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Design and evaluation of the production of 50,000 metric tonnes/year of methanol using pre-combustion carbon capture technology

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Abstract

Carbon dioxide (CO_2) emission contributes largely to the increasing level of greenhouse gases in the atmosphere. Carbon capture and storage (CCS) and carbon capture utilisation (CCU) are evaluated as a fundamental technology that contributing to the reduction of CO_2 emission. Thus, this study concerns about the design of 50,000 tonnes/year of methanol using pre-combustion CO_2 capture technology. Aspen HYSYS version 8.8 was used as a tool for simulating the methanol production process. The simulation mainly covered the pre-combustion CO_2 capture technology using Selexol method and methanol production plant from CO_2 as raw material. The methanol plant electric capacity was evaluated based on the capacity of three coal-fired power stations in Malaysia. The CO_2 was fed at 120 kPa and H_2 at 101.3 kPa, into the methanol plant which resulted in 21.9% purity of methanol and water. The CO_2 need to produce targeted 50, 000 tonne/year of methanol is 1500×10^4 kg/hr. The emission of CO_2 by the Sultan Salahuddin Abdul Aziz Shah Power Station is 326 kg/hr which produce 0.09 kg/hr of methanol.

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1.0 Introduction

It was in 1827, when the first role of gasses trapping heat close to earth was found by Jean-Baptiste Fourier. Later in 1896, the knowledge was spoken out by a Swedish chemist, showing that carbon dioxide (CO_2) emissions from the combustion of coal could worsen the greenhouse (McGinness, 2001). Carbon dioxide emission from combustion of fossil fuels particularly power plants, is the major contribution to global warming and climate change. According to Intergovernmental Panel on Climate Change (IPCC), the unhindered release of anthropogenic carbon dioxide to the atmosphere would lead to global warming, resulting in severe weather conditions and damaging to the ecosystem (Babu et al., 2013).

Based on the data taken from the United State Environmental Protection Agency as shown in Fig. 1, the highest greenhouse gasses released to the atmosphere in 2014 was reported as CO_2,with emission of 81% followed by methane (11%), nitrous oxide (6%), and lastly fluorinated gases (3%). According to the International Energy Agency (EIA), the demand for coal is estimated to elevate by 21% in the year 2015 to 2035. This is to ensure that the growing world primary energy demand is supported. On the other hand, the trend estimated is similar as in Malaysia.

The demand of coal is emerging based on information from EIA in 2017. Natural gas continues to provide the largest portion in this electricity generation mix with 56.6%, followed by coal and hydropower at 34.2%, and 6.9%, respectively. The remaining 2.3% is contribution from oil and others. As for the total coal energy consumption in Malaysia, Jones (2008) reported that coal formed 30% (~ca. 14,200 MW) in 2008 and is estimated to elevate to 42%(~ca. 17,600 MW) by 2013.

The total CO_2 emission produced will be continuing to increase with the increasing in the fuel consumption pattern. The emission pattern in this figure explains that increasing in energy sources for electricity generation have projected to the increases in CO_2 emission in Malaysia. From the total CO_2 emission in Malaysia, coal-fired power plants itself are estimated to reach 98 million metric tonnes by the year 2020 (Othman et al., 2009). Process industries such as cement, iron and steel as well as oil refineries have inherent CO_2 emission as a result of raw materials conversion. This CO_2 emission contributes largely to the increasing level of greenhouse gases in the atmosphere. In order to mitigate climate change or

specifically global warming, the constraints and solution on carbon emission should be improvised. Three technological pathways have been identified for CO_2 capture technology. They are pre-combustion, post-combustion, and oxy-combustion technologies. The CO_2 capture technology is viable for these three types of system which are an integrated gasification combined cycle (IGCC), a convectional combustion of pulverised coal (PC), and a natural gas combined cycle (NGCC). In the post-combustion capture, the CO_2 is removed from other flue gas constituents which is either initially present in the air or produced by the combustion process. In pre-combustion capture, carbon is separated from the fuel before combustion, and in an oxy-combustion, the fuel is burned in an oxygen stream that contains little or no nitrogen (Figueoa et al., 2008).

The pre-combustion captures CO_2 in synthesis gas after conversion of CO into CO_2 .The post-combustion captures CO_2 in the exhaust gases once the fuel has been completely burned with air. Lastly, the oxy-combustion consists of combustion in oxygen with recycling of exhaust gases and purification of the CO_2 flow, to remove incondensable gases (Figueoa et al., 2008). Much consideration shall be given in selecting suitable methods for capturing carbon dioxide, as not all systems are compatible with all capture methods. According to Franz et al. (2014), the IGCC system can only be practical with pre-combustion capture method. It is because the pre-combustion capture is applicable at high partial pressure. The pulverised coal (PC) power plant system can adopt the post-combustion as well as oxy-combustion capture methods. Lastly, three capture methods are feasible to be applied in the NGCC system.

CO_2 with an increasing potential for by-product end-use in the industrial and energy production sectors, would not only have economic benefits but would simultaneously mitigate the global climate change. Carbon capture and storage (CCS) is evaluated as one fundamental technology contributing to the reduction of CO_2 emission. According to Stryring et al. (2011), CCS is most generally defined as the capture of CO_2 from an industrial or power-sector point source combined with its transport and its storage in geological formations. Though CCS is seen as cost effective emission reduction, the past years have shown that significant drawbacks regarding the CCS option. The possibility of leakage, long term liability issues, problems with public acceptance of on-shore storage locations and limited cost effective storage capacity in some essential regions are the challenges with geological storage.

Therefore, carbon capture and utilisation (CCU) has been recommended as an alternative to divert some CO_2, since it can be used as raw material for other processes. This consists of synthesis of chemicals and materials such as methanol and formic acid, fuels like methane and kerosene and direct use in applications based on CO_2 physico-chemical properties (Styring et al., 2011).

One of the advanced technologies for carbon capture is pre-combustion capture. Pre-combustion capture relates to the treatment of synthetic gas composed of CO and hydrogen. Gasification of coal or reforming of natural gas with oxygen leads to a mixture of CO and H_2 (on dry basis) (Kanniche et al., 2010). Then CO is converted to CO_2 by conversion with steam to a mixture of CO_2 and H_2. CO_2 is then captured by using physical absorbent (the most frequent method). CO_2 is then sent to the compression unit while hydrogen is used as the input to a combined cycle to produce electricity.

Study from Jansen et al. (2015) mentioned that the pre-combustion capture involves reacting a fuel with oxygen or air and/or steam to give mainly a synthesis gas (syngas) or fuel gas which composed mainly of carbon monoxide and hydrogen. The carbon monoxide is reacted with steam in a catalytic reactor, called a shift converter, to give CO_2 and more hydrogen. CO_2 is then separated, usually by a physical or chemical absorption process, resulting in a hydrogen-rich fuel which can be used in many applications, such as boilers, furnaces, gas turbines, engines and fuel cells.

From Fig. 1, it shows that the pre-combustion in both coal and natural gas applications in principle are the same. However, when coal is used, more stages of gas purification are required. The power generation can be divided into basically five different sections. They are:

- Syngas island
- CO_2 separation
- CO_2 conversion
- Power island
- Oxygen island (optional for natural gas cases)

Presently, on-going study and development activities in pre-combustion capture concern all

process steps i.e. the syngas production, the oxygen production, the water gas section, the H_2/CO_2 separation, the CO_2 compression & cleaning section and finally the power island with the hydrogen fuelled gas turbine.

Selexol process is a process where stable acid gas removal system based on the use of a dimethyl ether of polyethylene glycol (DEPG) as a solvent. This process requires no chemical reaction. Selexol process is effective in reducing mass transfer rate and tray efficiencies since DEPG solvent is more viscous than other solvents. The advantages and disadvantages of the Selexol process include (Jansen et al., 2015):

Advantages:

- Chemically and thermally stable, less degradation occurs
- Low viscosity, enhances mass transfer
- High flash point gives ease of handling and safe conditions
- Low vapor pressure results in low solvent loss, reduces raw material costs
- No heat of reaction and small heat of solution
- No on-site formulation required
- Non-fouling, inherently non-foaming and low corrosion
- Requires little heat input, solvent regeneration by pressure let down
- Material of construction mainly carbon steel due to non-aqueous nature, reduce cost.

Disadvantages:

- Requires gas cooling to ~100 °F
- Sensitive to operating temperature and pressure, but can be used to advantage
- Absorption process may require some refrigeration.

Therefore, this study focuses on the simulation to design 50,000 tonnes/year of methanol production plant using pre-combustion CO_2 capture technology and to evaluate the methanol production capacity from different coal-fired based power plant in Malaysia using pre-combustion CO_2 capture technology.

2.0 Methodology

2.1 Tools

The tool used in the simulation is Aspen HYSYS version 8.8. The simulation will mainly cover two important sections namely, the pre-combustion CO_2

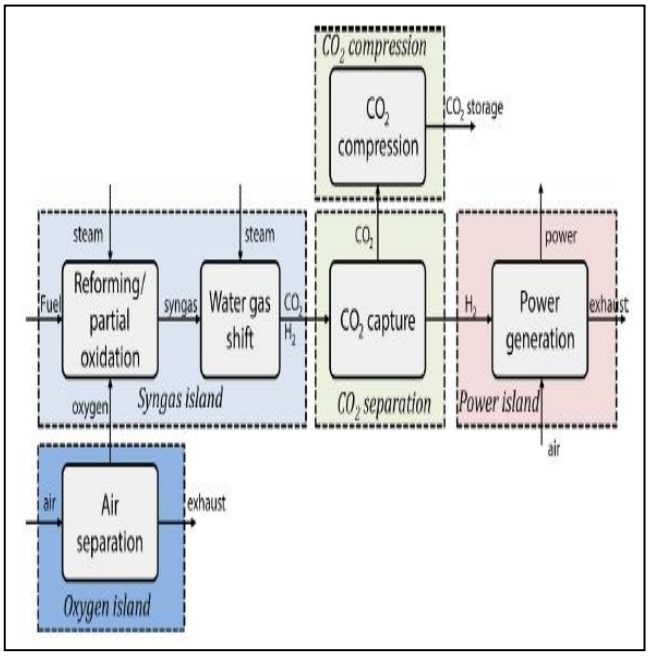

Fig. 1: Schematic diagram of pre-combustion capture for power generation (Jansen et al., 2015).

capture technology using Selexol method and methanol production plant from CO_2 as raw material. Upon completion with the design simulation, the calculation to produce the required 50,000 tonnes/year of methanol is necessary. The process plant is evaluated based on capacity from different coal-fired based power plant in Malaysia.

Pre-combustion carbon capture technology

There are two main routes to syngas production namely steam reforming; which is the addition of steam to the primary fuel, and partial oxidation when oxygen is applied to gaseous and liquid fuels. The syngas production is followed by the water gas shift (WGS) reaction to convert CO to CO_2 and H_2, by the addition of steam. The high pressure of the WGS product gas stream helps the elimination of CO_2. The concentration of CO_2 at the inlet of the CO_2/H_2 separation stage can be in the range of 15% to 60% (dry basis) at a total pressure typically between 2 and 7 MPa. This would mean that the CO_2 separation and compression process is less energy demanding than the post-combustion process where the total pressure and CO_2 concentration are lower (Jansen et al., 2015).

Cryogenic air separation unit (ASU)

Cryogenic distillation is a gas separation process which occurs at a lowest temperature and pressure, whereby it separates components of gaseous mixture instead of liquid based on their boiling points.

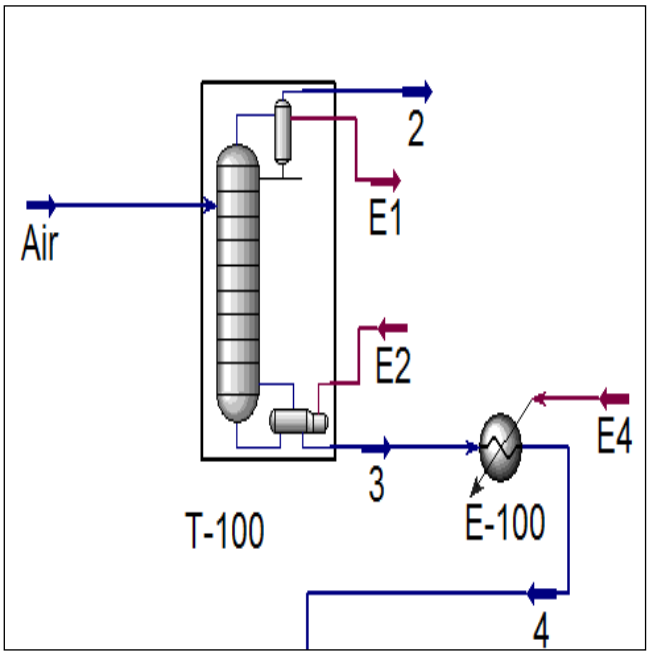

Fig. 2: ASU model in Aspen HYSYS.

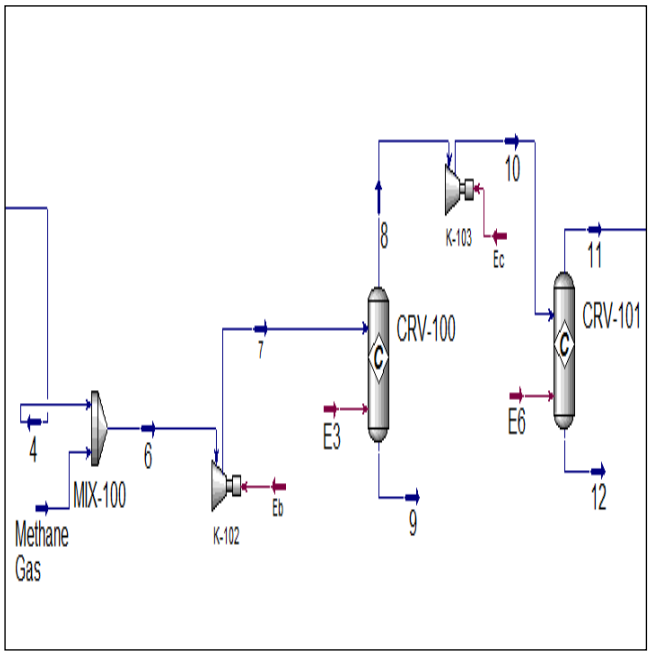

Fig. 3: Gasifier model in HYSYS.

Fig. 2 shows ASU simulated in Aspen HYSYS. Air contains 79% nitrogen and 21% oxygen were introduced at the feed inlet into a distillation column. Nitrogen and air were separated based on their boiling points. Table 1 shows the boiling points of both components. A nitrogen rich vapour product is collected at the top (stream 2) as the temperature is lower than oxygen. 99% oxygen rich liquid product was collected at stream 3. Table 2 shows the stream data of air.

Gasifier unit

Gasifier is needed to produce syngas as converting carbon containing fuel into syngas is the first step for pre-combustion CO_2 capture. CRV-101 and CRV-102 was modelled as fluidised bed reactors (Fig. 3). The composition of syngas produce is tabulated in Table 3. After being heated, stream 4 was mixed with methane gas in MIX-100, both at 25 °C and pressure of 101.325 kPa.

Table 1: Boiling points of nitrogen and oxygen.

Component	Boiling Point(°C)
Nitrogen	−195.8
Oxygen	−183

Table 2: Modelling assumptions for air stream.

Vapour fraction	1
Temperature (°C)	25
Pressure (kPa)	101.325

Stream 6 was then compressed to increase pressure to 200 kPa then into the CRV-101. Gaseous stream 8 leaves the reactor at 400 °C with methane composition of 0.74 and CO_2 of 0.04 only. Therefore, stream 8 was compressed to 1600 kPa before fed into CRV-102 to increase the composition of CO_2 leaving in stream 11.

Selexol process

Fig. 4 shows the Selexol absorption model in HYSYS. The unit integrates the process of selective removal of CO_2 from the gas in stream 11 using dimethyl ether polyethylene glycol (DEPG) as solvent. Selexol process is effective in reducing mass transfer rate and tray efficiencies since DEPG solvent is more viscous than other solvents. Through Selexol process, hydrogen is recycled as a fee along with CO_2. Hydrogen and carbon dioxide stream are then introduced into hydrogenation of methanol production.

Table 3: Composition of syngas at stream 11.

Component	Composition
CO	0.0008
CO_2	0.05
H_2O	0.1012
N_2	0.0015
Methane	0.7456
Methanol	0.1004

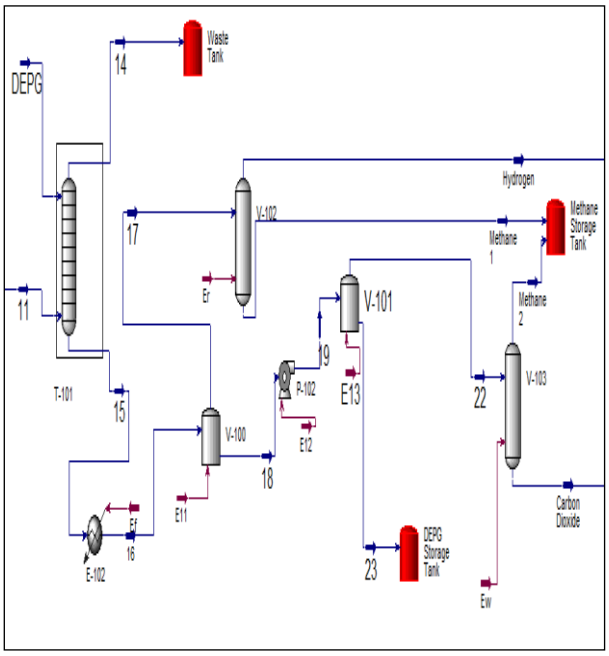

Fig. 4: Selexol absorption model in HYSYS.

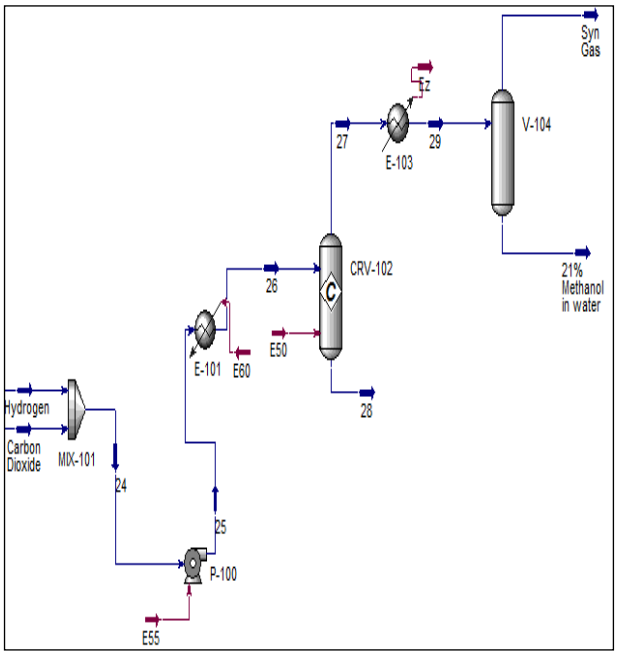

Fig. 5: Hydrogenation methanol model in HYSYS.

The modelling assumptions for the DEPG inlet used for this simulation is as shown in Table 4.

Methanol production

In methanol production plant, it is required to produce 50,000 tonne/year methanol using hydrogenation processes in which CO_2 and H_2 are the raw materials as depicted in Fig. 5. The two gases were mixed in MIX-101. The gases were then heated to 260 °C and introduced into CRV-102. The stream was then cooled and then sent to separator column (V-104). The water at the bottom column contains 21.90% of methanol at 25 °C and 101.325 kPa.

3.0 Results and discussion

3.1 50,000 Tonnes of methanol per year

A simulation design of pre-combustion carbon capture as well as methanol production using Aspen HYSYS was successfully simulated. The simulation was adjusted to the objective to obtain 50,000 tonnes/year of. Table 5 shows the mass flow from Aspen HYSYS for 50,000 tonnes/year of methanol.

Table 4: Modelling assumptions for DEPG inlet (Jansen et al., 2015)

Parameters	Values
Temperature (°C)	337.33
Pressure (kPa)	500
Molar Flow (mol/hr)	13, 964, 730

The 50,000 tonnes/year were generated when the mass flow of air achieved 3×10^9 tonnes/year. It was a huge value of air, methane gas, CO_2 emissions and other inlets consumed. According to Bhattacharya, et al. (2010), to design chemical and power plant processes, they are affected by several drawbacks in case of process simulators. General algorithms are most often not yet available in process simulation tools and which is the case for pre-combustion CO_2 capture plants, can be numerically challenging. Due to these limitations, there were problems of convergence and the results achieved were below expectation.

CO_2 can be recovered and separated from other gases or components by depressurizing it in three-stage depressurization using flash drum (commonly used). In this simulation, three-stage depressurisation was not included as the process was not solved by the Aspen HYSYS.

Table 5: Mass flow of component for 50,000 of methanol per year.

Component	Mass flow (10^4) (kg/hr)
Air	33,600
Methane gas	22,400
CO_2 emission	1,500
CO_2 captured	14.80
DEPG	391,000
H_2	14.80
Methanol	0.57

It was altered by changing the process by using vessel tanks, but the result was not satisfying as CO_2 captured was very low. According to Trapp, et. al. (2015), to obtain a high concentration of CO_2 capture from flash drum, it was then compressed to a pressure of 11 MPa in a single-stage low pressure (LP) and a four-stage medium pressure/high pressure (MP/HP) compressor with inter-stage cooling. Due to limited of information, this stage was not solved by the simulation to get the desired results of CO_2 captured.

3.2 Comparison of coal-fired power stations in Malaysia

The 50,000 tonnes/year of methanol production is compared to the three coal-fired power stations in Malaysia. The main objective is to evaluate the production of methanol from different coal-power plant. These are the three coal-fired power stations in Malaysia that had been selected. There are Sultan Salahuddin Abdul Aziz Shah Power Station, Jimah Power Station and Pulau Bunting Power Station. The electric capacities of each power station are 2420 MW, 1400 MW, and 700 MW, respectively as depicted in Fig. 6.

3.3 estimated methanol production from coal-fired power stations in Malaysia

The highest CO_2 emission, 326 kg/hr is from Sultan Salahuddin Abdul Aziz Shah Power Station as it produces the highest electric capacity, followed by Jimah Power Station, 189 kg/hr, and lastly, Pulau Bunting Power Station, 94 kg/hr. The simulations of these plants are using the same design for 50, 000 tonne/year of methanol. The calculated of CO_2 emission is used to design the amount of methane gas and air used.

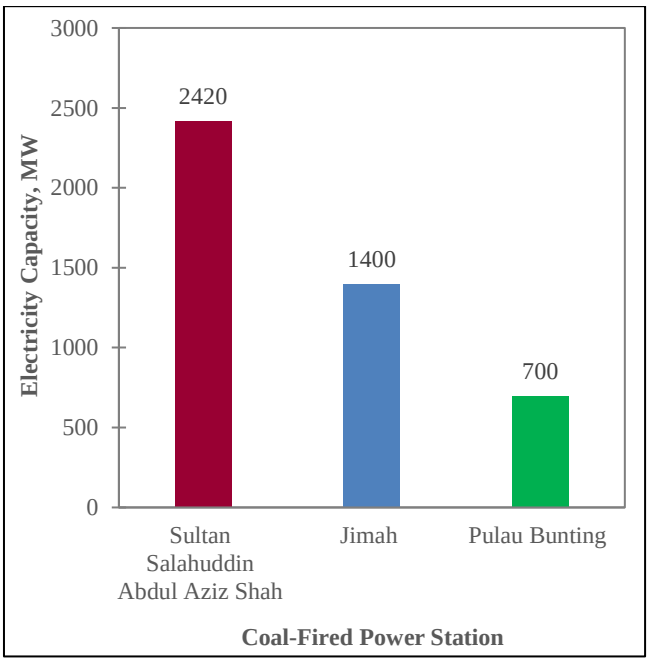

Fig. 6: Electric Capacity of Coal-Fired Power Stations in Malaysia (Lin et al., 2017).

CO_2 emission for a unit of electricity generation is calculated based on the research of Mahlia (2002). Table 6 shows the emission of CO_2 from various types of fuels. Sultan Salahuddin Abdul Aziz Shah Power Station with CO_2 emission of 326 kg/hr produces 0.09 kg/hr methanol. Jimah Power Station with CO_2 emission of 189 kg/hr produces 0.052 kg/hr methanol. Lastly, Pulau Bunting Power Station with CO_2 emission of 94 kg/hr produces 0.03 kg/hr methanol. These data are shown in Table 7.

Table 6: Emission of CO_2 from various fuel types (Mahlia, 2002).

Fuels	**Emission of CO_2 (kg/kWh)**
Coal	1.18
Petroleum	0.85
Gas	0.53
Hydro	0.00
Other	0.00

Table 7: CO_2 Capture from the CO_2 Emission and Estimated value of Methanol Produce.

Power Station	**CO_2 Emission (kg/hr)**	**Methanol (kg/hr)**
Sultan Salahuddin Abdul Aziz Shah	326	0.09
Jimah	189	0.052
Pulau Bunting	94	0.03

4.0 Conclusions

This paper has shown and evaluated the validity of methodology to estimate the potential of a carbon capture utilization plant. Its design has been simulated

in Aspen HYSYS version 8.8 in order to obtain 50,000 tonnes/year of methanol. This design need to use 1500×10^4 kg/hr of CO_2. Then, three coal-fired power stations in Malaysia are selected and simulated to estimate methanol production using calculated CO_2 emission respectively. The highest capacity of 2420 MW, Sultan Salahuddin Abdul Aziz Shah Power Station produce 0.09 kg/hr of methanol, in the simulated design plant based on 326 kg/hr of CO_2 emission.

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