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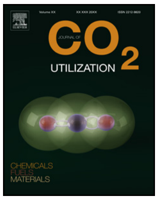

A model-based analysis of CO_2 utilization in methanol synthesis plant

Dia Milani [a], Rajab Khalilpour [a], Gholamreza Zahedi [b], Ali Abbas [a,*]

[a] *School of Chemical and Biomolecular Engineering, The University of Sydney, NSW 2006, Australia*
[b] *Ozone Solutions, Huntington, West Virginia Area, USA*

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ABSTRACT

Utilizing the greenhouse gas CO_2 as a feedstock in chemical processing could offer alternative solutions to long-term storage. Large-scale production of light hydrocarbons such as methanol (MeOH) is one of the predominant and sensible schemes for such utilization. This proposal will not only recycle the CO_2 gas within methanol synthesis process, but will also reduce the uptake of raw materials such as natural gas (NG) and reduce the greenhouse-gas (GHG) emissions of a comparable stand-alone NG-based methanol synthesis plant.

In this paper, a comprehensive model for CO_2 integration in NG-based methanol synthesis plant has been developed. The reformer product (syngas) is mixed with the high-purity CO_2 stream that comes out of power-plant carbon capture (PCC) process. It is found that this integration may reduce methane uptake by 25.6% and decrease the combined CO_2 emissions for both power-plant and MeOH-plant by 21.9%. The energy intensity for this integration is 33.45 $GJ_{th}/tonne_{MeOH}$ and 0.64 $GJ_{el}/tonne_{MeOH}$. The energy efficiency of this integration is 59% and the product to feed ratio is 2.27 $tonne_{MeOH}/tonne_{CH_4}$ higher than 1.69 $tonne_{MeOH}/tonne_{CH_4}$ calculated for a comparable standalone NG-based methanol synthesis plant with 68% efficiency.

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1. Introduction

Economic and population growth continue to be the most important factors behind increases in CO_2 emissions from fossil fuel combustion. The escalation of anthropogenic CO_2 emissions linked to global warming has attracted global efforts to find new and better ways of meeting the world's growing energy demand, while simultaneously reducing greenhouse-gas (GHG) emissions [1]. Despite a growing number of climate change mitigation initiatives and policies, global GHG emissions grew on average by 2.2% carbon dioxide equivalent (CO_2eq) per year from 2000 to 2010 compared to 1.3% CO_2eq per year from 1970 to 2000 [2]. Carbon dioxide emissions from fossil fuel combustion and industrial processes contributed about 78% of the total GHG emission increase from 1970 to 2010. In 2010 fossil fuel-related CO_2 emissions reached 32 (±2.7) Gt/y, and grew further by about 3% between 2010 and 2011 and by about 1–2% between 2011 and 2012 [2].

Large-scale carbon capture and sequestration (CCS) is considered as one of the effective emissions avoidance mechanisms. Other emissions avoidance mechanisms can also be achieved by either improving the energy efficiency of various industrial processes or shifting to non-fossil energy sources (renewable and nuclear). Traditionally, most of the world is heavily reliant on fossil fuel sources for their energy demand and trillions of dollars have already been invested in existing energy infrastructures. Shifting away from fossil fuel energy sources will require a huge investment in other resources and will also require long transitional periods. Employing CCS to reduce CO_2 emissions would allow continued use of fossil energy, while buying time to ease the transition to clean energy sources systematically. However, there is a strong debate on the feasibility of CCS in general and the high energy penalty imposed by such processes. This debate is more intensified on CO_2 sequestration part where the gas is arguably considered as a waste. Uncertainty is also associated with the eternity of the stored CO_2 and the high cost involved [3–6]. Conversely, CO_2 can be captured and utilized (CCU) as a feedstock or commodity which can be converted to a variety of commodity chemicals, fuels and building blocks for other products [7].

One of the transitional strategies is to use NG for power generation. Natural gas is the fastest growing primary energy source where the global consumption has increased from 118.4 trillion cubic metre (TCM) in 1993 to reach 185.7 TCM at the end of 2013 [8]. The geographical mismatch between most NG resources and markets usually involves higher handling and transportation costs in comparison with transportation of liquid

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[*] Corresponding author. Tel.: +61 2 9351 3002; fax: +61 2 9351 2854.
E-mail address: ali.abbas@sydney.edu.au (A. Abbas).

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Abbreviations and symbols

ASU	air separation unit
ATR	auto-thermal reforming
BAU	business as usual
CCS	carbon capture and sequestration
CCU	carbon capture and utilization
CO_{2eq}	carbon dioxide equivalent
FT-GTL	Fischer–Tropsch gas to liquid
GHG	greenhouse-gas
GTL	gas-to-liquid
KTPA	kilo-tonnes per annum
LHHW	Langmuir–Hinshelwood–Hougon–Watson kinetics
MEA	monoethanolamine
MeOH	methanol
MTBE	methyl tertiary-butyl ether
NG	natural gas
PCC	power-plant carbon capture
POX	partial oxidation
PP	power-plant
RWGS	reverse water–gas shift reaction
SMR	steam-methane reformer
S/M	steam to methane ratio
TCM	trillion cubic metre
WGS	water–gas shift reaction
E	activation energy (kJ/kmol)
k	pre-exponential factor
k_b	reversible reaction coefficient
k_f	forward reaction coefficient
M	stoichiometric number
r	rate of reaction
R	gas law constant (kJ/kmol K)
T	absolute temperature (K)

petroleum. Fischer–Tropsch gas to liquid (FT-GTL) is a well-developed technology that converts NG to a variety of liquid fuels [9]. The FT-GTL technology may provide a sensible solution to avoid the larger expense of gas transport by transforming this gas into liquid fuel which is easier to confine, control and transport. Global FT-GTL demand for NG is projected to increase from 4 billion m^3 in 2000 to 170 billion m^3 in 2030 [10]. One possible outcome of the GTL process is correlated with light hydrocarbon products which can be regarded as building blocks for more complex hydrocarbons such as gasoline and diesel.

Methanol (methyl alcohol, CH_3OH or MeOH) is the simplest liquid hydrocarbon that can be regarded as a fuel, a hydrogen carrier or a feedstock for producing more complex chemical compounds. Methanol production can be achieved by using fossil fuel sources (NG, coal) or renewable sources (biomass, waste wood, atmospheric CO_2). More than 80% of the MeOH produced worldwide is obtained from NG [11]. However, the process of producing MeOH from NG only is often associated with extremely high GHG emission. In common practice, each GJ of produced MeOH will emit between 17 and 72 kg of CO_2 excluding the CO_2 equivalent of CH_4 loses and the energy consumed in the NG extraction, purification and transport. Part of the NG input is contained in the energy content of the produced MeOH (18.82 kg_{carbon}/GJ_{MeOH}) and not resulting in CO_2 emissions while the other part is used as process fuel causing CO_2eq emissions [12]. Two possible pathways of reducing CO_2 emissions and producing “renewable methanol” are either by the syngas resulting from biomass gasification or by hydrogenation of carbon dioxide captured from flue gases of large industrial processes [13].

This paper presents and analyses the strategy of CO_2 utilization with methanol synthesis process to generate liquid methanol at lower energy and GHG emissions intensities. By blending the CO_2 outlet of a carbon capture plant retrofitted at the end of a coal-fired power plant (PP), this study shows how the NG feedstock can be reduced for the equivalent amount of produced MeOH. This practice will not only reduce the GHG emissions due to the extra NG portion, but also will have the CO_2 stream recycled in the methanol production chain at lower net energy intensity (GJ/$tonne_{MeOH}$). For this purpose, a 660 MW_{el} base case power plant is considered. The flue gas of this PP is treated in post-combustion carbon capture plant and the outlet CO_2 stream is blended with a syngas stream that is coming from an existing and detached steam-methane reforming (SMR) process (Fig. 1). These two streams enter a methanol synthesis reactor to generate MeOH.

In this paper, an assessment for CCS and CCU technologies is presented and the diverting point from CCS to CCU is identified. A comprehensive model of CO_2 utilization paired with methanol synthesis process using Aspen Plus V8.4 (Aspentech, USA) is developed in this work. The flowsheet parameters are explained and the operational conditions of the predominant unit operation are analysed. The mass and energy balance for the entire system is discussed and the results are compared with an equivalent standalone NG-based methanol synthesis plant. The overall efficiency, the energy intensity and the CO_2 emissions for both cases are highlighted and discussed.

2. Sequestration and/or utilization

The harvest of a typical carbon capture processes is a highly concentrated and high-pressurized CO_2 stream ready for sequestration procedures. Gaseous CO_2 is typically compressed to a pressure more than 110 bar in order to avoid two-phase flow regimes and increase the density of the CO_2 which makes it easier and less costly to transport. Depending on the storage option, several factors may affect CO_2 transportation and storage cost including the amount of CO_2, the transport distance, the storage medium (gas field, oil field, aquifer or ocean bed) and the depth of the storage. Among several CO_2 storage options, three major options can be named; geological, oceanic and chemical storage. Detailed analyses of the cost and benefits, advantages and disadvantages of these options can be found in literatures [3,14–16].

There is a growing recognition that CO_2 sequestration which treats CO_2 as a waste stream to be sequestered may not be the silver bullet for the reduction of GHG emissions. Alternatively, CO_2 can be viewed and utilized as a valuable feedstock or commodity. Historically, CO_2 has been directly used in many useful chemicals such as urea, dry ice and polycarbonates (Fig. 2), but this small-scale utilization is incomparable with the large-scale CO_2 production from fossil fuel combustions. Some of these products are commodity chemicals, fuels and building blocks for other products (Fig. 2). A productive utilization of CO_2 as a feedstock for liquid fuels may provide an attractive alternative over sequestration. This also would help to satisfy part of the increasing demand for conventional petroleum. Therefore, recycling CO_2 as a fuel feedstock may provide a reasonable opportunity to consume CO_2 at a scale proportionate with its production by conversion to liquid hydrocarbon fuels [7,17]. Multiple processes can be combined to utilize CO_2 with syngas, a mixture of hydrogen (H_2) and carbon monoxide (CO), including methanol synthesis reaction. The production of methanol from syngas is a mature process and there have been numerous studies into the synthesis and commercialization of methanol [11,18–20].

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