

Mass and Energy Balance Analysis of Methanol Production Using Atmospheric CO₂ Capture with Energy Source from PCMSR

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Abstract. The rising of atmospheric CO₂ concentration is the major source to global warming system. Many methods have been proposed to mitigate global warming, such as carbon penalty, carbon trading, CO₂ sequestration, etc. However these proposed methods are usually uneconomical, i.e., these methods do not produce economic valuable substances. This paper will propose a method to absorb atmospheric CO₂ to produce economic valuable substances such as methanol, dimethyl ether, ethylene, several hydrocarbon substances and derivatives and several graphite substances. This paper is focused on methanol production using atmospheric CO₂ capture. The overall process is endothermic. Thus a sufficient energy source is needed. To avoid more CO₂ emission, the energy source must not use conventional fuels. To assure the continuity of energy deliberation, nuclear energy will be used as the energy source of the process. In this paper, the Passive Compact Molten Salt Reactor (PCMSR) will be used as the energy source. The 460 MWth PCMSR is coupled with atmospheric CO₂ capture, desalination, hydrogen production and methanol production facilities. The capturing CO₂ capacity is 7.2 ton/h of atmospheric CO₂. The valuable outputs of this system are 3.34 ton/h of H₂, 34.56 ton/h of O₂, 5.24 ton/h of methanol and 86.74 MWe of excess electricity. **Keywords**—CO₂; methanol; economic product; PCMSR

1 Introduction

The increasing of atmospheric CO₂ concentration becomes the most important environmental issue recently. The increase of CO₂ in the earth atmosphere gives the effect of global warming which in turn causes global climate change [1]. The global climate change will cause many serious problems to human civilization. The examples of serious effects global climate are several natural disasters such as flooding, drought, harvesting failure, etc. [2]. Several actions have been proposed, and some of them have been implemented. The common goal of these actions is to reduce human-made CO₂ emission and to increase CO₂ absorption of both naturally or human-made. Some of the examples of actions to reduce CO₂ emission are carbon penalty to every entity who emit CO₂ by using conventional energy resources or other emitting CO₂ process, carbon certificate and carbon trading for every entity who able to substitute the emitting CO₂ processes with the other processes that emit less CO₂ [3]. The examples of actions to increase CO₂ absorption or to limit the decreasing of CO₂ absorption are deforestation penalty and CO₂ sequestration.

Most of these proposed methods do not produce real economics products, so the implementation of these actions will be viewed as an economic burden of human civilization. The consequence, massive law enforcement is required to guarantee these actions to be a success. It is

interesting to invent a method of atmospheric CO₂ increasing mitigation that able to produce real economics valuable products. This will promote the global warming mitigation by natural human behavior.

2 Basic Theory

2.1 Valuable substances from CO₂

The CO₂ can be reacted with H₂ to produce methanol (CH₃OH) [4]. The methanol itself is a valuable substance. The methanol also can be processed to produce more valuable substance. For example, the methanol can be dehydrated to produce dimethyl ether (DME) [5]. Dimethyl ether can be dehydrated to produce ethylene [6]. Ethylene can be polymerized to produce several synthetic hydrocarbon substances. All of these substances are economically valuable and also feedstock to produce more valuable substances. Thus CO₂ is actually can be processed to produce several economically valuable substances.

In recent technology industrial scale, CO₂ is produced form other economically valuable substances. Production cost consideration and limiting the availability these substances limit the amount of CO₂ production, and thus limit the number of several valuable substances produced from CO₂. If it can be captured economically, the

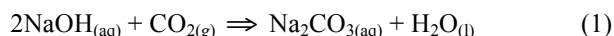
atmospheric CO₂ will become huge and cheap CO₂ resources to produce several economically valuable materials. The consequence, by this method the mitigation of global warming will boost economic development and will be no longer viewed as an economic burden for human civilization.

2.2 Atmospheric CO₂ Capture

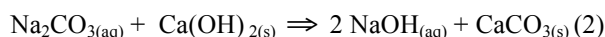
There are two types CO₂ capture method. The first is CO₂ capture from concentrated CO₂ sources such as exhaust stack of coal or oil-fueled power plants or engines. The types of methods are relatively well established. However, these methods are not suitable to capture CO₂ from diffuse sources such as vehicles or other diffuse sources in which emit far more CO₂ than concentrated sources around the world. Thus the method to capture CO₂ directly from earth atmosphere is far more interesting.

Stolarrof et al. propose a method to capture CO₂ directly from earth atmosphere [7]. CO₂ will not be utilized after capturing but will be sequestered. However, the Stolarrof method is interesting due to the ability to capture atmospheric CO₂ in a simple manner. This method will be referred in this paper.

In the Stolarrof method, atmospheric air is contacted with NaOH solution, and the CO₂ will be captured by this following reaction [7] :

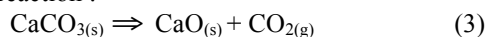


The Na₂CO₃ is then regenerated by this following reaction [7] :

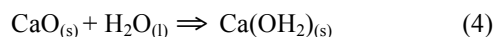


Thus the CO₂ is trapped in solid CaCO₃. In the original Stolarrof proposal, the CaCO₃ is directly sequestered. This means the overall process is costly and unsustainable because need Ca(OH)₂ continually.

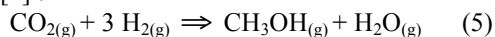
In this paper, the CaCO₃ is regenerated by this following reaction :



The CaO is then reacted with water to obtain Ca(OH)₂ with the following reaction :



The overall process will be sustainable in term of NaOH and Ca(OH)₂. However, it is useless if the CaCO₃ regeneration is done in an atmospheric condition, so the CO₂ is released back into the atmosphere. In this paper, the CaCO₃ regeneration must be done in a reactor which supplied with hydrogen so the released CO₂ will react with hydrogen to produce methanol by this following reaction [4] :



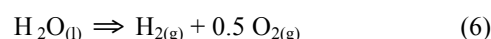
The overall system of atmospheric CO₂ capture followed by methanol synthesis, methanol dehydration,

DME dehydration and synthetic hydrocarbon synthesis is shown in Fig. 1.

2.3 Hydrogen Production

According to equation (4), hydrogen is needed to convert CO₂ to methanol. Free hydrogen is unavailable naturally in a sufficient amount. Thus free hydrogen must be produced from naturally abundant feed materials. Hydrogen can be produced from conventional energy resources by using steam reforming method [8]. However, this method emits CO₂ thus this method is not suitable to the ultimate goal of mitigation of global warming by reducing atmospheric CO₂ concentration.

Hydrogen can be produced by using water as feedstock with the following reaction :



The production of hydrogen from water does not emit CO₂. There are several methods to produce hydrogen from water. The high-temperature steam electrolysis (HTSE) using solid oxide electrolyze cell is the efficient and low-cost method for producing hydrogen from water [9][10]. This method is used as a reference method in this paper. Fig. 2 shows the schematic diagram of solid oxide electrolyzer cell.

2.4 Energy Consumption

The overall reaction of capturing CO₂ to become the final product of methanol is endothermic, means input energy is needed.

The reaction (1) is exothermic with $\Delta h_0 = -109.4$ kJ/mole of CO₂ and $\Delta g_0 = -56.1$ kJ/mole of CO₂. With the negative value of Δg_0 , the reaction (1) is spontaneous. The reaction (2) is exothermic with $\Delta h_0 = -5.3$ kJ/mole of Na₂CO₃ and $\Delta g_0 = -18.2$ kJ/mole of Na₂CO₃. Also, the reaction (2) is spontaneous.

The reaction (3) is endothermic with $\Delta h_0 = 177.99$ kJ/mole of CaCO₂. The reaction (4) is exothermic with $\Delta h_0 = -65.3$ kJ/mole of CaO. The reaction (5) or methanol synthetic reaction is exothermic with $\Delta h_0 = -102.42$ kJ/mole of CO₂.

The reaction (6) or hydrogen production is the most energy consume reaction. Fig. 3 the energy needed to produce hydrogen from water per mole of hydrogen [11].

To produce 1 mole of methanol, 3 moles of hydrogen must be produced, 1 mole of CO₂ must be captured, 1 mole of Na₂CO₃, of CaCO₃ and of CaO must be regenerated. Thus the energy needed per mole methanol production in ideal condition is $(3 \times 250 - 109.4 - 5.3 + 177.99 - 65.3 - 102.42)$ kJ/mole = 645.79 kJ/mole. The energy needed in real condition is higher due to energy losses and the fact that not all of energy released by the exothermic reactions are recoverable.

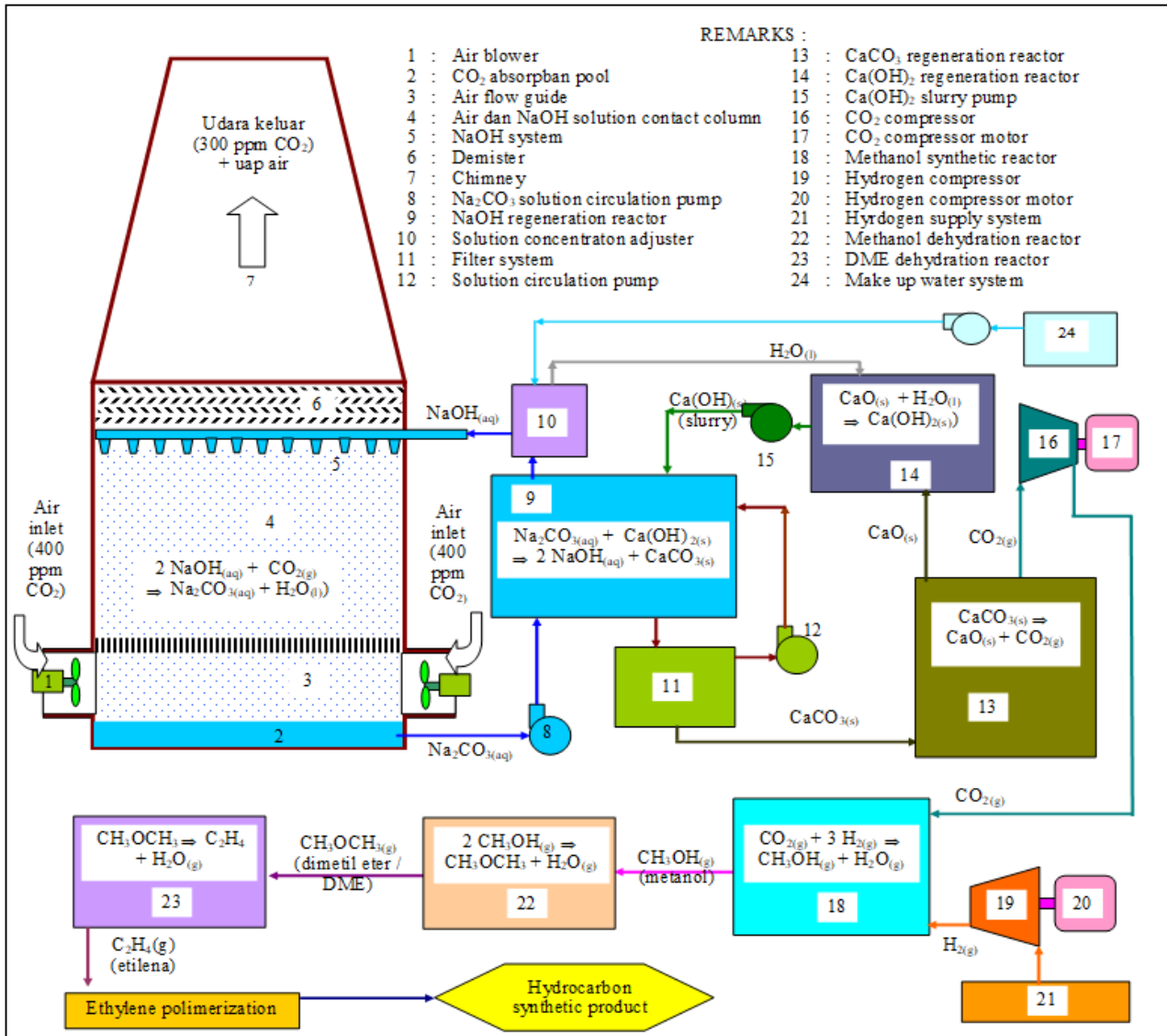


Fig. 1. The overall system of atmospheric CO₂ capture followed by methanol synthesis, methanol dehydration, DME dehydration and synthetic hydrocarbon synthesis.

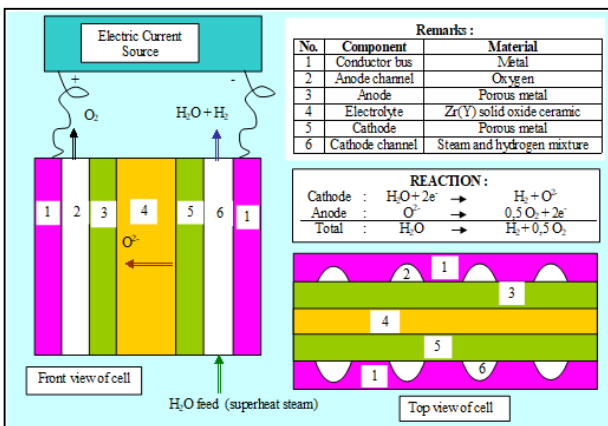


Fig. 2. Schematic diagram of Solid Oxide Electrolyze Cell

2.5 Energy Source

The fact that the overall reaction is endothermic means that an energy source is needed. The fossil energy sources must be excluded because of the emitted CO₂ and thus

contra productive with the ultimate goal to mitigate global warming by absorbing CO₂.

Due to the fact that the overall process is extensive energy consume, the massive and continuous energy sources is needed. Thus nuclear energy source is the most suitable for this system.

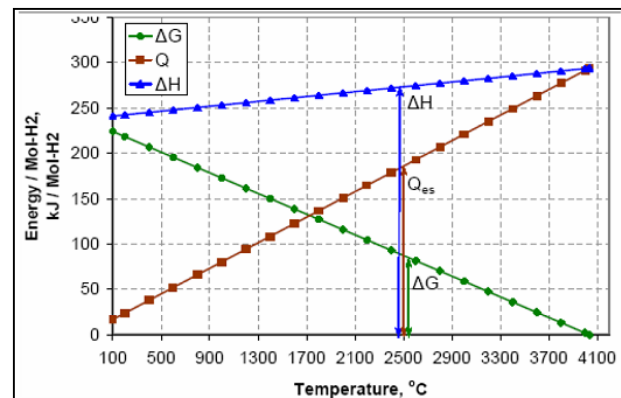


Fig. 3. Energy needed to produce hydrogen from water [11]

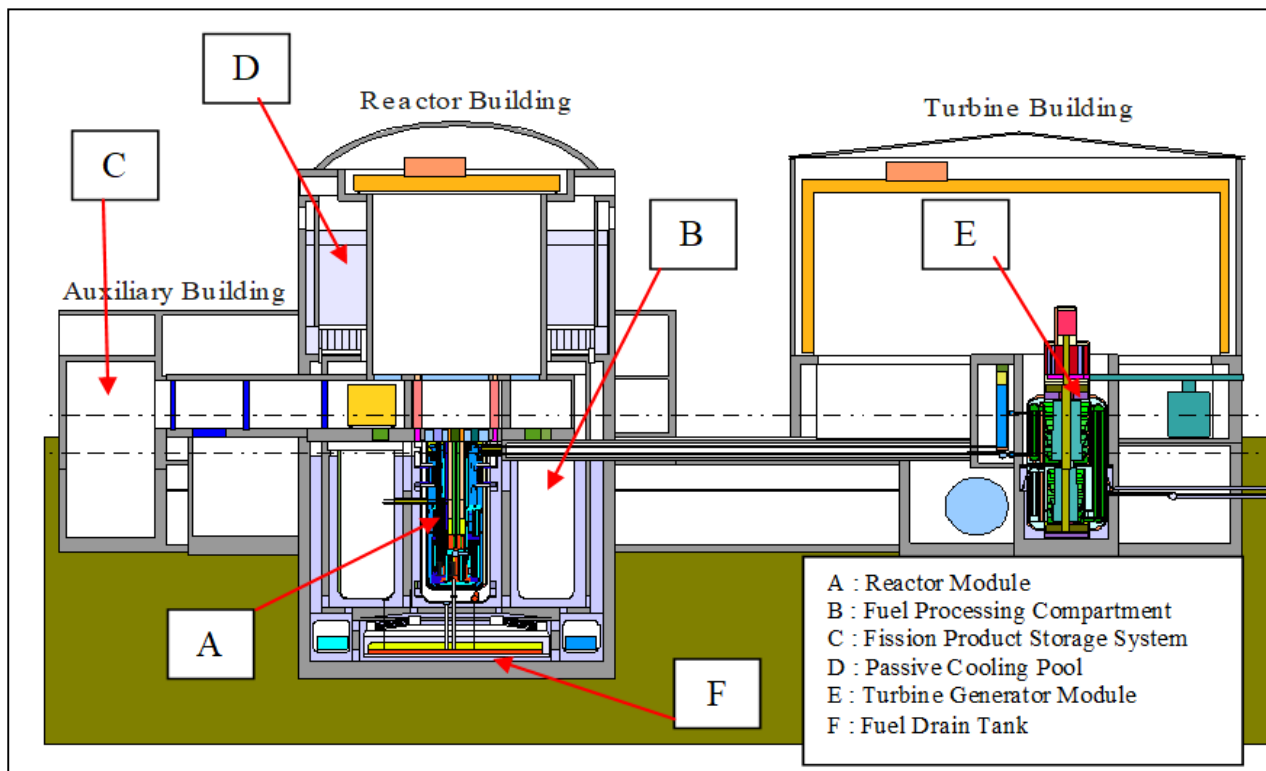


Fig. 4. The schematic diagram of PCMSR [12]

Regarding the consideration of long-term nuclear resources sustainability, the recent nuclear reactor technology that uses U-235 as fissile material is not recommended due to the natural U-235 resources scarcity.

The advanced breeder reactor utilizes more abundant fertile natural resources is more suitable. In this paper, the PCMSR (Passive Compact Molten Salt Reactor) which utilizes thorium nuclear fuel resources is applied to the energy source of the capturing CO₂ to produce methanol process.

2.6 PCMSR (Passive Compact Molten Salt Reactor)

PCMSR is a variant of molten salt reactor that uses liquid fluoride salt mixture of 70 % mole LiF, 29 % mole ThF₄ and 1 % mole UF₄. The thorium is converted to fissile U-233 which undergoes fission reaction and produces the reactor power. The PCMSR use graphite as moderator and LiF-NaF-KF as intermediate coolant [12]. The schematic diagram of PCMSR is shown in Fig. 4.

3 Result and Discussion

1) Energy balance of hydrogen production

Schematic diagram of energy balance of hydrogen production using High Temperature Steam Electrolysis using energy source from PCMSR is shown in Fig. 5. In Fig. 5, Q is heat energy, W is electrical energy, and η is efficiency. The index of R refer to the reactor, HE refers to a heat exchanger for hydrogen production heat supply, TG refers to a turbine generator, AC/DC refer to the

electrical supply system for electrolysis process, P refers to pump. In this analysis, it assumed that $\eta_{HE} = 0.99$, $\eta_{electrolyzer} = 0.98$, $\eta_{AC/DC} = 0.97$, $\eta_{TG} = 0.53$, $\eta_P = 0.70$ and $\eta_{Blower} = 0.70$.

The thermal power of PCMSR is assumed to be 460 MWth. The hydrogen production capacity is set as 1.2 kg/s (4.32 ton/h) or 0.6 kmole/s = 600 mole/s. The HTES is assumed to be operated at 1000 °C. According to Fig. 3, $\Delta g = 171$ kJ/mole of H₂ and $\Delta h = 251$ kJ/mole of H₂ and thus $T\Delta s = \Delta h - \Delta g = (251 - 171)$ kJ/mole = 80 kJ/mole of H₂.

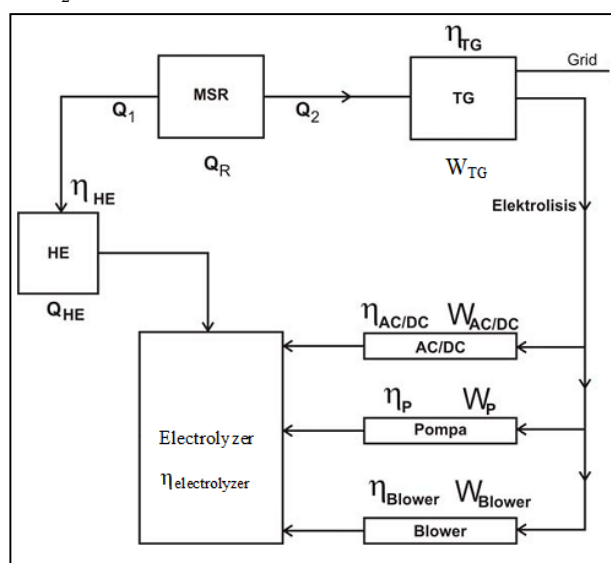


Fig. 5. Schematic diagram of energy balance of hydrogen production using High-Temperature Steam Electrolysis using energy source from PCMSR

The Δg component must be supplied as electrical energy. Thus the electrical power needed to supply the Δg component is

$$W_{EG} = \frac{\dot{m}_{H_2} \Delta g}{\eta_{electrolyzer}} = \frac{600 \text{ (mole/s)} \times 171 \text{ (kJ/mole)}}{0.98} = 104 \text{ MWe}$$

The electrical energy also must be supplied to feed heater pump, recirculation water pump and gas mixture blower. The calculated overall water pumping power is small, i.e., 0.4 kWe and the calculated blower power is 2 MWe. Thus the total electrical power to be supplied for overall electrolyze process is

$$W_E = \frac{W_{EG}}{\eta_{AC/DC}} + \frac{W_P}{\eta_P} + \frac{W_{blower}}{\eta_{blower}} = \left(\frac{104}{0.97} + \frac{0.0004}{0.7} + \frac{2}{0.7} \right) \text{ MWe} = 110.36 \text{ MWe}$$

The $T\Delta s$ component must be supplied as heat energy from the reactor. The electrical energy loss in electrolyzer will become heat energy, and thus the thermal power to be supplied to reactor is

$$\begin{aligned} Q_{EG} &= \frac{\dot{m}_{H_2} T\Delta s}{\eta_{HE}} - (1 - \eta_{electrolyzer}) W_{EG} \\ &= \frac{600 \text{ (mole/s)} \times 80 \text{ (kJ/mole)}}{0.99} - (1 - 0.98) \times 104 \text{ MWth} \\ &= 48.48 \text{ MWe} - 2.1 \text{ MWth} = 46.38 \text{ MWth} \end{aligned}$$

Heat also must be supplied to evaporate the feed water. To produce 0.6 kmole/s of hydrogen, 0.6 kmole/s or 10.8 kg/s of water is needed. The heat of evaporation of water is 2400 kJ/kg of water. Thus the evaporation heat needed to produce 0.6 kmole/s of hydrogen is

$$Q_{evap} = \frac{\dot{m}_{H_2O} \Delta h_{evap}}{\eta_{HE}} = \frac{10.8 \text{ (kg/s)} \times 2400 \text{ (kJ/kg)}}{0.99} = 26.18 \text{ MWth}$$

The total thermal power to be supplied by reactor to produce 0.6 kmole/s of hydrogen is

$$Q_1 = Q_{EG} + Q_{evap} = 46.38 \text{ MWth} + 26.18 \text{ MWth} = 72.56 \text{ MWth}$$

The PCMSR has the thermal power $Q_R = 460 \text{ MWth}$ and the overall turbine-generator efficiency of 0.53. A part of this thermal power must be supplied to the hydrogen production system, i.e., $Q_1 = 72.56 \text{ MWth}$. Thus the thermal power supplied to the turbine system is

$$Q_2 = Q_R + Q_1 = 460 \text{ MWth} + 72.56 \text{ MWth} = 532.56 \text{ MWth}$$

The electrical output of turbine system is therefore

$$W_{TG} = \eta_{TG} Q_2 = (0.53 \times 532.56) \text{ MWe} = 282.26 \text{ MWe}$$

A part of the turbine electrical output power must be supplied to the hydrogen production system, i.e. $W_E = 110.36 \text{ MWe}$. Thus the turbine still produces extra electrical power of

$$W_{EX} = W_{TG} - W_E = (282.26 - 110.36) \text{ MWe} = 171.90 \text{ MWe}$$

2) Energy balance of atmospheric CO₂ capture

The atmospheric CO₂ capture system is assumed to be designed capture 2 kg/s (7.2 ton/h) or 45.45 moles/s of CO₂. The ambient air inlet is assumed to contain 400 ppm of CO₂. The capture system is assumed able to reduce the CO₂ content to become 300 ppm as the air flows out from the capture system. This means the mass flow rate of air is 20 ton/s.

To capture 45.45 mole/s of CO₂, 45.45 moles/s of Na₂CO₃, CaCO₃ and CaO must be regenerated. The energy released from the exothermic reaction of the capturing CO₂ cycle is assumed to be unrecoverable. Thus the energy needed for capturing CO₂ process cycle is equal to the energy needed for the endothermic reaction of this cycle, i.e., reaction (3). The energy is supplied in the form of heat energy. It is assumed that the heat energy is supplied via an electrical heater, which the electricity is supplied by the extra electrical power of the PCMSR turbine system. The efficiency of electrical heater is assumed to be 0.98. The electrical power to be supplied for reaction (3) is :

$$\begin{aligned} W_3 &= \frac{\dot{m}_{CaCO_3} \Delta h_3}{\eta_{heater}} = \frac{45.45 \text{ (mole/s)} \times 177.99 \text{ (kJ/mole)}}{0.98} \\ &= 8.26 \text{ MWe} \end{aligned}$$

The electrical energy also must be supplied for air blower and slurry pumps. The pumping powers are small. The calculated pumping power of NaOH solution is 0.67 kWe. The calculated pumping power of Na₂CO₃ solution is 0.67 kWe. The calculated pumping power of NaOH-CaCO₃ slurry is 1 kWe. The calculated pumping power of CaCO₃ slurry is 0.68 kWe. The calculated pumping power of CaO slurry is 0.45 kWe. The calculated pumping power of Ca(OH)₂ slurry is 0.64 kWe. The calculated pumping power of H₂O make up is 0.22 kWe. The calculated air blower power is 2.67 kW. Thus the overall air blower pumping power of the capturing CO₂ cycle is 7.00 kWe.

Electrical energy also must be supplied for the operation of mixer agitators in Na₂CO₃ regeneration reactor, CaCO₃ regeneration reactor, and CaO-water reactor. The calculated mixer agitator power of Na₂CO₃ reactor is 18.33 kWe. The calculated mixer agitator power of CaCO₂ regeneration reactor is 30 kWe. The calculated mixer agitator power of CaO-water reactor is 3.55 MWe. Thus the total mixer agitator power is 46.88 kWe.

Therefore, the total electrical power to be supplied to the atmospheric CO₂ capture system is

$$\begin{aligned} W_C &= W_3 + W_{pump} + W_{agitator} \\ &= (8.26 + 0.007 + 0.047) \text{ MWe} = 8.32 \text{ MWe} \end{aligned}$$

3) Energy balance of methanol synthesis

The methanol synthesis reaction (reaction (3)) is an exothermic reaction. The energy released is assumed to be unrecoverable. Thus it is no energy needed to supply the reaction (3). However, the reaction (3) needs pressurization until 300 MPa. Thus both of H₂ and CO₂ must be compressed. The electrical energy supply needed for H₂ and CO₂ compression.

The calculated compressor power for CO₂ compression is 0.17 kW. The calculated compressor power for H₂ compression is 5.58 kW. Thus the total electrical power must be supplied for compressor system is

$$W_{compressor} = 5.75 \text{ kWe}$$

4) Overall energy and material balance

The total electrical power needed for overall process is

$$W_{process} = W_E + W_C + W_{compressor} = (110,36 + 8,23 + 0,00575) \text{ MWe} \\ = 118,6 \text{ MWe}$$

Therefore the surplus of electrical power is

$$W_{surplus} = W_{TG} - W_{process} = (205,34 - 118,6) \text{ MWe} = 86,74 \text{ MWe}$$

The surplus electrical power can be supplied to commercial electric consumers or commercial grid.

This atmospheric CO₂ capture system is assumed to have a capturing capacity of 7.2 ton/h (45.45 moles/s) of CO₂. All of the captured CO₂ is converted to methanol. Thus according to reaction (5), the production capacity of methanol is 45.45 mole/s or 5.24 ton/h of methanol.

To produce 45.45 mole/s of methanol, according to reaction (5), $3 \times 45.45 \text{ mole/s} = 136.35 \text{ mole/s}$ of hydrogen is needed. However, the hydrogen production capacity of the HTSE system powered by 460 MWth PCMSR is 600 moles/s of hydrogen. Thus there is an excess hydrogen production of $(600 - 136.35) \text{ mole/s} = 463.65 \text{ mole/s}$. The 463.65 mole/s or 3.34 ton/h of the excess can be considered as the commercial hydrogen product.

According to reaction (6), the HTSE with a production capacity of 600 moles/s of hydrogen produces $0.5 \times 600 \text{ moles/s} = 300 \text{ moles/s}$ of oxygen by-product. The 300 mole/s or 34.56 ton/h of the by-product can also consider as the commercial oxygen product.

4 Summary

It can be summarized that the global warming mitigation is not always an economic burden for human civilization. It is possible to mitigate global warming as well as produce several economics valuable products from this mitigation action. The atmospheric CO₂ capture is the endothermic reaction in overall. Thus the key to this process to be a success is the availability of the abundant, cheap and not CO₂ emitter energy sources. The MSR that utilizes abundant thorium resources is the prominent candidate for the energy source of this system. The analysis has been performed for 460 MWth PCMSR which is coupled with atmospheric CO₂ capture, desalination, hydrogen production and methanol production facilities. For the capturing CO₂ capacity of 7.2 ton/h of atmospheric CO₂, this system can produce valuable outputs of 3.34 ton/h of H₂, 34.56 ton/h of O₂, 5.24 ton/h of methanol and 86.74 MWe of excess electricity.

The results showed that mussel shells contain 14.15% CaO. The optimum yield was 95.12% which was achieved at NaOH concentration of 30% and the catalyst amount of 15%. The biodiesel produced was fulfilled the national standards and had a better quality compared to the conventional homogeneous catalyst. The GC-MS analysis

showed that the biodiesel containing methyl ester with the largest component was methyl oleic (61.39%).

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