions on the Performance of a Combined Cycle Gas Turbine. *J. Appl. Res. Technol.* **2012**, *10*, 567–577.

(6) Leung, D.; Caramanna, G.; Maroto-Valer, M. An overview of current status of carbon dioxide capture and storage technologies. *Renew. Sust. Energ. Rev.* 2014, 39, 426–443.

(7) Mancuso, L.; Ferrari, N.; Chiesa, P.; Martelli, E.; Romano, M. Oxycombustion turbine power plant. International Energy Agency Report. Copyright IEA Environmental Projects Ltd.(IEAGHG), 2015. Via https://ieaghg.org/docs/General_Docs/Reports/2015-05.pdf, Accessed Jan 10, 2020

(8) Ferrari, N.; Mancuso, L.; Davison, J.; Chiesa, P.; Martelli, E.; Romano, M. Oxy-turbine for Power Plant with CO2 capture. *Energy Procedia* **2017**, *114*, 471–480.

(9) Thorbergsson, E.; Gröonstedt, T.; Sammak, M.; Genrup, M. A comparative analysis of two competing mid-size oxy-fuel combustion cycles (GT2012-69676). *Proceedings of ASME Turbo Expo 2012*; Copenhagen, Denmark, 2012.

(10) Heitmeir, F.; Jericha, H.; Sanz, W. Graz cycle – a zero emission power plant of highest efficiency. *The gas turbine handbook*; US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, 2006 Via https://www.netl.doe.gov/coal/ turbines/handbook, Accessed Jan 10, 2020

(11) Banaszkiewicz, T.; Chorowski, M.; Gizicki, W. Comparative analysis of oxygen production for oxy-combustion application. *Energy Procedia* **2014**, *51*, 127–134.

(12) Alavandi, S.; Seaba, J.; Subbaraman, G. Emerging and existing oxygen production technology scan and evaluation. *Gas Technology Institute* (*GTI*) project (report) number 22164; 2018, Via https://www. cosia.ca/sites/default/files/attachments/22164-%20Oxygen%20Generation%20Technologies%20Review%20-%20Rev0.pdf. Accessed Jan 10, 2020

(13) Rabovitser, J.; Nester, S.; White, D. Partial Oxidation Gas Turbine (POGT). *The gas turbine handbook*; US Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory, 2006 Via https://www.netl.doe.gov/coal/turbines/handbook, Accessed Jan 10, 2020 (14) Granovskii, M.; Gerspacher, R.; Pugsley, T.; Sanchez, F. An effect of tar model compound toluene treatment with high-temperature flames. *Fuel* **2012**, *92*, 369–372.

(15) Granovskii, M.; Gerspacher, R.; Pugsley, T.; Sanchez, F. Decomposition of tar model compound toluene by treatment with the high-temperature hydrogen/oxygen flame. *Proceedings of 19th European Biomass Conference and Exhibition*; Berlin, Germany, 2011, 1530–1538.

(16) Granovskiy, M. Method and reactor to produce syngas. *Provisional patent* **12 Aug 2020**, Attorney Ref. No. 19044.0445U1.

(17) Gopan, A.; Kumfer, B. M.; Phillips, J.; Thimsen, D.; Smith, R.; Axelbaum, R. L. Process design and performance analysis of a staged, pressurized oxy-combustion (SPOC) power plant for carbon capture. *Appl. Energy* **2014**, *125*, 179–188.

(18) Khallaghi, N.; Hanak, D. P.; Manovic, V. Staged oxy-fuel natural gas combined cycle. *Appl. Therm. Eng.* **2019**, *153*, 761–767.

(19) Granovskii, M. S.; Safonov, M. S. New integrated scheme of the closed gas-turbine cycle with synthesis gas production. *Chem. Eng. Sci.* **2003**, *58*, 3913–3921.

(20) Hietala, J.; Vuori, A.; Johnsson, P.; Pollari, I.; Reutemann, W.; Kieczka, H. Formic Acid. *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley Online Library, 2016.

(21) Process for the production of methyl formate. US 4,661,624, 1987.

(22) Process for recovering carbon monoxide from fuel gas. US 3,716,619. 1973

(23) Putten, R.; Wissink, T.; Swinkels, T.; Pidko, E. A. Fueling the hydrogen economy: Scale-up of an integrated formic acid-to-power system. *Int. J. Hydrog. Energ.* **2019**, *44*, 28533–28541.

(24) Rahbari, A.; Ramdin, M.; Broeke, L. J. P.; Vlugt, T. J. H. Combined steam reforming of methane and formic acid to produce syngas with an adjustable H_2 :CO ratio. Ind. Eng. Chem. Res. **2018**, 57, 10663–10674.

(25) Chua, W.; Cunha, S.; Rangaiah, G.; Hidajat, K. Design and optimization of Kemira-Leonard process for formic acid production. *Chem. Eng. Sci.:X* **2019**, *2*, No. 100021.