Restored CO$_2$ from Flue Gas and Utilization by Converting to Methanol by 3 Step Processes: Steam Reforming, Reverse Water Gas Shift, and Hydrogenation

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Abstract—Flue gas discharging from coal fired or gas combustion power plant is containing partially carbon dioxide (CO$_2$). CO$_2$ is a greenhouse gas which has been concerned to the global warming. Carbon Capture Storage and Utilization (CCSU) is a topic which is a tool to deal with this CO$_2$ realization. In this paper, the Flue gas is drawn down from the chimney and filtered then it is compressed to build up the pressure until 8 barg. This compressed flue gas is sent to three stages Pressure Swing Adsorption (PSA) which is filled with activated carbon. The experiment showed the optimum adsorption pressure at 7 barg at which CO$_2$ can be adsorbed step by step in 1st, 2nd, and 3rd stages obtaining CO$_2$ concentration 29.8, 66.4, and 96.7% respectively. The mixed gas concentration from the last step composed of 96.7% CO$_2$, 2.7% N$_2$ and 0.6% O$_2$. This mixed CO$_2$ product gas obtained from 3 stages PSA contained high concentration of CO$_2$ which is ready to be used for methanol synthesis. The mixed CO$_2$ was experimented in 5-liter methanol synthesis reactor skid by 3 step processes: steam reforming, reverse water gas shift then hydrogenation. The result showed that the ratio of mixed CO$_2$ and CH$_4$ 70/30, 50/50, 30/70 and 10/90 yielded methanol 2.4, 4.3, 5.6 and 5.3 L/day and saved 40, 30, 15, and 7% CO$_2$ respectively. The optimum condition (positive in both methanol and CO$_2$ consumption) was mixed CO$_2$/CH$_4$ ratio 47/53% by volume which yielded 4.2 L/day methanol and saved 32% CO$_2$ compared with traditional methanol production from methane steam reforming (5 L/day) but no CO$_2$ consumption.

Keywords—Carbon capture storage and utilization, pressure swing adsorption, reforming, methanol.

I. INTRODUCTION

GLOBAL warming is the topic of this century and it is projected that is occurring by human activity and resulting to tremendous climate change such as monsoons in Asia, blizzard snow, cloud burst, drought, and unpredictable weather around the world. The claim that the global warming situation is unnatural and is related to scientific evidence observed of human carbon emissions. It was focused on data showing that the world temperatures and atmospheric CO$_2$ levels have been equally high or higher in the past century as shown in Fig. 1.

The CO$_2$ concentration had been recorded since 1958 and continue monitoring more than 40 years. Fig. 1 showed zigzag pattern because of changing of the season cycle. It was seen that rising CO$_2$ concentration results in increasing global

temperature. The rise of CO$_2$ in the Earth's system may occur in two ways. The first is caused by nature such as volcanic eruptions and forest fires. The second is caused by man-made activities after the Industrial Revolution such as the use of coal and petrochemicals, which are carbon sources, for energy production and processing. CO$_2$ from the first activity is out of control, but the second activity is alleviated by human hands. There are two approaches to managing CO$_2$. The first approach is to reduce this gas generation and the second one is to store and recycle CO$_2$ as well-known Carbon Capture Storage and Utilization (CCSU).
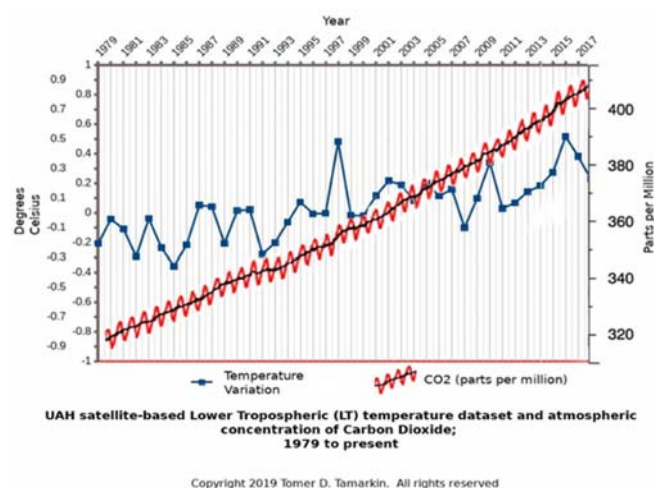
Fig. 1 CO$_2$ related to Global temperature from Historic Atmospheric CO$_2$ Concentration (ppm) for 50 Years from [1]

In this article, the discussion is on the second approach concerning CO$_2$ recovery, storage, and utilization. CO$_2$ from human being is normally produced by burning coal or petroleum sources for producing energy in terms of heat and electricity and generating from organic fermentation. In the present, organic waste from industry is closely absolutely managed by biogas technology which is circularly transformed to energy. By the way, CO$_2$ is generated from coal and petroleum burning called flue gas which is a major part of CO$_2$

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released to the global. Normally, flue gas contained 10-15% CO_2, 4-8% O_2, 70-80% N_2 and small number of others such as SO_x and NO_x [1].
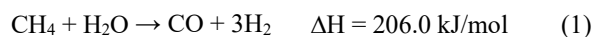
There are several methods to capture CO_2 from from Carbon Dioxide Emitting Industries. In summary, there are three main methods: Membrane Separation (MBS), Pressure Swing Adsorption (PSA) and chemical absorption.

In this article, the CO_2 carrying from the exhaust gas from coal-fired power plant is emphasized for further use in the methanol synthesis process. Therefore, the technique to be considered is the technique that is suitable for obtaining CO_2 for further reaction of CO_2 with methane for methanol purpose. It is found that MBS is not appropriate because some contaminated in flue gas may affect or destroy membrane and it is also highly cost comparing with other techniques [3]. Therefore, it is not good for environment. For PSA, an overview of several adsorbents was collected by Riboldi and Bolland [4]. They summarized that CO_2 capture technology by PSA is a mature technology which can be installed in post- and pre-combustion of power plants. However, installing at post combustion of power plant is an interested because it can recover CO_2 more than 95%. The CO_2 separation by PSA needs only absorbent materials for trapping CO_2. The development of adsorbent materials and separation processes is worldwide studied and collected [4]. Zeolites, MOF and amine functionalized adsorbents exhibited CO_2 capture potentials, but they are still under development combining with process steps to achieve CO_2 separation performance with the minimum energy. In several number of adsorbents, activated carbon from organic sources is interesting because it is feasible and environment friendly. However, if a hot gas separation process is demonstrated feasible, PSA which filled with activated organic carbon may become advantageous in terms of performance of CO_2 capture and energy efficiency. Yin et al. [5] displayed the difference of activated carbon from organic and coal sources. They found that ash in biomass-derived Activated Carbon (coconut), composing of mainly K compound, promoted certainly effect on CO_2 adsorption. In addition, results indicated that the surface properties of AC had little influence on CO_2 adsorption, while the volume of ultra-micropore (< 0.7 nm) had a significant effect on excess CO_2 adsorption capacity.
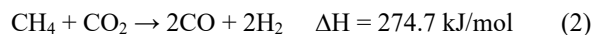
CO_2 utilization is a global topic which is interesting study for CO_2 direct using and CO_2 transforming to other products. In this view, transforming CO_2 to methanol is a challenge topic to substitute commercial methanol (produced from fossil sources such as coal or natural gas). Methanol is a value chemical in various sectors such as solvent, biodiesel, biofuels and additives [6], [7]. Methanol is directly used as a solvent and a raw material by reacting with vegetable oil to produce biodiesel [8]. Indirect consuming, it is transformed to formaldehyde, Methyl Tertiary Butyl Ether (MTBE)/ Tert-Amyl methyl ether (TAME) (blending component for gasoline), dimethyl ether (DME), MTO (methanol to olefin), and MTP (methanol to paraffin), etc. [9], [10]. Global methanol demand is rising an average of 5% to 6% each year by 64 Million Metric Ton, MMT (2014), 92 MMT (2016), and 97 MMT (2020) [13]. In case of Thailand,

methanol was absolutely imported and approximately consumed around 10% of the global methanol usage from 0.66 MMT (2014), 0.78 MMT (2016), 0.88 MMT (2018), 0.81 MMT (2020) and predicted 1.7 MMT (2036) [14]. As a result, the methanol generated by CO_2 transforming is not only solving CO_2 problem but also supporting the utilization of CO_2 and methanol downstream by reducing petroleum sources. Methanol can be produced by combining CO_2 with CH_4 under steam reforming and dry reforming by following (1) and (2) respectively. However, CO_2 obtained from flue gas separation is not absolutely pure, it is contaminated with oxygen and nitrogen. Therefore, methane can be reacted in partial oxidation with oxygen by following (3). There is a side reaction of CO with H_2O becoming to CO_2 and H_2 called Water Gas Shift (WGS) by (4) and also having a side reaction of CO_2 with H_2 reversing to CO and H_2O called Reverse Water Gas Shift (RWGS) by (5). All equations are opportunely appeared in the first reactor of transforming CO_2 to syngas. The product contained water and syngas composing of CO, CO_2 and H_2. The syngas is an intermediate for producing methanol. However, the composition of syngas containing appropriate ratio of $CO/CO_2/H_2$ is significant to obtain high yield methanol. There are two concepts of methanol synthesis by hydrogenation on CO or CO_2 shown in (6) and (7) respectively. The first concept focused that CO is the primary reactant to produce methanol which is supported by several researchers: Leonov et al. [12], Natta et al. [13], Natta et al. [14], and Klier et al. [21]. They proposed that hydrogenation on CO was better than CO_2 and obtained more purity methanol contaminated with small amount of water. The second concept emphasized that CO_2 is the primary reactant for methanol synthesis which is advocated by several researchers: Liu et al. [15], Chinchen et al. [16], Takagawa and Ohsugi [17], McNeil et al. [18], Rozovskii et al. [19], Fujitani et al. [20], and Liu et al. [22]. They agreed that CO_2 plays the domination rate of methanol production, but they accepted that water is a by-product.
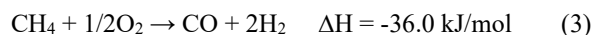
Steam Reforming (SR)

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H = 206.0 \text{ kJ/mol} \quad (1)$$

Dry Reforming (DR)

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H = 274.7 \text{ kJ/mol} \quad (2)$$

Partial Oxidation (PO)

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \quad \Delta H = -36.0 \text{ kJ/mol} \quad (3)$$

Water Gas Shift (WGS)

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H = -41.12 \text{ kJ/mol} \quad (4)$$

Reverse Water Gas Shift (RWGS)

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad \Delta H = 41.12 \text{ kJ/mol} \quad (5)$$

Methanol Synthesis (MS)

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$$CO + 2H_2 \leftrightharpoons CH_3OH \qquad \Delta H = -90.55 \ kJ/mol \qquad (6)$$

$$CO_2 + 3H_2 \leftrightharpoons CH_3OH + H_2O \quad \Delta H = -49.43 \ kJ/mol \qquad (7)$$
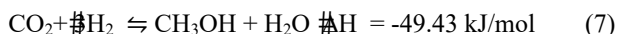
The purpose of this article is to give guidance for capturing and transforming CO_2 for methanol production by using three steps: flue gas compression, CO_2 separation by three stages Pressure Swing Adsorption (PSA), and CO_2 transforming by three steps of Methanol Synthesis (MS).

II. MATERIAL AND METHODS

A. Raw Material

1. Simulation gas containing CH_4, CO_2, N_2, and O_2 obtained from Thai Special Gas Co., Ltd.
2. Flue gas obtained from Coal fire Power Plant.
3. Mixed gas controlled by mass-flow controller
4. Activated Carbon Code HR AT-460 obtained from Right Solution Public Co., Ltd. which is used for CO_2 separation in PSA process. Catalyst A (Ni/Al_2O_3) obtained from Tianjin catalyst new material technology Co., Ltd. used in Reforming reaction of CO_2 and CH_4 in 1st step of MS section. Catalyst B ($Cu/ZnO/Al_2O_3$) obtained from Xi'an Sunward Aeromat Co. Ltd. used in RWGS reaction in 2nd step of MS section. Catalyst C ($Cu/ZnO/Al_2O_3$) obtained from Xi'an Sunward Aeromat Co., Ltd. used in Hydrogenation reaction in 3rd step of MS section.

B. Apparatus

1. The gas product amount was measured by a gas rotameter.
2. The gas composition was measured by gas analyzer obtained from MRU Co., Ltd. model Vario luxx and gas chromatography was obtained from Agilent model 7850 B.
3. The liquid product was measured by weighting balance.
4. The 9 m^3/min CO_2-Flue Gas Treatment (FGT) skid was obtained from PEM Co., Ltd. as shown in Fig. 2 (a).
5. The Feed 13 L/min Product (2.8 L/min) of 3 stages PSA skid was obtained from Wisdom Innovation Co., Ltd. as shown in Fig. 2 (b).
6. The 5 L/day of 3 steps of Methanol Synthesis skid was obtained from Owner Food Machinery Co., Ltd. as shown in Fig. 3.
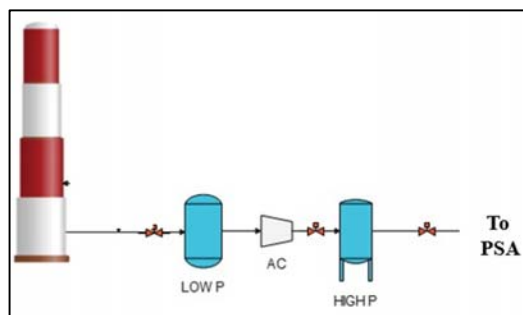

Fig. 2 (a) CO_2-FG preparation

Fig. 2 (b) 3 Stages of PSA

Fig. 3 The 3 Steps of MS

C. Process Flow Diagram

The process flow diagram of experiments showing the combination of CO_2-FGT and preparation (Section A), CO_2 separation by 3 stages PSA (Section B), and CO_2 reaction in 3 steps MS is given in Fig. 4.

The FGT operation (Section A): After the flue gas is treated, then it is drawn out by a blower to increase the flow rate. The flue gas is collected in buffer tank before pressurized by a flue gas compressor. Oil and water are trapped in a dryer, then the flue gas is cleaned and stored in flue gas storage tank obtaining 8 barg pressure.

The PSA operation (Section B): The optimum condition of PSA is under copyright of Thailand Institute of Scientific and Technological Research (TISTR). Pressurized flue gas from storage tank is fed to the 1st stage PSA composing of 4 steps: 1) Feeding to the column by entering at the bottom until obtaining 7 barg pressure, 2) holding time 40 seconds for adsorption of CO_2 in activated carbon, 3) purging the gas out at the top of column until 0.1 barg pressure, then 4) starting vacuum pump to draw the gas out the bottom of the column, and CO_2 out of activated carbon until -0.4 barg column pressure. The operation is the same cycle in the second column. Flue gas is passed from the 1st stage to the 2nd stage and the 3rd stage obtaining higher CO_2 concentration. The highest CO_2 concentration is stored in CO_2 storage for using in the Section C. Flue gases which are

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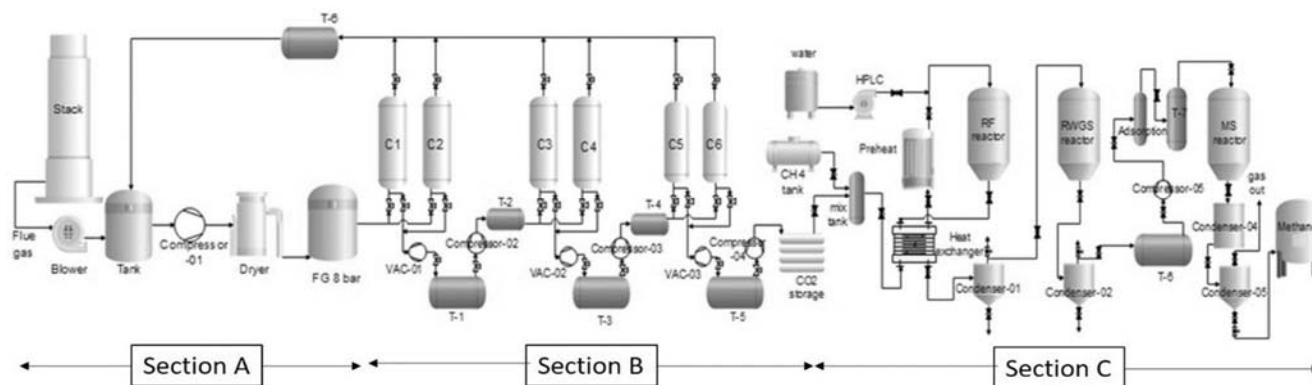removed at the top of all stages are returned to the buffer tank of Section A.

Fig. 4 Process Flow Diagram of CO_2-FGT preparation, 3 stages PSA and 3 steps MS

The MS operation (Section C): The optimum condition of MS is under copyright of TISTR. The process of MS consists of three main reactions: 1) Reforming reaction is starting by total feed 5 L/min mixed gas containing CO_2 from CO_2 storage and CH_4 combining with water to the 1st reactor which is contained 5 kg of catalyst A. The 1st reactor is operated under 600 °C and 1 barg. CO_2, CH_4 and H_2O are reacted then generated syngas composing CO, H_2 and CO_2. 2) RWGS reaction is operated by obtaining syngas from the first step. The second reactor is the same size as the first reactor and contains 5 kg of catalyst B. The second reaction is operated under 500 °C and 1 barg. Syngas is balanced and generated the ratio of H_2/CO around 1.8 and obtained %CO more than %CO_2. The by-product from this step is water. 3) MS reaction is operated by obtaining balanced syngas from the second step. The third reactor is the same size as the 2nd reactor and contains 5 kg of catalyst C. The gas is compressed by compressor and stored at high pressure tank, then the gas 40 barg was reacted by CO hydrogenation to give methanol. The reaction operated under 40 barg and 170 °C.

III. Results and Discussions

A. PSA Experiments

PSA testing for building CO_2 in-out concentration curve was experimented in one stage by maintaining optimum condition: pressure 7 barg, holding time 40 sec, purging pressure until obtaining 0.1 barg and vacuum gas out until obtaining -0.4 barg. The relationship of CO_2 in and CO_2 out was plotted when test with mixed gas by varying CO_2 concentration in range of 12, 30, 50, 70% combination with O_2 7, 4, 2, 1%, and balance with N_2 81, 66, 48, and 29% respectively as shown in Fig. 5. The comparison result showed that PSA was running by activated carbon under the condition. It can absorb CO_2 resulting to obtain CO_2out/CO_2in as 30.07/12.12, 64.09/30.22, 90.4/50.7, and 95.48/70.35 respectively. The CO_2 was increased in CO_2 range 10 to 50%, but it was almost saturated when CO_2 in range 50 to 70%. The data from Fig. 5 support the significant forecast that this PSA condition can be used for real flue gas obtained from coal-fired power plant which comprised of 12% CO_2, 7%
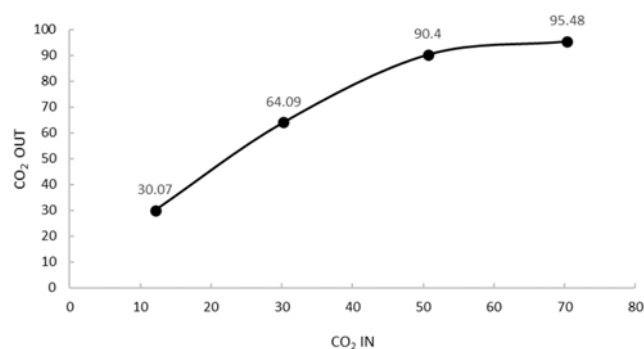
O_2 and 81%N_2.

Fig. 5 The combination of CO_2 in VS CO_2out using one step PSA packed with activated carbon under conditions: pressure 7 barg, holding time 40 sec, purging pressure until obtaining 0.1 barg and vacuum gas out until obtaining -0.4 barg
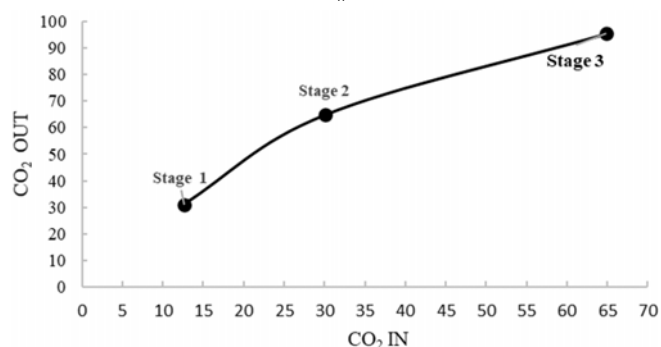

Fig. 6 The relationship of %CO_2 feed in and %CO_2 product out after each stage using the optimum condition with 4 steps: feeding until obtained pressure 7 barg, holding 40 second, purging until obtaining 0.1 barg, and vacuum until obtaining -0.4 barg

PSA testing was experimented with flue gas comprised of 12% CO_2, 7% O_2 and 81% N_2 by using the optimum condition with 3 stages. The relationship of CO_2 in and CO_2 out in each stage was plotted in series from 1st, 2nd and 3rd PSA as shown in Fig. 6. The result was graphed by CO_2out/CO_2 as 29.8/12,

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66.4/29.8, and 96.7/66.4 respectively. It was found that % CO_2 final from 3 stage PSA was very close to CO_2 obtained from the CO_2 concentration curve in Fig. 5 which showed the same trend when higher concentration was input to the PSA system. The product gas from the last step contained 96.7% CO_2, 0.6% O_2 and 2.7 % N_2.

B. MS Experiments

Methanol production consists of 3 steps process: Reforming, Reverse Water Gas Shift, and Methanol Synthesis. The flue gas (CO_2 12%) was separated by 3 stages PSA until obtaining high concentration CO_2 (CO_2 96.7%, O_2 0.6%, and N_2 2.7%) ready for MS. In this process, 3 step MS was applied by using high concentration CO_2 from flue gas as CO_2 feed. The total feed rate 5 L/min of varying ratio of CO_2/CH_4 30/70, 50/50, 70/30, and 90/10 was combined with 6 ml/min water then fed to 1st reactor (Reforming reaction) by operating conditions: 5 kg of Ni/Al_2O_3 catalyst, temperature 600 °C, and 1 bar pressure. Products obtained from 1st reactor are water and syngas containing H_2, CO_2, and CO respectively. The syngas obtained from 1st reactor was CO/CO_2 and H_2/CO around 0.8 and 2.3 respectively. Water in the product was separated out and syngas was sent to the 2nd reactor. The 2nd reactor (RWGS) was operated by operating conditions: 5 kg of $Cu/ZnO/Al_2O_3$ catalyst, temperature 500 °C, and 1 bar pressure. Products obtained from 2nd reactor were water and syngas. Water was generated by the RWGS reaction following (5) and syngas was containing H_2, CO, and CO_2 and receiving CO/CO_2 ratio 1.2 and H_2/CO around 1.8. This RWGS reaction is needed for the MS system which promoted CO being primary dominant in the MS by following (7). The syngas obtained from the 2nd reactor was compressed to boost pressure until 50 barg before sending to the 3rd reactor. The 3rd MS reactor was operated by operating conditions: 5 kg of $Cu/ZnO/Al_2O_3$ catalyst, temperature 170 °C, and pressure 40 barg. The product was methanol which was 98% purity containing small amount of water, 1 to 2%, ethanol around 0.2% and tiny amount of propanol. The liquid product (methanol) obtained from 3 steps MS process was plotted by varying feed ratio of CO_2/CH_4 against liquid product combining with CO_2 consumption as shown in Fig. 7. The graph showed that feed ratios CH_4/CO_2 30, 50, 70, and 90 yielded liquid products (98% CH_3OH) 2.45, 4.35, 5.60, and 5.30 kg/day and consumed CO_2 40.32, 30.10, 15.40, and 7.20 % respectively. It can be seen from Fig. 7 that the optimum condition (both produce methanol and consume CO_2) was at the crossing of liquid product line and CO_2 consumption line which showed CH_4/CO_2 feed ratio 54/46 and obtained CO_2 consumption 31.5%.

The optimum condition was compared feed ratio CH_4/CO_2 obtained from 3 steps MS (Case1) with commercial MS (CH_4/CO_2 90/10) in 3 steps process (Case 2) and CH_4/CO_2 90/10 in 2 steps process without RWGS reaction (Case 3). The high concentration of CO_2 gas (96.7% CO_2, 0.6% O_2, and 2.7% N_2) was used for reacting with CH_4 in ratios following conditions of case1, case2, and case 3 by total gas feed 5 L/min. Fig. 8 showed results of liquid product (98% CH_3OH) 4.3, 5.3, and 5.1 kg/day with CO_2 consumption 1.7, 0.1, and -0.7 kg/day

respectively. It means that 3 steps MS consumed more CO_2 than 2 steps MS, because RWGS reaction supported transform of CO_2 to CO and obtaining CO/CO_2 ratio more than 1. However, CO/CO_2 was lower than 1 which showed in 2 steps MS (without RWGS). The 2 steps system did not consume CO_2, moreover it generated new CO_2 to the system. At the optimum feed CH_4/CO_2 ratio comparing with CH_4/CO_2 90/10, the product was decreased 18.86% (4.3 from 5.3 kg/day), but CO_2 consumption was increased 320% (31.5 from 7.20% CO_2 consumption as shown in Fig. 7).
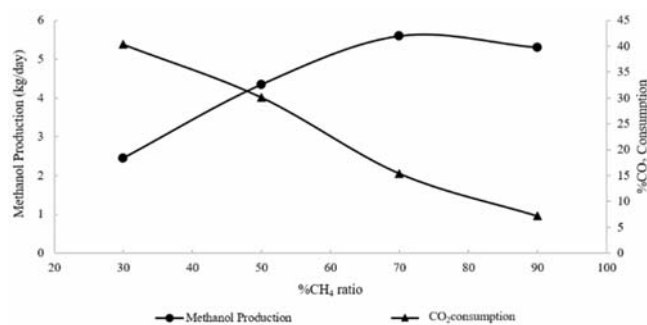

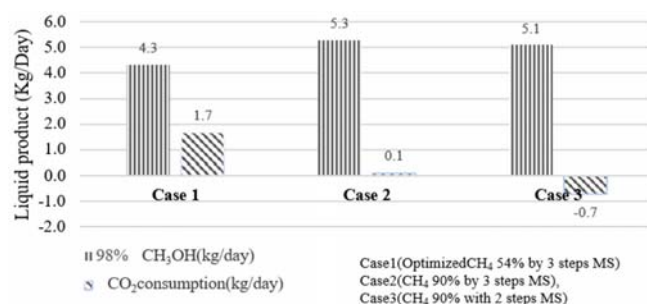Fig. 7 The relationship of Feed ratio CH_4/CO_2 with Methanol production and CO_2 consumption in 3 steps MS

Fig. 8 The comparison of the optimum feed CH_4/CO_2 in 3 steps MS with CH_4/CO_2 90/10 3 steps MS and 2 steps MS by total gas feed 5 L/min

IV. CONCLUSIONS

Flue gas from coal fired power plant or the similar sources can be a major source of CO_2. CO_2 is trapped and compressed for separation in 3 stages PSA packed with activated carbon until obtaining high concentration CO_2 (CO_2-flue gas), then stored in high pressure tank. The CO_2-flue gas is utilized by combining with CH_4 in 3 steps methanol process for producing methanol which is a major chemical for several industries. In this experiment, the methanol production required CO_2, CH_4 and H_2O as raw materials. The by-product is off gas composed of 33% CO, 33% CO_2 and 34% H_2 which is unconverted. The off gas can be recycled to mix with raw gases to compensate raw gas feed in methanol synthesis or it can be used in electricity generator causing of its having heating value.

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