Malaysian Journal of Chemical Engineering & Technology

Methanol production using carbon capture technology: An overview

*Mohd Aizad Ahmad, Zulkifli Abdul Rashid

Faculty of Chemical Engineering, Universiti Teknologi MARA, Selangor, Malaysia

*Corresponding email: mohdaizad@salam.uitm.edu.my

Abstract

Carbon emission to environment cause global warming problems. Research on carbon capture technology has been widely established including pre-combustion, post-combustion and oxyfuel method. Utilisation of carbon from capture process has been developed for methanol production. Various separation method of CO2 from gas has been highlighted. Challenges and potentials of methanol production using carbon capture utilisation (CCU) should be taken into account. The major challenge for methanol production from carbon capture is to produce catalysts which are selective, lower cost and long term recyclable which will allow the reduction of carbon dioxide to methanol. Researchers also discussed how to produce minimum cost of sustainable hydrogen supply to react with CO_2. For oxyfuel combustion technology, the challenges are the capital cost and energy consumption mostly from cryogenic air separation unit (ASU). An overview of methanol production using various method of carbon capture has been discussed in this paper.

1.0 Introduction

Methanol (CH_3OH) also known as a methyl alcohol is a monochrome liquid. Methanol is one of the large uses chemical product and the constituents of methylated spirits in the home. Antifreeze, solvent, and fuel are some example of the used for domestic and industrial applications. Although, it has half of the gasoline energy density, methanol has outstanding combustion properties which consents its use as a fuel in vehicles (Ganesh, 2014). Furthermore, it can be raw material in the processing of various organic chemical compounds, and in the industrial production such supplies as paints and plastics are the example of the uses of the methanol.

Methanol has toxic properties which are suitable to produce biodiesel via transesterification reaction and for ethanol manufacturing; it is recurrently used for industrial purposes as a denaturant additive. Toxic properties give high possibility to get very bad conflict in health when deal with this chemical. The toxic effect can occur when someone is inhaling the high concentrations of methanol vapor by inhalation system and absorption of methanol through the skin. Methanol is also one of the raw materials for many chemicals such as dimethyl terephthalate, formaldehyde, methylamines, methyl methacrylate, and acetic acid.

High energy density per mass and per volume is several benefits of the methanol products (Ganesh, 2014). Methanol has been proven as an attractive compound as a direct fuel for the fuel cell and automotive industry. Besides that, methanol has been used as a feedstock for chemical synthesis to produce various compounds. Methanol can also be produced from resources such as coal, oil and natural gas, or by conversion of biomass. On a worldwide basis, methanol have a total annual capacity of more than 50 million tonne that were produced by over 90 methanol plants.

1.1 Methanol manufacturing process

Currently, more than 75% of methanol is produced from natural gas. Methanol synthesis is based on three fundamental steps including: Synthesis gas (syngas) production through steam reforming or partial oxidation of methane, methanol synthesis, methanol purification and hydrogen separation process (Olah et al., 2009).

Steam reforming involved endothermic reaction as decreasing pressure, rising temperature and higher steam to carbon S/C ratio could lead to higher conversion (Mouljin et al., 2001). Steam reforming is limited by equilibrium as in the radiant section of a furnace, where nickel catalyst-packed tubes located.

Meanwhile, methanol synthesis need combining design of methanol synthesis reactor, feed quenching, boiler feed or unheated reactants are cooling service in order to remove reaction heat. Higher conversions with higher pressures, stoichiometric ratios and lower temperatures of isothermal cooling in shell and reactor tube setups can be achieved, if it is modelled under conditions known to approach equilibrium.

As for methanol purification, the products of methanol synthesis containing methanol and syngas are flash in order to separate crude methanol and unconverted light ends. To separate remaining light-ends, methanol at 98wt.% and water, crude methanol is distilled, in an atmospheric column with a partial condenser.

Hydrogen separation has the objective to avoid recycle accumulation the flashed light-ends contain excess hydrogen which these must be purged for furnace fuelling or purified for hydrogen credit via pressure swing adsorption, cryogenic distillation or membrane separation with the latter being cheaper at the low recoveries and purities required (Mivechian and Pakizeh, 2013). As hollow fibre tubes in a shell, and separation for this, polyimide membranes are fabricated is achieved by partial pressure differences.

1.2 Carbon emissions

Human activities are produced carbon dioxide (CO_2), which is emitted as the primary greenhouse gas (GHGs). Activities from human which produced carbon dioxide (CO_2) in 2014 accounted about 80.9% of all U.S greenhouse gas (GHGs) emissions. Part of the earth's carbon cycle (the natural circulation of carbon among the atmosphere, oceans, soil, plants, and animals) that is naturally present in the atmosphere is carbon dioxide (CO_2). To remove carbon dioxide (CO_2) from the atmosphere, human activities are altering the carbon cycle — both by adding more carbon dioxide (CO_2) to the atmosphere and by influencing the ability of natural sinks, like forests. The increasing that has been occurred in the atmosphere is because from human-related emissions while carbon dioxide (CO_2) emissions come from natural sources, since the industrial revolution.

According to U.S carbon dioxide (CO_2) emissions, about 37% is contributed from electricity, 31% from transportation, 15% from industry, 10% is residential and commercial, and 6% from other activities (non-fossil fuel combustion). The combustion of fossil fuels (coal, natural gas, and oil) for energy and transportation is the main human activity that emits carbon dioxide (CO_2) even though certain industrial processes and land-use changes also emit carbon dioxide (CO_2) (Climate and Weather, 2016).

1.3 Carbon capture storage and utilisation

The aim of carbon capture storage (CCS) and carbon capture utilisation (CCU) is to capture carbon dioxide (CO_2) emissions from sources of power plants and processes from industrial to overcome the release of carbon dioxide (CO_2) emissions into the atmosphere (Markewitz et al., 2012). The final destination of the captured carbon dioxide (CO_2) is the difference between CCS and CCU. Captured carbon dioxide (CO_2) is transferred to a suitable site for long-term storage in CCU (Metz et al., 2005). In CCU, captured carbon dioxide (CO_2) is converted into commercial products (Yu et al., 2008). In Fig. 1, different CCS and CCU options are being summarised and described below.

According to Azapagic and Rosa (2015), carbon dioxide (CO_2) can be produced from energy sector, oil refineries, cement industry, iron and steel industry, biogas sweetening, and chemical sectors. Then the carbon dioxide (CO_2) can be captured by using techniques of post-conversion capture, pre-combustion capture, and oxy-fuel combustion capture. Every technique has their ways in how to separate the carbon dioxide (CO_2) and purified that carbon dioxide (CO_2). This is because, carbon dioxide that has been captured can be utilised to form other types of chemical or also can be stored but it need to be purified first.

Post-combustion is the process where carbon dioxide is separated after the combustion of fuel source. In power plants, production of biogas sweetening, iron, fuels, cement and steel, and ethylene oxide, this technique can be used to remove carbon dioxide (CO_2) (Metz et al., 2005). Vacuum and pressure swing adsorption, membranes, frameworks of porous organic, solvent absorption, and solid sorbents adsorption are the methods of post-combustion (Kuramochi et al., 2012). Among these, monoethanolamine (MEA) is the most commonly used absorption method for the post-combustion purpose (Li et al., 2013). As MEA regeneration consumes high amount of energy in the form of heat, this method is not economically viable for all industries.
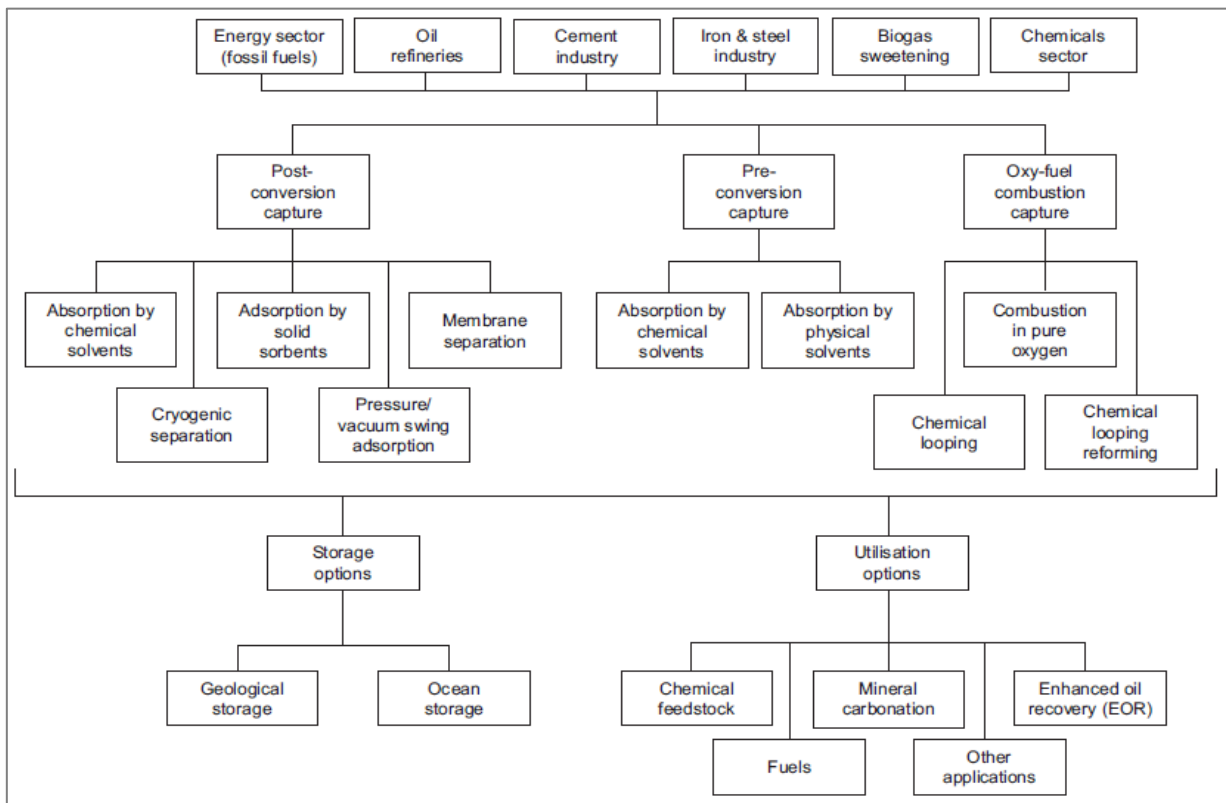
Fig.1: Different carbon capture, storage and utilization options chart (Azapagic and Rosa, 2015).

In cement plant, the utilisation of MEA absorption incurred additional energy costs. Carbon dioxide (CO_2) is less well suited than in a combined heat and power plant as the former lacks recoverable heat.

According to UNIDO (2011), pre-combustion capture refers to capturing carbon dioxide (CO_2) generated as an undesired co-product of an intermediate reaction of a conversion process. The production of ammonia and coal gasification in power plants can used this type of technique (Singh et al., 2011). Carbon dioxide (CO_2) that is co-produced with hydrogen in ammonia production, take place the ammonia synthesis before remove the steam reforming. Commonly for these purposes absorption in MEA is used (Metz et al., 2005). In an integrated gasification combined cycle (IGCC) power plant the hydrogen must be separated from carbon dioxide (CO_2). This is typically achieved using physical solvents such as Selexol and Rectisol (Viebahn et al., 2007). Applications with high operating pressure Physical solvents are, reportedly, more suitable because they are also more efficient for concentrated carbon dioxide (CO_2) stream (Markewitz et al., 2012).

In oxy-fuel combustion is one of the leading technologies. Instead of air, the process of burning the fuel in this process is with pure oxygen (Stanger et al., 2015). Furnace or boiler is where the flue gas is recycled back to control the temperature of flame. The main purpose of using oxy-fuel combustion technology in order to capture the carbon dioxide (CO_2) from a power plant is to generate a flue gas with high concentration of carbon dioxide (CO_2) and water vapor. At low temperature, the process of purification and dehydration is carried out to separate carbon dioxide (CO_2) from flue gas. Oxy-fuel combustion has principal attraction which is it can avoid the need for a costly post-combustion carbon dioxide (CO_2) capture system. To generate the pure oxygen needed for combustion, it requires an air separation unit (ASU). Generally, the major units of power generation in oxy-combustion consist unit of separation of air (ASU) to produce oxygen, gas turbine or boiler for heat generation and combustion of fuel, unit to process flue gas for flue gas cleaning or gas quality control system (GQCS) and unit to process carbon dioxide (CO_2) (CPU) for storage and transport the carbon dioxide (CO_2) that have been purified (Stanger et al., 2015).

Fig. 2 shows that carbon dioxide (CO_2) which is present originally in the air or produced by combustion mixed with other constituent flue gas is separated are the post-combustion capture. For pre-combustion capture, before combustion carbon is eliminated from the fuel. Little or no nitrogen that contains in oxygen stream is burned with fuel is oxy-combustion capture.

1.4 Carbon dioxide (CO_2) separation method from gas

Numerous technologies for separating or capturing CO_2 from mixture of gases are commercially accessible and widely practices which are absorption, adsorption, cryogenics, membrane and microbial system. Chemical absorption is the most developed method for CO_2 separation. Monoethanolamine (MEA), diethanolamine (DEA) and methyl diethanolamine (MDEA) are a family of organic compounds of alkanolamine. Alkanolamine is the most effective solvent that chemically absorb H_2S in the presence of CO_2. The absorption is more than 90% efficiency. Based on review on various CO_2 capture technologies, it has been concluded that the most promising method for CO_2 absorption is using MEA. An absorption pilot plant with one tonne per hour of CO_2 for post-combustion capture technology for coal-fired power plant was positively tested using a solvent containing 30% MEA (Leung et al., 2014).

Physical absorption used physical solvents to separate CO_2 and H_2S from flue gases from oil and coal gasification. The physical absorption of CO_2 in the solvent is mostly depends on temperature and pressure. As an example, high partial pressures and low temperatures of CO_2 facilitates the absorption. The consequent pressure reduction regenerates the solvent with a comparatively small energy requirement. Hence, it is suitable for recovering CO_2 from Integrated Gasification Combined Cycle (IGCC) systems where the exhaust CO_2 would leave the gasifier at elevated pressures.

Typical physical solvents used in IGCC pre-combustion capture are Selexol, Rectisol and Purisol (Jansen et al., 2015). Separation by adsorption relies on the thermodynamic properties of a solid sorbents to bind the CO_2 on its surfaces. The main criteria for sorbent selection are great regeneration ability, large specific surface area and high selectivity. Examples of the most used sorbents for this process are activated carbon, molecular sieves, calcium oxides, zeolites and hydrotalcites (Leung et al., 2014).

Membrane which is a thin selective layer is made of a composite polymer is mechanically supported to a non-selective, low-cost and thicker layer. It can be used to disregard else constituents of flue gas while allowing only CO_2 to pass through. Proceeding from highly efficient membranes' development, Audus (2000) had successfully achieved a CO_2 separation of 82% to 88%.

There is possibility that through the development and on-going research of membrane, production of membranes that is better for CO_2 separation can be done.

Cryogenic distillation is a gas separation process which occurs at a lowest temperature and pressure. CO_2 in flue gas is cool to desublimation temperature ranging from −100 °C to −135 °C. After that, separation of solidified CO_2 from other light gases occurs. Then, compression of solidified CO_2 to a high pressure of 100 °C to 200 °C takes place. From the process up to 90% to 95% amount of CO_2 recovered from flue gas. The energy of the intensive process is calculated to be 600 kWh to 660 kWh per tonne of CO_2 recovered in liquid form (Leung et al., 2014).

2.0 Challenges and potentials of methanol production using CCU

According to the report by CO_2 Chem Network in 2012, the major challenge in cluster of solvents is to produce catalysts which are selective, lower cost and long-term recyclable which will allow the reduction of carbon dioxide to methanol in the absence of carbon monoxide. There are also lack of life cycle analysis (LCA) on catalyst supply and use. Another challenge is to produce sustainable hydrogen supply to react with CO_2 and produce methanol. Current hydrogen production relies heavily on hydrocarbon reforming reactions, while water electrolysis consume higher cost of energy and there are also lack of scale up to produce hydrogen from electrolyser. For oxyfuel combustion technology, the challenges are the capital cost and energy consumption for a cryogenic air separation unit (ASU), boiler air infiltration that dilutes the flue gas with N_2, and excess O_2 contained in the concentrated CO_2 stream (EPA, 2015). However, potentials of methanol productions by using CCU have been highlighted by several reports and studies. CO_2 Chem Network has listed methanol production from CCU is one of the brightest potential to become economic friendly in the future.

Methanol is used for energy storage media and synthons for further production of another solvents or chemicals. They also suggest that possible solution for sustainable hydrogen supply is to integrate photochemical water splitting with CO_2 reduction. EPA in Technical Support Document 2015 has reported the potential of producing methanol using carbon capture instead of storage CO_2 in geology sequestration. They also reported development of post-

combustion CO_2 capture for incorporation into pulverized coal power plants and pre-combustion CO_2 capture for integration into the new generation of coal gasification power plants by The National Carbon Capture Centre (NCC) at the Power Systems Development Facility (PSDF) in Wilsonville, Alabama. NCC is a consortium between DOE/NETL and electric power producers which conducts multiple projects, such as testing of solvents, enzymes, gas separation membranes, sorbents, and catalysts, as well as other novel processes.
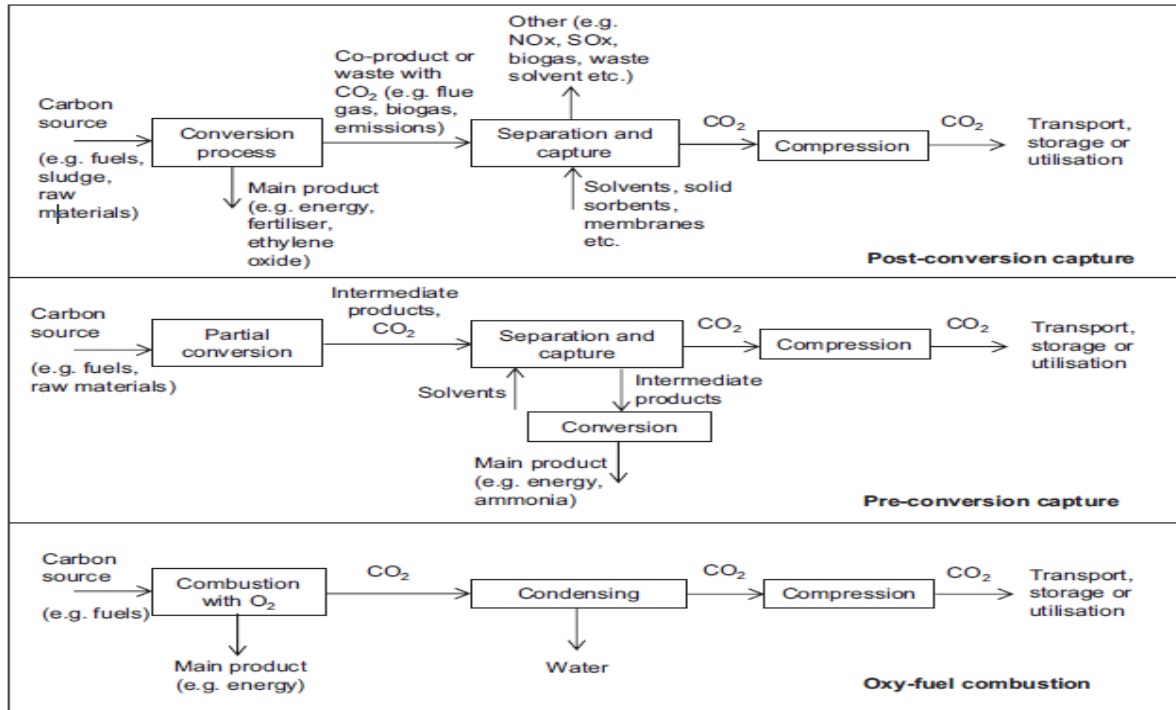

Fig. 2: Route on different carbon capture technology (Azapagic and Rosa, 2015).

3.0 Conclusions

Methanol production using various carbon capture technology has been discussed including methanol manufacturing, carbon capture storage and utilization, challenges and potentials of producing methanol via carbon capture technology.

It is understood that methanol production via CCU has tremendous potential to become new approach for replacing natural gas as the raw material in methanol production. Therefore, further studies on designing and optimizing plant integrating carbon capture and methanol production need to be conduct. Economic and safety analysis of this plant must be simulated to get minimum benchmark of operating this plant in the future.

Acknowledgment

References

A. Azapagic and M. Rosa (2015). Carbon capture, storage and utilisation technologies: A critical analysis, *Journal of CO₂ Utilization*. 82–102.

A. Mivechian and M. Pakizeh (2013). Performance comparison of different separation systems for H₂ recovery from catalytic reforming unit off-gas streams. *Chemical Engineering Technology*. 519–527.

B. Metz, O. Davidson, H. de Coninck, M. Loos, L. Meyer (2005). IPCC Special report on carbon dioxide capture and storage, intergovernmental panel on climate change.

B. Singh, A.H. Strømman, and E.G. Hertwich (2011). *Int. J. Greenhouse Gas Control*. 5. (4). 911–921.

Climate and Weather (2016). Retrieved 11 15, 2016, from Mother Nature Network :http://www.mnn.com/earth-matters/climate-weather/stories/co2-101-why-is-carbon-dioxide-bad.

D. Jansen, M. Gazzani, G. Manzolini, E.v. Dijk and M. Carbo (2015). Pre-combustion CO₂ capture. *International Journal of Greenhouse Gas Control*. 40, 167–187.

D.Y. Leung, G. Caramanna and M. M. Maroto-Valer (2014). An overview of current status of carbon dioxide capture and storage technologies. *Renewable and Sustainable Energy Reviews*. 39.426–443.

Environmental Protection Agency: Literature Survey of Carbon Capture Technology, Technical Support Document (2015).

G.A. Olah, A. Goeppert, and G.K. Surya (2009). Beyond oil and gas: the methanol economy. Wiley-VCH Verlag GmbH and Co. KgaA.

Ganesh (2014). Conversion of carbon dioxide into methanol – a potential liquid fuel: fundamental challenges and opportunities (A Review). *Renewable and Sustainable Energy Reviews*.221–257.

J. Moulijn, M. Makkee and A.V. Diepen (2001). Chemical Process Technology, England: John Wiley & Sons Ltd.

K.M. Yu, I. Curcic, J. Gabriel and S.C. Tsang (2008). *Chem. Sus. Chem.* 1 (11).893–899.

L. Li, N. Zhao, W. Wei, and Y. Sun (2013). A review of research progress on CO2 capture, storage, and utilization in Chinese Academy of Sciences *Fuel*. 108.112–130.

Leung, Dennis Y.C., Giorgio Cand Mercedes, M. and Valer, M (2014). An Overview of Current Status of Carbon Dioxide Capture and Storage Technologies. *Renewable and Sustainable Energy Reviews*. 39. 426-443.

P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber, and T.E. Mu¨ller (2012). Worldwide innovations in the development of carbon capture technologies and the utilization of CO_2. *Energy Environ. Sci.* 5 (6). 7281–7305.

P. Viebahn, J. Nitsch, M. Fischedick, A. Esken, D. Schuwer, N. Supersberger, U. Zuberbuhler and O. Edenhofer (2007). Comparison of carbon capture and storage with renewable energy technologies regarding structural, economic, and ecological aspects in Germany, *Int. J. Greenhouse Gas Control* .1.121–133.

R. Stanger, T. Wall, R. Spörl, M. Paneru, S. Grathwohl, M. Weidmann, G. Scheffknecht, D. McDonald, K. Myöhänen, J. Ritvanen, S. Rahiala, T. Hyppänen, J. Mletzko, A. Kather, S. Santos, (2015). Oxyfuel combustion for CO_2 capture in power plants. *International Journal of Greenhouse Gas Control*.40.55–125.

Roadmap for the Future of CO2Chem and CCU, Spring (2012).

T. Kuramochi, A. Ramı´rez, W. Turkenburg and A. Faaij (2012). *Prog. Energy Combust. Sci.* 38 (1). 87–112.

UNIDO (2011). Technology roadmap: carbon capture and storage in industrial applications, United Nations Industrial Development Organization, Organisation for Economic Development & International Energy Agency.