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—CO$_2$; 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 CO$_2$

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.
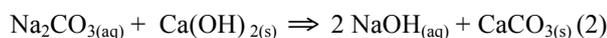
2.2 Atmospheric CO_2 Capture

There are two types CO_2 capture method. The first is CO_2 capture from concentrated CO_2 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 CO_2 from diffuse sources such as vehicles or other diffuse sources in which emit far more CO_2 than concentrated sources around the world. Thus the method to capture CO_2 directly from earth atmosphere is far more interesting.

Stolarrof et al. propose a method to capture CO_2 directly from earth atmosphere [7]. CO_2 will not be utilized after capturing but will be sequestrated. However, the Stolarrof method is interesting due to the ability to capture atmospheric CO_2 is a simple manner. This method will be referred I this paper.

In the Stolarrof method, atmospheric air is contacted with NaOH solution, and the CO_2 will be captured by this following reaction [7] :

$$2NaOH_{(aq)} + CO_{2(g)} \Rightarrow Na_2CO_{3(aq)} + H_2O_{(l)} \qquad (1)$$
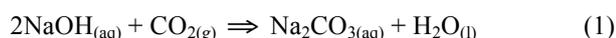
The Na_2CO is then regenerated by this following reaction [7] :

$$Na_2CO_{3(aq)} + Ca(OH)_{2(s)} \Rightarrow 2 NaOH_{(aq)} + CaCO_{3(s)} \ (2)$$

Thus the CO_2 is trapped in solid $CaCO_3$. In the original Stolarrof proposal, the $CaCO_3$ is directly sequestrated. This means the overall process is costly and unsustainable because need $Ca(OH)_2$ continually.

In this paper, the $CaCO_3$ is regenerated by this following reaction :
$$CaCO_{3(s)} \Rightarrow CaO_{(s)} + CO_{2(g)} \qquad (3)$$
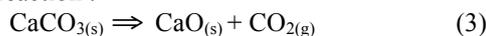
The CaO is then reacted with water to obtain $Ca(OH)_2$ with the following reaction :

$$CaO_{(s)} + H_2O_{(l)} \Rightarrow Ca(OH_2)_{(s)} \qquad (4)$$
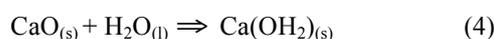
The overall process will be sustainable in term of NaOH and $Ca(OH)_2$. However, it is useless if the $CaCO_3$ regeneration is done in an atmospheric condition, so the CO_2 is released back into the atmosphere. In this paper, the $CaCO_3$ regeneration must be done in a reactor which supplied with hydrogen so the released CO_2 will react with hydrogen to produce methanol by this following reaction [4] :
$$CO_{2(g)} + 3 H_{2(g)} \Rightarrow CH_3OH_{(g)} + H_2O_{(g)} \qquad (5)$$

The overall system of atmospheric CO_2 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 CO_2 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 CO_2 thus this method is not suitable to the ultimate goal of mitigation of global warming by reducing atmospheric CO_2 concentration.

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

$$H_2O_{(l)} \Rightarrow H_{2(g)} + 0.5 O_{2(g)} \qquad (6)$$
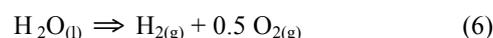
The production of hydrogen from water does not emit CO_2. There are several methods to produce hydrogen from water. The high-temperature steam electrolysis (HTSE) using solid oxide electrolyze cell is the efficient and low-cost method for producing hydrogen from water [9][10]. This method is used as 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 CO_2 to become the final product of methanol is endothermic, means input energy is needed.

The reaction (1) is exothermic with Δh_0 = -109.4 kJ/mole of CO_2 and Δg_0 = -56.1 kJ/mole of CO_2. With the negative value of Δg_0, the reaction (1) is spontaneous. The reaction (2) is exothermic with Δh_0 = -5.3 kJ/mole of Na_2CO_3 and Δg_0 = -18.2 kJ/mole of Na_2CO_3. Also, the reaction (2) is spontaneous.

The reaction (3) is endothermic with Δh_0 =177.99 kJ/mole of $CaCO_2$. The reaction (4) is exothermic with Δh_0 = -65.3 kJ/mole of CaO. The reaction (5) or methanol synthetic reaction is exothermic with Δh_0 = -102.42 kJ/mole of CO_2.

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 CO_2 must be captured, 1 mole of Na_2CO_3, of $CaCO_3$ and of CaO must be regenerated. Thus the energy needed per mole methanol production in ideal condition is (3×250 - 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.
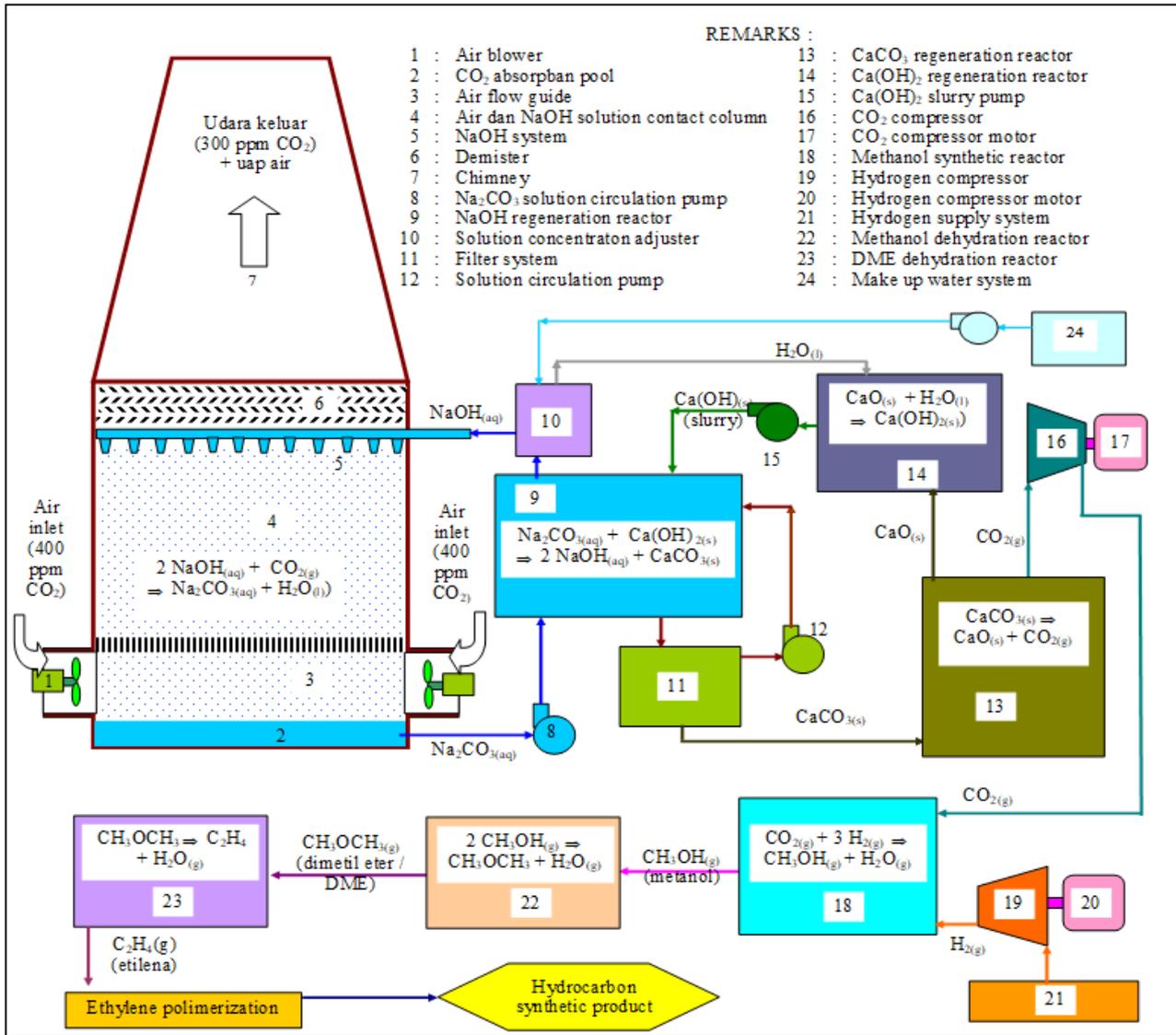
Fig. 1. The overall system of atmospheric CO_2 capture followed by methanol synthesis, methanol dehydration, DME dehydration and synthetic hydrocarbon synthesis.
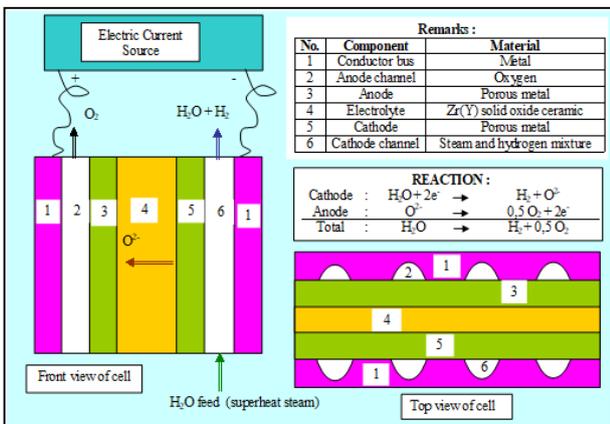

Fig. 2. Schematic diagram of Solid Oxide Electrolyze Cell

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 CO_2 and thus contra productive with the ultimate goal to mitigate global warming by absorbing CO_2.

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.
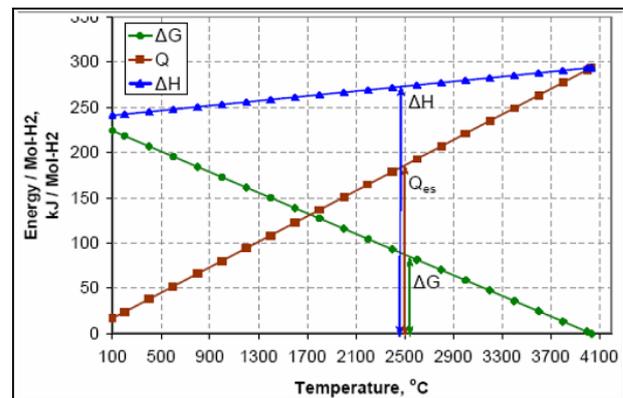

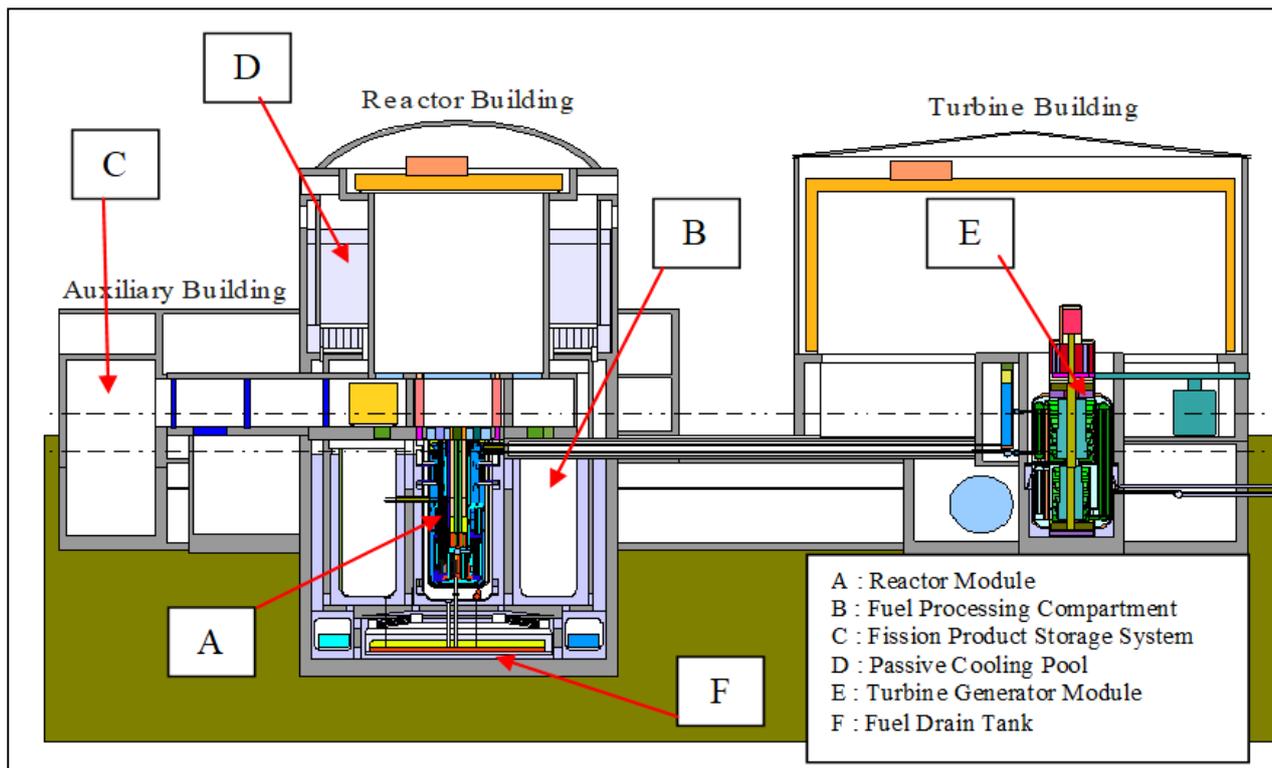**Fig. 3.** Energy needed to produce hydrogen from water [11]

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 ThF$_4$ and 1 % mole UF$_4$. 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 $\eta_{HE} = 0.99$, $\eta_{electrolizer} = 0.98$, $\eta_{AC/DC} = 0.97$, $\eta_{TG} = 0.53$, $\eta_{P} = 0.70$ 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 ºC. According to Fig. 3, $\Delta g = 171$ kJ/mole of H$_2$ and $\Delta h = 251$ kJ/mole of H$_2$ and thus $T\Delta s = \Delta h - \Delta g = (251 - 171)$ kJ/mole = 80 kJ/mole of H$_2$.
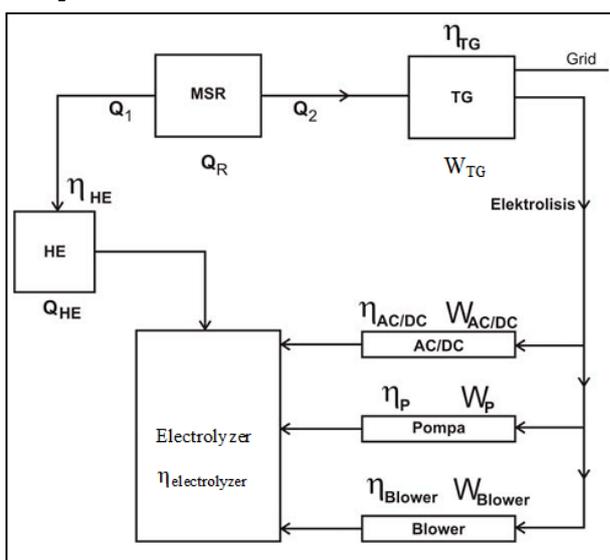

Fig. 5. Schematic diagram of energy balance of hydrogen production using High-Temperature Steam Electrolysis using energy source from PCMSR

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

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

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

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

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 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 MWth. Thus the thermal power supplied to the turbine system is

$$Q_2 = Q_R + Q_1 = 460\,\text{MWth} + 72.56\,\text{MWth} = 387.44\,\text{MWth}$$

The electrical output of turbine system is therefore

$$W_{TG} = \eta_{TG}Q_2 = (0.53 \times 387.44)\,\text{MWe} = 205.34\,\text{MWe}$$

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

$$W_{EX} = W_{TG} - W_E = (205.34 - 110.36)\,\text{MWe} = 94.98\,\text{MWe}$$

2) Energy balance of atmospheric CO_2 capture

The atmospheric CO_2 capture system is assumed to be designed capture 2 kg/s (7.2 ton/h) or 45.45 moles/s of CO_2. The ambient air inlet is assumed to contain 400 ppm of CO_2. The capture system is assumed able to reduce the CO_2 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 CO_2, 45.45 moles/s of Na_2CO_3, $CaCO_3$ and CaO must be regenerated. The energy released from the exothermic reaction of the capturing CO_2 cycle is assumed to be unrecoverable. Thus the energy needed for capturing CO_2 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 :

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

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 Na_2CO_3 solution is 0.67 kWe. The calculated pumping power of NaOH-$CaCO_3$ slurry is 1 kWe. The calculated pumping power of $CaCO_3$ 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 H_2O 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 CO_2 cycle is 7.00 kWe.

Electrical energy also must be supplied for the operation of mixer agitators in Na_2CO_3 regeneration reactor, $CaCO_3$ regeneration reactor, and CaO-water reactor. The calculated mixer agitator power of Na_2CO_3 reactor is 18.33 kWe. The calculated mixer agitator power of $CaCO_2$ 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 CO_2 capture system is

$$W_C = W_3 + W_{pupm} + W_{agitator}$$
$$= (8.26 + 0.007 + 0.047)\,\text{MWe} = 8.32\,\text{MWe}$$

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 H_2 and CO_3 must be compressed. The electrical energy supply needed for H_2 and CO_2 compression.

The calculated compressor power for CO_2 compression is 0.17 kW. The calculated compressor power for H_2 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 CO_2 capture system is assumed to have a capturing capacity of 7.2 ton/h (45.45 moles/s) of CO_2. All of the captured CO_2 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 × 45.45 mole/s = 136.35 mole/s oh 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) mole/s = 463.65 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 × 600 moles/s = 300 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 CO_2 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 CO_2 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 CO_2 capture, desalination, hydrogen production and methanol production facilities. For the capturing CO_2 capacity of 7.2 ton/h of atmospheric CO_2, this system can produce valuable outputs of 3.34 ton/h of H_2, 34.56 ton/h of O_2, 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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