# CO<sub>2</sub> Abatement by Methanol Production from Flue-Gas in Methanol Plant

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**Abstract**—This study investigates  $CO_2$  mitigation by methanol synthesis from flue gas  $CO_2$  and  $H_2$  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  $O_2$  delivery and marketing. On the other hand, onboard hydrogen storage and consumption; in methanol plant; make the project economically more competitive.

*Keywords*—Biomass, CO<sub>2</sub> 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  $CO_2$  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  $CO_2$  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  $CO_2$ emission from fossil fuels could be obtained in three ways: Improving the energy efficiency of equipments; using renewable energy sources; development and deployment ofcarbon 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  $CO_2$  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  $CO_2$  and  $H_2$  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  $CO_2$ 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  $CO_2$  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.

$$CO_2 + 3H_2 \to CH_3OH + H_2O \tag{1}$$

$$CO + 2H_2 \to CH_3OH \tag{2}$$

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

$$SN = \frac{[H_2] - [CO_2]}{[CO] + [CO_2]}$$
(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  $CO_2$  is produced from natural gas combustion and vented to atmosphere. To ensure a sustainable development it is necessary to achieve zero emissions. Capturing  $CO_2$  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	Sm3/hr	152,458
Temp	<sup>0</sup> C	141
Pressure	bar	1
CO <sub>2</sub>	Mol%	10.74
$N_2$	Mol%	65.73
O <sub>2</sub>	Mol%	1.53
H <sub>2</sub> 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  $CO_2$  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  $CO_2$  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  $CO_2$  can be described by electrochemical reaction in the aqueous solution according to equations: 4-7.

 $CO_2 + 2H_2 \ 0 \Leftrightarrow H_3 O^+ + HCO_3^- \tag{4}$ 

$$HCO_3^- + H_2O \Leftrightarrow H_3O^+ + CO_3^{2-} \tag{5}$$

 $MEA + H_3O^+ \Leftrightarrow MEA^+ + H_2O \tag{6}$ 

$$MEA + HCO_3^- \Leftrightarrow MEACOO^- + H_2O \tag{7}$$

Flue gas is cooled and dehumidified, it then enters a separator.  $CO_2$  rich flue gas then passes through an absorption column wherein it is contacted with monoethanolamine (MEA) in counter-current pattern.

The CO<sub>2</sub> 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 CO<sub>2</sub> 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 CO<sub>2</sub> [19]. Alie, C. found that the lowest energy requirement of 176 kJ/kmol CO<sub>2</sub> (4GJ/ton CO<sub>2</sub>) can be achieved at lean solvent loading between .25-.3 mol CO<sub>2</sub>/mol MEA [17]. Mohamad Abu-Zahra realized that energy equivalent of 3.3 GJ/ton CO<sub>2</sub> is required for solvent regeneration with 30 wt% [2]. Here we consider regeneration energy demand equal to 3.5 GJ/ton CO<sub>2</sub> 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 CO<sub>2</sub> 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.

Electrolyte: 
$$4H_2 0 \rightarrow 4H^+ + 40H^-$$
 (8)

Cathode:  $4H^+ + 4e^- \rightarrow 2H_2$  (9)

Anode: 
$$40H^- \to 0_2 + 2H_20 + 4e^-$$
 (10)

Sum:

(11)

The produced  $H_2$  and  $O_2$  are transferred into storage tanks to be used later.  $O_2$ , 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, elecetrolyzers with today's efficiencies would need to have access to electricity prices lower than \$.045-.055/kWh [20], [21].



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 CO<sub>2</sub>; indeed the recovered CO<sub>2</sub> can be introduced to former synthesis unit without any extra modification. In this unit the CO<sub>2</sub> 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  $\Delta h_f$  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°C.

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  $CO_2$  capturing unit. The product stream is cooled near dewpoint 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/Sm<sup>3</sup> 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
CO2 capturing	40-60\$/ton <sup>1</sup>

## V.CONCLUSION

Fossil fuels are the major source of  $CO_2$  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  $CO_2$  as feedstock for producing other chemicals like methanol is a promising solution for making  $CO_2$  balance in the environment.

Basically, methanol synthesis requires hydrogen in proportion of 3/1 with respect to CO<sub>2</sub>. 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 CO<sub>2</sub> 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.

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