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Autothermal Reforming of Methane into Syngas and its Conversion into Methanol, Powered by Combustion of Excess Hydrogen or Excess Carbon Monoxide

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ABSTRACT

The proposed technical solution harnesses the **Autothermal Methane Reforming (ATR)** as an industrial process for **"Blue" hydrogen (H2) production** from natural gas, by converting of methane (CH_4) into **synthesis gas / syngas** ($CO + H_2$) using oxygen (O_2) and either carbon dioxide (CO_2) or steam (H_2O) in an **Exothermic Reaction** with methane (CH_4), the released heat of exothermic reaction satisfying heat requirements of the steam-reforming part of the ATR, so that the outlet temperature of the produced syngas is between **950–1100°C**, while the outlet pressure is about **100 bar**. Such high syngas pressures and temperatures employed in the ATR process are obtained by **pressurization** of **atmospheric air** and oxygen (contained in the air and extracted from it using an **air separation unit**) and the **natural gas / methane** (the main feedstock for the ATR reaction), by means of an **air/oxygen compressor** and a **methane/ natural-gas compressor**, respectively. High-pressure steam necessary for the ATR process is raised by harnessing of a huge (thermal and mechanical) energy potential of the waste heat contained in the stream of products (syngas). The proposed technical solution thus envisions **conversion** of a suitable amount of the **waste heat contained in the produced syngas**, so that the temperature of the syngas products reduces up to an **optimum temperature** for the process of **Methanol Synthesis (~250°C)** and also **conversion** of the **heat of combustion** of the **excess hydrogen** or **excess carbon-monoxide** (remaining **after methanol synthesis** of the syngas products) into the mechanical energy/ power using a **simple-reheat-cycle steam-turbine power plant**, so that after satisfying/covering of the mechanical energy needed to drive the **process compressors** (for air, oxygen and methane), eventual **surplus of mechanical energy** remains that can be converted into an **extra electrical energy**. Thus, methanol is here produced **without combustion of any additional external fuel** (natural gas, fuel oil, coal or any other) and hence **without any GHG emissions**.

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Introduction

The standard method of world-scale **Methanol Production** has been based on the methanol synthesis process which generally uses **synthesis gas** (CO and H_2) produced from natural gas or coal as a feedstock to produce methanol. Since the steam reforming process of methane is very energy consuming and, in addition, the current **CO_2 to methanol processes** is very energy and capital intensive, large oil & gas companies, like **ExxonMobil**, actively research **Direct Hydrogenation of Carbon Dioxide** (CO_2) into methanol (CH_3OH) by the **hydrogen** (H_2). However, the main problem of such an approach (direct conversion of CO_2 to methanol) is that a **stable and ample source of hydrogen** has to be provided, which typically means the use of either water/steam electrolysis (fueled by fossil fuels or renewables, like Solar or biomass) or some suitable thermochemical water-splitting method, or perhaps the use of sponge iron reaction (with high-temperature steam), with a subsequent reduction of the formed iron oxide (magnetite). That complicates this approach a great deal. In addition, some typical problems of the **direct CO_2 hydrogenation** are: the per pass methanol yield is severely limited by thermodynamic equilibrium to approximately 20–40%; lower temperatures and higher pressures would favor higher equilibrium yields, however, reaction rates are typically too low at the lower temperatures (e.g. < 200 °C) required for significant equilibrium conversion improvements; while operating at higher pressures (e.g. > 100 bar) can improve yields as well, it would lead to a significant increase in capital and operational expenses. In addition to the thermodynamic limitations, an **equimolar amount of water** is formed in the reaction of CO_2 to methanol, which contributes to **catalyst deactivation** and complicates reactor design and downstream separations. In addition, it has to be considered that the gaseous CO_2 that is to participate in the reaction of **direct CO2 hydrogenation** into **methanol**, will probably have to be adequately/sufficiently pressurized (up to ~100 bar) by a carbon-dioxide compressor, most likely with intercooling.

Materials and Methods and Results/Observations

The herewith envisioned technical solution thus proposes an alternative, the **Autothermal Methane Reforming (ATR)** as an industrial process for **"Blue" Hydrogen (H_2) production** from natural gas, by converting of methane (CH_4) into **synthesis gas / syngas** ($CO + H_2$) (https://en.wikipedia.org/wiki/Methane_reformer#:~:text=Autothermal%20reforming%20(ATR)%20uses%20oxygen,exothermic%20due%20to%20the%20oxidation). **Autothermal reforming (ATR)** uses oxygen (O_2) and either carbon dioxide (CO_2) or steam (H2O) in a reaction with methane (CH_4) to form syngas. When the ATR uses **carbon dioxide** the H_2:CO ratio produced is **1:1**; when the ATR uses **steam** the H_2:CO ratio produced is **2.5:1**. The following ATR chemical reaction with steam (H_2O) and oxygen (O_2) has been chosen herewith and it proceeds as follows:

$$\mathbf{4\cdot CH4+O_2+2\cdot H_2\,O \rightarrow 4\cdot CO+10\cdot H_2 - Q_{ATR,1}}$$

The above chemical reaction takes place in a single chamber and is **exothermic**, due to **partial oxidation** of the methane (https://en.wikipedia.org/wiki/Exothermic_reaction), whereby the released heat of exothermic reaction ($Q_{ATR,1}$) serves to satisfy heat requirements of the steam-reforming part of the ATR. The **ATR** process operates at such temperatures so that the outlet temperature of the produced syngas is between **950–1100°C**, while the outlet pressure can be as high as **100 bar** (which is also very suitable for the methanol synthesis process). The produced syngas (**4*CO + 10*H_2 or CO + 2.5*H_2**) can be further used for the production of **Methanol** (CH_3OH), by its conversion over a **catalyst** (the most widely used being a mixture of copper and zinc oxides, supported on alumina), at favorable pressures of **5–10 MPa** (50–100 atm) and a temperature of **~250°C** (482°F), according to the following well-known **Exothermic** (also) reaction:

$$CO + 2\cdot H_2 \rightarrow CH_3OH - \sim 90.5\,\frac{kJ}{mol} \equiv \frac{MJ}{kmol}$$

$$=>\ \textit{equivalent to}:\quad 4\cdot CO + 8\cdot H_2 \rightarrow 4\cdot CH_3OH - \sim 362\,\frac{kJ}{4\ mol} \equiv \frac{MJ}{4\ kmol}$$

To obtain such high syngas pressures and temperatures employed in the ATR process, **atmospheric air** containing **oxygen** (extracted from the air using an **air separation unit**) and the natural gas (containing its overwhelmingly major ingredient – methane, CH_4), used as the main feedstock for the ATR reaction, would both have to be pressurized by means of an **air/oxygen compressor** and a **methane/natural-gas compressor**, respectively. In addition, high-pressure steam necessary for the ATR process has to be raised using the syngas waste heat (and additionally heated by an excess of fuel – syngas, if and when necessary). The parameters (temperature and pressure) of the produced synthesis gas are very high (**~950–1100°C** and up to **100 bar**, respectively), resulting in a huge (thermal and mechanical) energy potential contained in the stream of products (syngas) that can be harnessed. The proposed technical solution thus envisions **conversion** of a suitable amount of the **waste heat contained in the produced syngas (4*CO + 10*H_2)** (so that the temperature of the syngas products reduces up to an **optimum temperature** for the process of methanol synthesis, **~250°C**) and also **conversion** of the **heat of combustion** of the **excess hydrogen** (remaining **after methanol synthesis** (**2*H_2**) of the syngas products) into the mechanical energy/power using a **simple-reheat-cycle steam-turbine power plant**, so that after satisfying/covering of the mechanical energy needed to drive the **process compressors** (for air, oxygen and methane), eventual **surplus of mechanical energy** remains that can be converted into an **extra electrical energy** (either to be sold to the grid or used to satisfy the self-consumption). The described technical solution thus proposes a high-temperature high-pressure **autothermal reforming** of the natural gas/methane using **oxygen and steam** into a **pressurized cooled syngas**, with the resulting subsequent **synthesis of methanol**, powered by the combustion of **excess hydrogen** with a possibility of **additional generation of electricity, without any GHG emissions**. Since the huge heat that is released in the methanol synthesis process is unfortunately at a fairly moderate temperature level (~250°C), the proposed technical solution does not foresee any useful use of that heat for power generation purposes, other than for the purposes of process, space or residential heating.

In the disclosed technical solution, a **single-reheat non-extraction steam-turbine-cycle (Rankine-cycle) power plant** (using water/steam circulating in a closed-ST-cycle loop as a working fluid) is used as a prime mover of both the said **process compressors** (for air, oxygen and methane) and a producer of an eventual extra electrical energy. The below-depicted flow diagram (**Figure 1**) shows a basic configuration of the proposed technical solution, comprising: a **syngas reactor vessel** of the ATR system with internals/equipment, an **air compressor** (in complete with an **air aftercooler**) within an **air-separation unit** (ASU), a **compressor of oxygen** separated from the air in the said ASU and a **natural-gas/methane compressor**, for adiabatic compression of air, oxygen and methane, respectively, a **heat recovery boiler** containing its own water economizer, evaporator and steam superheater (for isobaric heating of the water/ steam by the sensible heat of the produced HT syngas), a **steam generator/boiler** with integrated **economizer, evaporator**, steam **superheater** and **reheater** (for isobaric heating of the steam-cycle water/steam by the heat of combustion of the excess hydrogen), a **first high-pressure (HP) stage** and a **second intermediate-pressure (IP) stage** of the **steam turbine** for a full adiabatic expansion of the working fluid (superheated and reheated steam, respectively) to the condensation pressure and the heat conversion into the mechanical work, a **condenser** for isobaric-isothermal condensation and liquefaction of the exhaust vapor from the said ST, and a **feedwater pump** for adiabatic compression of the condensed water and closure of the ST cycle. The cooling water for the said **condenser** and the said **air aftercooler** can be recirculated in a **closed-circuit/loop** (like the one shown), embodying a **cooling-water system** comprising a **forced-circulation cooling tower**, with its own **air fan** and its own **cooling-water pump** for circulation of cooling water within the closed loop. Alternatively, an **open-circuit/loop** cooling-water system may be chosen, which can take cooling water directly from a river or a lake.

Also, it is shown that the said **HP & IP steam turbine stages** are both connected on the **same shaft** with the said **process compressors**, together with an **electrical generator** via which it converts the extra produced mechanical work to electricity. Such a **single-shaft** way of the equipment interconnecting is a very desirable in practice, thus simplifying the entire system. The said **process compressors** can instead be connected on a different shaft together with a **separate electrical motor** (supplied by electricity from the said electrical generator), which can be their chosen prime mover.

The waste heat energy contained in the produced syngas is used extensively to heat, evaporate and superheat the incoming water from the said heat-recovery economizer into the steam of a necessary temperature level (preferably **900°C** to **1000°C**), whereby the temperature of the produced syngas products lowers up to an **optimum temperature** for the process of methanol synthesis, **~250°C**. General assumptions used are as follows:

- Outlet temperature of the produced syngas is T_{1s} = **950°C = 1223 K**;
- Temperature of the environment/ambient is T_1 = **293 K = 20°C**;
- Temperatures of cooling water from outcoming line and return line of the cooling-water system are T_{1c} **= 20°C = 293 K** and T_{2c} = T_{3c} **= 27°C = 300 K**, respectively;
- Minimum attainable temperature of the cooled pre-compressed air at the aftercooler outlet is T_{III} **= 30°C = 303 K**; Natural-gas temperature in the transmission line is $T_{CH4,1}$ = T_{1g} = **~298 K = 25°C**;

- Natural-gas pressure in the transmission line (https://www.softdig.com/blog/differences-between-gas-line-types/) is $p_{CH4,1g}$ = **200 psi = ~13.79 bar**;
- Chosen compression pressure ratio of the methane compressor is $\mathbf{CPR}_{CH4}$ = **7.25: 1**;
- Chosen compression pressure ratio of the oxygen/CO2 compressor is $\mathbf{CPR}_{O2}$ = **100: 1**;
- Assumed compression pressure ratio of the air compressor (ahead of the air separation unit) is $\mathbf{CPR}_{air}$ = **10: 1**;
- Isentropic efficiency of air/oxygen/methane/CO2 compressors is $\eta_{COM,is}$ = **85%**;
- Desirable maximum temperature to which the steam-turbine live steam is heated (steam-turbine inlet temperature) is T_1 **= 813 K = 540°C**;
- Desirable maximum temperature to which the steam-turbine cold intermediate steam is reheated (reheat-steam-turbine inlet temperature) is $T_1 = T_1 = 813\ K = 540°C$;
- Desirable maximum pressure of the live steam is $p_1 = p_6$ = **175 bar (17.5 MPa)**;
- Optimum pressure of the reheated steam is $p_2 = p_3$ = **40 bar (4 MPa)**;
- Minimum attainable condensation temperature is $T_{cond} = T_3$ **= 30°C = 303 K**;
- Steam turbine isentropic efficiency is $\eta_{ST,is}$ = **87%**;
- Overall efficiency of the water pump and cooling-water pump is η_{pump} = **75%**;
- Average ratio of specific heats of the ambient air is γ_{air} = **1.40**, resulting in the constant-pressure specific heat of approx. $c_{p,air}$ = **~1 kJ/(kg*K)**;
- Average ratio of specific heats of the oxygen (O_2) is γ_{O_2} = **1.40**, resulting in the constant-pressure specific heat of approx. $c_{p,O2}$ = **0.91 kJ/(kg*K)**;
- Average ratio of specific heats of the hydrogen (H2) is $\gamma H2$ = 1.40, resulting in the constant-pressure specific heat of approx. $c_{p,H2}$ = **14.55 kJ/(kg*K)**;
- Average ratio of specific heats of the carbon monoxide (CO) is γ_{CO} **= 1.40**, resulting in the constant-pressure specific heat of approx.$c_{p,O2}$ = **~1.04 kJ/(kg*K)**;
- Average ratio of specific heats of the natural gas/methane is γ_{CH4} = **1.32**, resulting in the constant-pressure specific heat of approx. $c_{p,CH4}$ = **~2.143 kJ/(kg*K)**;
- Average ratio of specific heats of the steam/water vapor (H_2O) is γ_{H2O} = **1.30**, resulting in the constant-pressure specific heat of approx. $c_{p,air}$ = **~2.0 kJ/(kg*K)**;
- Average ratio of specific heats of the carbon dioxide (CO_2) is γ_{CO2} = 1.29, resulting in the constant-pressure specific heat of approx. $c_{p,co2}$ = **~0.84 kJ/(kg*K)**.

Using the above listed general assumptions, extra mechanical work divided by the heat input from the excess hydrogen combustion, that is, the **overall corrected** Rankine cycle thermal efficiency according to the First Law of Thermodynamics, can reach ~**19%**, in addition to the resulting **synthesis of methanol** and **without any GHG emissions**. However, in the flow diagram depicted in **Figure 1** it is shown that the entire waste heat from the produced HP syngas is used to raise HP process steam necessary for the ATR process. This is not 100% true, since only estimated ~**55%** of the total syngas waste heat is necessary to raise the needed quantity of the ~**950°C**-temperature superheated process steam; hence, there is additional ~**45%** of the total syngas waste heat that can be used for additional power generation. With that additional waste-heat power generation (and considering that the estimated thermal efficiency of the original single-reheat non-extraction Rankine cycle amounts to ~40% under the above general assumptions), the **overall corrected** Rankine cycle thermal efficiency according to the First Law of Thermodynamics could then reach ~**30% (29.6%)**.

Alternatively, the second ATR chemical reaction could be chosen instead of the previous one, which uses carbon dioxide (CO_2) (instead of steam) and oxygen (O_2) and proceeds as follows:

$$\mathbf{2 \cdot CH_4 + O_2 + CO_2 \rightarrow 3 \cdot CO + 3 \cdot H_2 + H_2O - Q_{ATR,2}}$$

Similarly, the produced syngas **(3*CO + 3*H_2)** can be further used for the production of **methanol** (CH_3OH), by its conversion over a **catalyst** (a mixture of copper and zinc oxides, supported on alumina), at favorable pressures of **5–10 MPa** (50–100 atm) and a temperature of ~**250°C** (482°F), according to the following well-known **exothermic** reaction:

$$\mathbf{CO + 2 \cdot H_2 \rightarrow CH_3OH - {\sim}90.5\ \frac{kJ}{mol} \equiv \frac{MJ}{kmol}}$$

$$=>\ \mathbf{equivalent\ to:\quad 1.5 \cdot CO + 3 \cdot H_2 \rightarrow 1.5 \cdot CH_3OH - {\sim}136\ \frac{MJ}{1.5\ kmol}}$$

The above depicted ATR reaction conveniently uses **CO_2**, which either comes from the process itself, after combustion of the excess CO, or from an external source, in which case the CO_2 would need to be adequately pressurized, like the oxygen and the methane. The **excess part** of the formed **carbon monoxide** (**1.5*CO**), which remains after occurrence of the associated methanol-synthesis reaction: **1.5*CO + 3*H_2 = 1.5*CH_3OH**, is to be used as a fuel for powering of the process compressors (and generation of the excess electricity). Although the final product of the excess CO combustion will still be CO_2: **1.5*CO + 0.75* O_2 = 1.5*CO_2**, using the second ATR reaction is still beneficial, since for each mol of CO_2 taken from the process/ atmosphere, the second ATR reaction emits 1.5 moles of CO_2, meaning that the net excess of CO_2 is only half a mole of CO_2. However, there would still be **no any GHG emission of CO_2** to the atmosphere, since any unused/ excessive CO_2 would remain at a high process pressure (close to 100 bar) and could then be readily **captured and sequestered** (please see **Figure. 2**).

Similar to the first ATR reaction, the parameters of the produced synthesis gas in the second one would also remain very high (**~950–1100°C** and up to **100 bar**), thus enabling **conversion** of a suitable amount of the huge (thermal and mechanical) energy potential contained in the **waste heat contained in the produced syngas (3*CO + 3*H_2 + H_2O)** (so that the temperature of the syngas products reduces up to an **optimum temperature** for the process of methanol synthesis, ~**3**). Applying the technical solution in accordance with the second ATR equation involves also **conversion** of the **heat of combustion** of the **excess carbon monoxide** (remaining **after methanol synthesis** (**1.5*CO**) of the syngas products) into the mechanical energy/power using a **simple-reheat-cycle steam-turbine power plant**, so that after satisfying/covering of the mechanical energy needed to drive the **process compressors** (for air, oxygen and methane, plus optionally for CO_2), an eventual **surplus of mechanical energy** remains that can be converted into **extra electrical energy** (either to be sold to the grid or used to satisfy the self-consumption). Thus, this version of the described technical solution applies the second high-temperature high-pressure **autothermal methane reforming** reaction using **oxygen and carbon dioxide**, followed by the subsequent **synthesis of methanol**, whereby the entire ATR process is self-powered by the combustion of **excess carbon monoxide** with eventual **additional generation of electricity, without any GHG emissions** and with **capture/sequestration** of a part (33.33% or 0.5 kmol) of the formed high-press. CO_2.

The below-depicted altered flow diagram (**Figure. 2**) shows a configuration of the proposed technical solution using the second ATR reaction and **without a carbon-dioxide compressor**, wherein the only difference between two depicted flow diagrams is that both the said **heat recovery boiler** and the said **steam generator/boiler in Figure. 2** are used for heat input to the single-reheat non-extraction Rankine cycle, thus both contributing to the power generation. In addition, **Figure. 2** also shows the **drainage of the condensate** that could expectedly form due to the cooling of the produced synthesis gas mixture and possible **condensation** of an **equimolar amount/part** of the water vapor contained in it at the high pressure of the ATR process (~100 bar). Using the above listed general assumptions, the extra mechanical work divided by the heat input from the excess hydrogen combustion, that is, the **overall corrected** Rankine cycle thermal efficiency according to the First Law of Thermodynamics, can reach ~**21% (20.8%)**, considering that the estimated thermal efficiency of the original single-reheat non-extraction Rankine cycle amounts to ~40% under the above general assumptions.

For the purposes of paper space saving, the flow diagram depicted in **Figure. 2** does not show the **carbon-dioxide compressor** that would suck in and compress an **externally-supplied CO_2**, which can optionally be used in addition to other process compressors (methane, air, oxygen) and also on the same shaft with them and the steam turbines. Should such a CO_2-compressor be used, the **overall corrected** Rankine cycle thermal efficiency according to the First Law of Thermodynamics could then reach ~**28% (27.9%)**; however, in this case the entire amount of the HP CO_2 resulting from the combustion of the excess CO (1.5 kmol) would need to be captured and sequestered. In this case there would also be no any GHG Emissions.

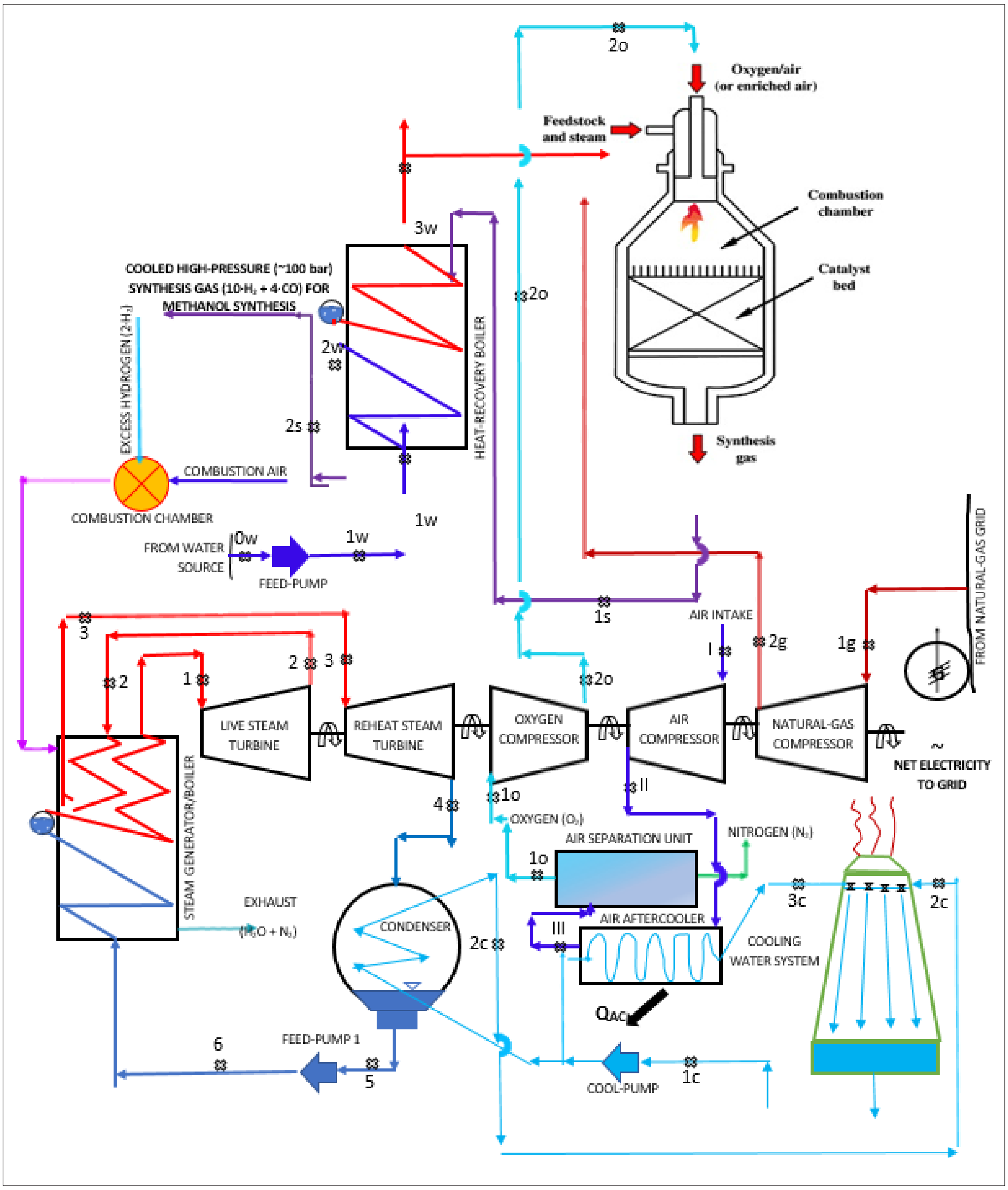

Figure 1

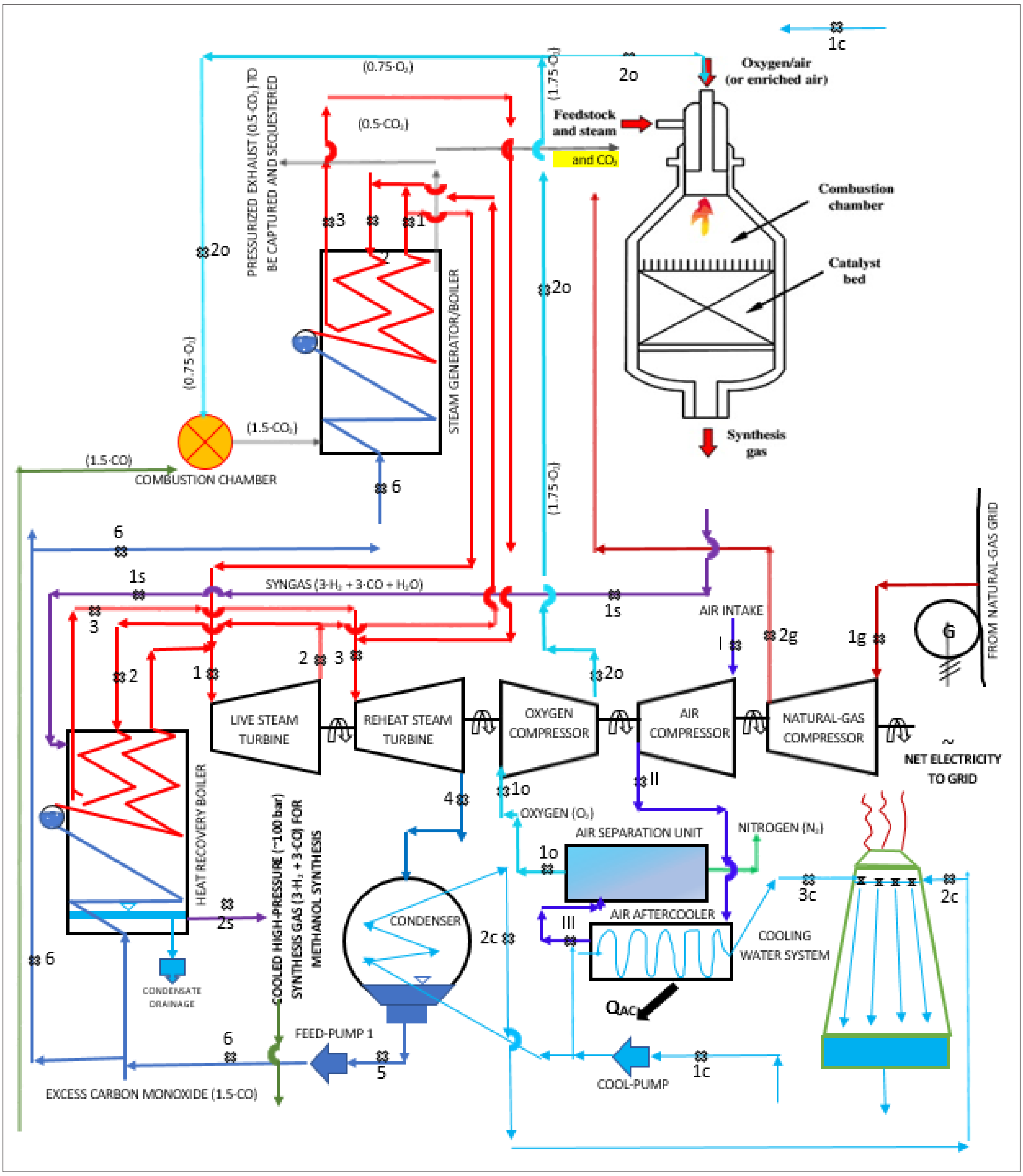

Figure 2

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