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Comparative energetic assessment of methanol production from CO_2: Chemical versus electrochemical process

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HIGHLIGHTS

- We model two emission-to-fuel processes which convert CO_2 to fuels.
- We optimize the heat exchanger networks for the two processes.
- We compare the two processes in terms of energy requirement and climate impact.
- The process based on CO_2 electrolysis is more energy efficient.
- Both of the processes can reduce CO_2 emissions if renewable energies are used.

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ABSTRACT

Emerging emission-to-liquid (eTL) technologies that produce liquid fuels from CO_2 are a possible solution for both the global issues of greenhouse gas emissions and fossil fuel depletion. Among those technologies, CO_2 hydrogenation and high-temperature CO_2 electrolysis are two promising options suitable for large-scale applications. In this study, two CO_2-to-methanol conversion processes, i.e., production of methanol by CO_2 hydrogenation and production of methanol based on high-temperature CO_2 electrolysis, are simulated using Aspen HYSYS. With Aspen Energy Analyzer, heat exchanger networks are optimized and minimal energy requirements are determined for the two different processes. The two processes are compared in terms of energy requirement and climate impact. It is found that the methanol production based on CO_2 electrolysis has an energy efficiency of 41%, almost double that of the CO_2 hydrogenation process provided that the required hydrogen is sourced from water electrolysis. The hydrogenation process produces more CO_2 when fossil fuel energy sources are used, but can result in more negative CO_2 emissions with renewable energies. The study reveals that both of the eTL processes can outperform the conventional fossil-fuel-based methanol production process in climate impacts as long as the renewable energy sources are implemented.

1. Introduction

Carbon dioxide (CO_2) is the main greenhouse gas responsible for the climate change all over the world. How to reduce CO_2 emissions is a main agenda in many countries and has received substantial research attention [1–4]. Emission-to-liquid (eTL) conversion is a promising technology to reduce carbon emissions as it directly consumes CO_2 as a reactant and at the same time produces useful liquid fuels compatible to the current energy infrastructure. Among various possible fuel products, methanol is of particular interest as it is an energy carrier that can be used for gasoline blending or direct methanol fuel cells [5,6]. In addition, it is a chemical feedstock for production of many valuable chemicals such as formaldehyde, acetic acid, methyl methacrylate, dimethyl terephthalate, methylamines, chloromethanes, dimethyl carbonate and methyl tertiary butyl ether [7]. It can also be transformed to ethylene and propylene via methanol-to-olefin (MTO) processes [8]. The current annual consumption of methanol is over 60 million metric tons globally, and it keeps growing [9]. However, almost all methanol produced worldwide is synthesized from fossil-fuel-based syngas, which is neither sustainable nor environmentally-friendly [10,11]. The eTL process kills two birds with one stone by enabling sustainable methanol production, and at the same time, reducing atmospheric CO_2 levels.

So far, the synthesis of methanol from CO_2 has been successfully demonstrated using photocatalytic, electrochemical and chemical (catalytic hydrogenation) methods. Though photocatalytic reduc-

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Nomenclature

A	kinetic model constant
B	kinetic model constant (J mol^{-1})
A_{cell}	total active area in SOEC stack (m^2)
ASR	mean area specific resistance of SOEC stack (Ω cm^2)
F	Faraday constant (96,485 C mol^{-1})
I	total current (A)
i	current density (A m^{-2})
K_{eq}	equilibrium constant
k	kinetic model constant as a function of A and B
LHV	lower heating value (J mol^{-1})
m	mass (kg)
N	number of moles of species (mol)
p	partial pressure (bar)
Q_{in}	heat input to the system (J)
R	molar gas constant (8.314 J mol^{-1} K^{-1})
r	reaction rate (mol kg_{cat}^{-1} s^{-1})
T	temperature (K)
V_N	mean Nernst potential (V)
V_{op}	average cell voltage during operation (V)
W	electrical power required by SOEC (W)
Greek letters	
η	energy efficiency
λ	stoichiometric ratio of syngas

tion of CO_2 is an attractive option as it allows for a direct use of solar energy, it is limited to lab-scale studies due to the sluggish kinetics and extremely low efficiency [12–14]. In contrast, CO_2 electrolysis in a high temperature solid oxide electrolytic cell (SOEC) and catalytic CO_2 hydrogenation show great potential for large-scale applications and thereby large-scale CO_2 consumption [15,16]. After decades of efforts in exploiting effective catalyst materials and developing advanced reactors, catalytic CO_2 hydrogenation has become technically competitive with the industrial production of methanol from syngas [17–20]. Different pilot plants have been constructed in Japan and Iceland to produce methanol from hydrogenation of CO_2 with renewable H_2 [20]. A recent techno-economic study revealed that the use of CO_2 hydrogenation for methanol production can be economically viable as long as the costs of raw materials, i.e., H_2 and captured CO_2, can be reduced [21]. On the other hand, R&D activity for high-temperature CO_2 electrolysis is accelerating [16]. One attractive feature of the electrochemical conversion of CO_2 is that it provides a possible solution to the storage of intermittent renewable electricity [22]. To date, substantial studies have been reported in various technical aspects of CO_2 electrolysis, including new electrocatalysts, reaction mechanisms, catalyst degradation, cell design and system design [23–28]. Despite significant technical advances in both of the technologies, there has been a lack of systematic comparison of different CO_2-to-methanol processes. Once technologically mature, there is an ambiguity in selection between the processes.

In this study, the two CO_2-to-methanol conversion processes, i.e., production of methanol by CO_2 hydrogenation and production of methanol based on high-temperature CO_2 electrolysis, are simulated and analysed using Aspen HYSYS. Using Aspen Energy Analyzer (AEA), heat exchanger networks (HEN) are optimized for both the processes, and their associated minimal energy requirements are determined. The two processes are finally compared in terms of energy requirement and climate impact. The results in this study will shed light on the further development of various eTL processes.

2. Methods

2.1. Process description

2.1.1. Methanol production from CO_2 hydrogenation

The process of methanol production from CO_2 hydrogenation is illustrated in Fig. 1(a), which consists of four main steps, i.e., CO_2 capture, H_2 production, methanol synthesis and methanol purification. The input streams to this process are flue gas (2 bar, 313 K) and water (1.01 bar, 298 K). In a global context, fossil-fuel-based power plants which are responsible for ~57% of the total CO_2 emissions are reported as the largest CO_2 emitter [29], and thus they are considered as the source of CO_2 in this study. Carbon capture process is firstly employed to separate CO_2 from flue gases from a thermal power plant. Substantial efforts have been made, particularly in recent years, to develop effective carbon capture technologies as a potentially immediate way to reduce the carbon intensity. The existing technologies for CO_2 separation and capture for power plants can be divided into three different categories, namely, post-combustion processes for a traditional coal-fired power plant, pre-combustion processes for gasification or reforming and oxy-fuel processes [30]. Post-combustion capture by liquid absorption using monoethanolamine (MEA) has been identified to be the most promising technology to date in terms of effectiveness and cost [31–33]. Water is here used as a source of H_2. With an electrolysis system, water is decomposed into stoichiometric amounts of H_2 and O_2. Compared to other available hydrogen production methods, water electrolysis has advantages of wide availability, flexibility and high purity of products. Though the high cost associated with the use of precious-metal catalysts remains an issue for the widespread application of this technology, it provides the best way for large-scale storage of intermittent renewable electricity. The produced H_2, together with the captured CO_2, are sent to a methanol synthesis unit for methanol production, which is normally operated in a temperature range of 493–543 K [13]. Following the methanol synthesis step, methanol purification is applied where a series of distillation columns are used to remove impurities from the methanol product. Fig. 1(b) shows our model layout.

2.1.2. Methanol production based on a high-temperature SOEC system

Fig. 2(a) schematically shows the process of methanol production based on a high-temperature SOEC system. Four steps are involved in this process, which are CO_2 capture, high-temperature electrolysis, methanol synthesis and methanol purification. Similar to the CO_2 hydrogenation process, water (1.01 bar, 298 K) and flue gas (2 bar, 313 K) are the input streams to the system. With a carbon capture unit, CO_2 is firstly captured from flue gases of a thermal power plant. The captured CO_2 is then sent to an SOEC system for syngas production together with water after being heated up to 1073 K (i.e., the operating temperature of the SOEC [26]). The resultant gas consisting of CO, CO_2 and H_2O is then passed to a methanol synthesis reactor for methanol generation. Methanol purification is finally performed to ensure the purity of the produced methanol. The corresponding Aspen HYSYS model is shown in Fig. 2(b).