

CO₂ Abatement by Methanol Production from Flue-Gas in Methanol Plant

A. K. Sayah, Sh. Hosseinabadi, M. Farazar

Abstract—This study investigates CO₂ mitigation by methanol synthesis from flue gas CO₂ and H₂ generation through water electrolysis. Electrolytic hydrogen generation is viable provided that the required electrical power is supplied from renewable energy resources; whereby power generation from renewable resources is yet commercial challenging. This approach contribute to zero-emission, moreover it produce oxygen which could be used as feedstock for chemical process. At ZPC, however, oxygen would be utilized through partial oxidation of methane in autothermal reactor (ATR); this makes ease the difficulties of O₂ delivery and marketing. On the other hand, onboard hydrogen storage and consumption; in methanol plant; make the project economically more competitive.

Keywords—Biomass, CO₂ abatement, flue gas recovery, renewable energy, sustainable development.

I. INTRODUCTION

COMBUSTION of fossil fuels such as oil, gas and coal are the main source of energy in today industry; and CO₂ exhausted from that is the major cause of global warming in today industry [1], [2]. As a result of the greenhouse-gas emissions (GHG), the average global surface temperature and sea level have increased by 0.4^{0C} and 15cm over the last century, respectively. The effect of GHG emissions on climate change is currently believed to be one of the most dangerous problems threatening human's life. And if any supplementary actions for GHG reduction are not taken in the near future, 40% of the species worldwide may be threatened with extinction [3].

Fossil fuels provide more than 80% of the world's total energy demands; the atmospheric CO₂ concentration will continue to rise in direct proportion to fossil fuels use, with significant consequences for global climate [4]. The necessity to achieve zero-emissions has attracted attention toward developing clean industries. A considerable reduction in CO₂ emission from fossil fuels could be obtained in three ways: Improving the energy efficiency of equipments; using renewable energy sources; development and deployment of-

carbon capture and storage (CCS) technologies [5], and converting CO₂ to other useful materials, for instance methanol.

The first method can't solve the problem thoroughly; and switch to other energy sources is not accessible in short term. The latter option, however, is more likely to be efficient since it makes use of the value in the waste CO₂ rather than to make another kind of "landfill" for it [6]. On the other hand, it can be applied on any source of flue gas in current industry.

Methanol synthesis from flue gas involves in combination of CO₂ and H₂ over CuO-ZnO based catalysts, according to equation (1). Hydrogen could be supplied through water electrolysis with renewable power supply or from biomass. Having lower production cost, hydrogen from biomass may appear to be more feasible, but it implicates in some CO₂ emission.

Like electricity, hydrogen is an 'energy carrier', which must be produced using energy from another source. It has an advantage over electricity, however, in that it can be stored more easily. Current interest in hydrogen stems from environmental and energy policy concerns including global climate change, local air quality, noise and security of energy supply, together with breakthrough in fuel cell technology [7]. It is also the lightest chemical element, and so has very low energy per unit volume. There are, however, some challenges for hydrogen utilization including: requirement of large installation because of low energy density, low controllability and endurance due to frequent fluctuations [8] and demand for infrastructure modification. Indeed, conversion of hydrogen and CO₂ to methanol is regards as an alternative method to use hydrogen energy more efficiently.

Despite the associated conversion efficiency, the conversion of gaseous hydrogen to liquid methanol results in a more convenient alternative energy carrier; it has the advantage of higher density for storage and transportation and can be handled by the existing infrastructure. Methanol can be used in the direct methanol fuel cells, where there is no need for onboard reformer, for the power industry, fuel grade methanol is clean and efficient alternative fuel for gas turbines. It can be mixed with conventional petrol [8].

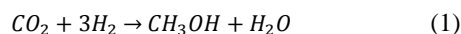
II. APPROACH

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

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steam reforming or partial oxidation of methane, catalytic conversion of syngas to crude methanol, according to equation (1) and (2) and rectifying crude-methanol in distillation unit to obtain high grade methanol.



Highest yield of methanol is obtained while stoichiometry number (SN), presented in equation (3) approaches 2.

$$SN = \frac{[H_2]-[CO_2]}{[CO]+[CO_2]} \quad (3)$$

However, introducing flue gas composition into equation (3) results in $\frac{H_2}{CO_2} \cong 3$, as quoted before [9], [10], [11].

In every methanol plant, large amount of CO₂ is produced from natural gas combustion and vented to atmosphere. To ensure a sustainable development it is necessary to achieve zero emissions. Capturing CO₂ from flue gas and its recycle to synthesis unit helps to reduce the level of climate-relevant emissions. [12] Table 1 shows specification of studied exhaust gas.

TABLE I
METHANOL PLANT EXHAUST-GAS SPECIFICATION

| Spec | unit | |
|------------------|---------------------|---------|
| Flow | Sm ³ /hr | 152,458 |
| Temp | °C | 141 |
| Pressure | bar | 1 |
| CO ₂ | Mol% | 10.74 |
| N ₂ | Mol% | 65.73 |
| O ₂ | Mol% | 1.53 |
| H ₂ O | Mol% | 21.18 |

Hydrogen can be produced from a variety of feed stocks; from fossil resources such as natural gas and coal, and from renewable resources such as biomass or water electrolysis with power input from renewable energy sources [13], [14], [15]. Fossil resources are off-consideration here as they associate with CO₂ emission.

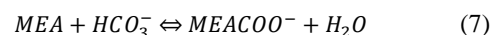
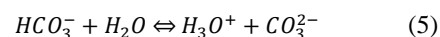
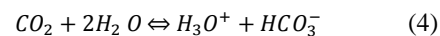
III. METHODOLOGY

Methanol synthesis from flue gas, is presumed to comprises 2 major principles in this study: Carbon capturing and electrolytic hydrogen production from renewable energy sources, and combining CO₂ and hydrogen in a conventional methanol synthesis unit.

A. CO₂ Capturing

Amine absorption is a proven technology for carbon dioxide recovery from flue gases. This method has been used by

former authors [16], [17], [18]. The reactions of MEA and CO₂ can be described by electrochemical reaction in the aqueous solution according to equations: 4-7.

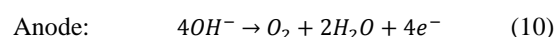
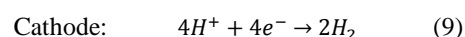
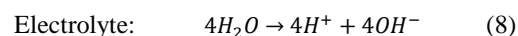


Flue gas is cooled and dehumidified, it then enters a separator. CO₂ rich flue gas then passes through an absorption column wherein it is contacted with monoethanolamine (MEA) in counter-current pattern.

The CO₂ is absorbed in MEA and leaves the column via its bottom, while the top product (N₂) leaves the tower and is vented to atmosphere. The bottom product (MEA) is fed into a stripping column and is separated by distillation. Several researchers have modeled and studied CO₂ capturing by MEA. Singh, D. found that the thermal energy requirement for a coal fired power of 400 MW is equal to 3.8 GJ/ton CO₂ [19]. Alie, C. found that the lowest energy requirement of 176 kJ/kmol CO₂ (4GJ/ton CO₂) can be achieved at lean solvent loading between .25-.3 mol CO₂/mol MEA [17]. Mohamad Abu-Zahra realized that energy equivalent of 3.3 GJ/ton CO₂ is required for solvent regeneration with 30 wt% [2]. Here we consider regeneration energy demand equal to 3.5 GJ/ton CO₂ due to higher MEA temperature. Therefore, 38.78GJ/hr energy is required for this process. The flue gas temperature is 141°C hence, total energy demand for CO₂ capturing can be supplied by heat recovery from exhaust gas. In addition, this energy could be supplied by medium pressure steam produced in boilers.

B. Water Electrolysis Unit

Water electrolysis is a process through which water is split into hydrogen and oxygen by application of electrical energy. Hydrogen, required for methanol synthesis, can be produced from splitting of water through various electrolytic processes. Alkaline, polymer electrolyte membrane (PEM), high temperature decomposition, photo-electrolysis (photolysis), photo-biological production (biophotolysis). However, amongst them, alkaline electrolysis and PEM are commercially available. PEM electrolysis is suitable for small capacities while alkaline have dominated high-capacity industrial market. Indeed alkaline electrolysis was adopted for hydrogen production in this study. Alkaline electrolysis uses an aqueous KOH solution as an electrolyte that usually circulates through the electrolytic cells [21], [22], [23]. The principle of alkaline electrolysis is presented in equation 7 and 8.



Sum: (11)

The produced H₂ and O₂ are transferred into storage tanks to be used later. O₂, however, is then conveyed to autothermal reactor (ATR) and contributes to the partial oxidation of methane (POX). Onsite consumption of oxygen lessens the difficulty of its market and dispatch.

Electricity costs are a major contributor to the overall cost of hydrogen. This accounts for nearly 80% of the cost of in electrolytic hydrogen using current state-of-the-art technology. Ideally, 39 kWh of electricity and 8.9 liters of water are required to produce 1 kg of hydrogen at 250C and 1 atmosphere pressure. A typical commercial electrolyzer system has lower efficiencies and corresponds to 48-60 kWh/kg. The US department of energy (DOE) has set a program long-term goal of delivered hydrogen costing \$2/kg to \$3/kg [20], [21].

Figure 1 shows hydrogen cost versus electricity costs, but takes into account only the cost of electricity used to split the water. The result demonstrate that to meet the DOE target of \$3.00/kg, electrolyzers with today's efficiencies would need to have access to electricity prices lower than \$.045-.055/kWh [20], [21].

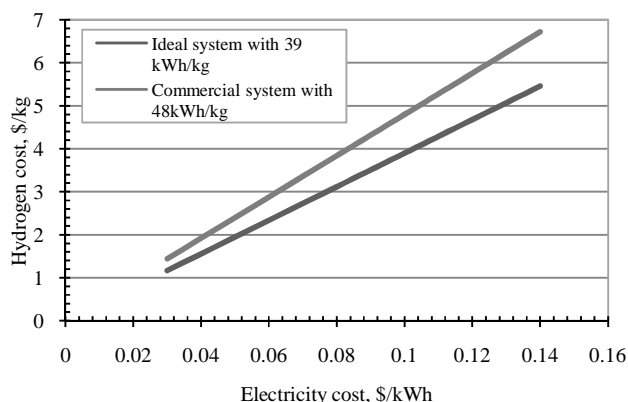


Fig. 1. Hydrogen cost vs. electricity (excluding other costs)

Considering today's electricity cost in Iran (.078\$/kWh) accompanying by available electrolytic technology, hydrogen production cost would be 4\$/kg.

C. Methanol Synthesis and Purification

Methanol synthesis unit at ZPC could be run over 110% of its normal capacity. The CuO-ZnO catalysts are selective to both CO and CO₂; indeed the recovered CO₂ can be introduced to former synthesis unit without any extra modification. In this unit the CO₂ stream will be mixed with hydrogen and pressurized to the required level to enter 2 shell and tube reactors called "water cooled", where the catalysts are filled inside the tubes while the shells are filled with water. The Δh_f released from methanol synthesis unit is delivered to water contained in shell. Warm water goes up through risers and enters the boiler to generate steam at 48 bar and 261^oC.

However, it is probably more efficient to design a new water-cooled reactor along with a boiler for synthesis unit. Generated steam could be fed to export steam line, utilized for

power generation in utility unit or used for supplying energy to CO₂ capturing unit. The product stream is cooled near dew-point and enters a flash-drum. Methanol product together with some impurities accumulates in liquid state in separator drum while unconverted gases are again recycled to process to enhance conversion factor of reactions. The distillation unit in ZPC could be operated over 115% load. Hence, there is no need to design a separate purification unit for extra methanol, produced.

D. Utility Unit

A utility unit of 200-254MW is assumed to generate renewable power for electrolytic hydrogen generation, considering 4.06-5.17kWh/Sm³ of hydrogen produced [14], [21].

IV. FEASIBILITY STUDY

Table 2 shows the expenditure for methanol production from flue gas. Designed natural gas intensity is defined equal to 860Sm³/ton methanol. Considering .069\$/m³ NG, the total material cost is evaluated 59.34\$ per ton methanol. However, 1ton methanol production from carbon capturing and electrolysis costs 19.48\$ for carbon and 476.76\$ for hydrogen, while ignoring conversion factor in catalytic reactors. This means that, to make the project feasible in economic aspects, electrolytic hydrogen cost needs to fall by a factor of 10 or even higher. In addition carbon capturing cost is rather high and need to fall by a factor of 2-3.

TABLE II
EXPENDITURE FOR METHANOL PRODUCTION FROM FLUE GAS

| Utility | Cost |
|---------------------------|--------------------------|
| Electrolysis | 48kWh/kg |
| Electricity | 0.078\$/kWh |
| Hydrogen | 3.74-4.68\$/kg |
| CO ₂ capturing | 40-60\$/ton ¹ |

V. CONCLUSION

Fossil fuels are the major source of CO₂ emission to the environment. Reducing the dependency of industry to fossil fuels and switch to other energy sources is not accessible until the next century. However, Carbon capturing and utilizing CO₂ as feedstock for producing other chemicals like methanol is a promising solution for making CO₂ balance in the environment.

Basically, methanol synthesis requires hydrogen in proportion of 3/1 with respect to CO₂. Hydrogen production from electrolysis has been investigated in this study. We found that today's electrolytic hydrogen, in considered location, costs between 3.74-4.68\$/kg which is rather expensive. However, flue gas has enough potential to provide energy demand for CO₂ capturing.

Although, Conventional methanol production from natural gas result in raw material cost equivalent to 59.34\$ per ton of methanol, but the peculiar low raw material cost comes from abandonment of gas resources and extra costs it implies in

environmental aspects and the depletion of natural resources have never and accounted in the price.

The carbon sequestration and electrolytic hydrogen via renewable resources are not still proven in commercial and economic terms; nonetheless, wide application of methanol as hydrogen carrier is likely to increase its price in the world. On the whole, accounting the environmental cost of fossil fuels, development of high-tech processes to drop the price sufficient for electrolytic hydrogen accompanied by burgeoning methanol market in future would make the process economically feasible.

National Renewable Energy Laboratory technical report NREL/TP-581-40605, September 2006. <http://www.osti.gov/bridge>.

- [21] "Hydrogen production cost estimate using water electrolysis," National renewable energy laboratory, September 2009. www.hydrogenenergy.gov/news_cost_goal.pdf

REFERENCES

- [1] F. Hasegawa, Sh. Yokoyama, K. Imou, "Methanol or ethanol produced from woody biomass: which is more advantageous? Bioresource-Technology," 101, S109-S111, 2010.
- [2] M. Abu-zahra, L. H. Schneiders, J.P.M. Niederer, P. H. M. Feron, G. F. Versteeg, et al., "CO₂ capture from power plants, part I. a parametric study of technical performance based on monoethanolamine," International journal of greenhouse gas control I. 37-46, 2007.
- [3] "IPCC fourth assessment report on climate change," www.ipcc.ch/publications_and_data/publications_and_data_reports.htm#1:2007.
- [4] M. E. Huntley, D. G. Redalje, "CO₂ mitigation and renewable oil from photosynthetic microbes, a new appraisal," Mitigation and Application Strategies for global change, 2006, www.drfriendly.tv/PDFs/-Huntley%2BRedalje200611.pdf
- [5] Jung-Ho wee. "Contribution of fuel cell systems to CO₂ emission reduction in their application fields," Renewable and Sustainable Energy Reviews, 14, pp 735-744, 2010.
- [6] "A new leading process for CO₂ mitigation," www.newenergyandfuel.com
- [7] "Prospects for hydrogen economy," parliamentary office of science and technology. October 2002, No.186, www.parliament.uk/post/home.htm
- [8] K. Hiraoka, "Prospects for a hydrogen-solar energy system," Translated from J Middle Eastern Stud 35(9), 2003. www.mesj.or.jp/~mesj_e/english/pub/english/-pdf/-mv29n022001p71.pdf, August 2005.
- [9] C.P. Galindo, O. Badr, "Renewable hydrogen utilization for the production methanol," Energy conversion and management, 48, pp 519-527, 2007.
- [10] M. Specht, A. Bandi, F. Staiss, "Comparison of CO₂ sources for synthesis of renewable methanol Studies on Surf Science and Catalyst," 14, pp 363-366, 1998.
- [11] Lurgi operating manual for Zagros Petrochemical Co.
- [12] M. Specht, A. Bandi, "The methanol cycle – sustainable supply of liquid fuels. Stuttgart, Germany: Centre for Solar Energy and Hydrogen Research (ZSW)," 1999, www.zsw-bw.de, January 2005.
- [13] D. Mignard, M. Sahibzada, J.M. Duthie, H.W. Whittington, "Methanol synthesis from flue-gas CO₂ and renewable electricity: a feasibility study," International Journal of Hydrogen Energy, 28, pp 455-464, 2003.
- [14] IEA Energy Technology Essentials, "Hydrogen production and distribution," 2007, www.iea.org/textbase/techno/-essentials.htm.
- [15] T. Riis, E. F. Hagen, P. J. S. Vie, O. Ulleberg, "Hydrogen production-Gaps and priorities," IEA Hydrogen Implementing Agreement (HIA) HIA-HCG-Production-2005-15-rev1-final.doc, www.bctia.org/files/-PDF/hydrogen_fuel_cells/Hydrogen_Production_Gaps_Priorities__IEA_2005.pdf
- [16] S. Freguia, G.T Rochelle, "modeling of CO₂ capture by aqueous Monoethanolamine," AIChE Journal, 49(7), 7, 1676-1686, 2003.
- [17] C. Alie, L. backham, E. Croiset, p. L. Douglas, "simulation of CO₂ capture using MEA scrubbing: a flow sheet decomposition method," Energy conversion and management. 46, 475-487, 2005.
- [18] L. Erik Oi, "Aspen Hysys simulation of CO₂ removal by amine absorption from a gas based power plant," Presented at SIMS2007 conference, Goteborg, October 30-31th 2007.
- [19] D. Singh, E. Croiset, P. L. Douglas, M. A. Douglas, "techno economic study of CO₂ capture from an existing coal-fired power plant: MEA scrubbing vs. O₂/CO₂ recycle combustion," Energy Converse Manage, 44, pp 3073-3091, 2003.
- [20] B. Kroposki, J. Levene, K. Harrison, P.K. Sen, F. Novachek, "Electrolysis: information and opportunities for electric power utilities,"