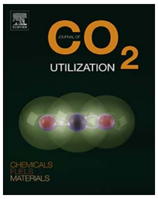
Journal of CO_2 Utilization 24 (2018) 555–563

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

journal homepage: www.elsevier.com/locate/jcou



Improving methanol synthesis from carbon-free H_2 and captured CO_2: A techno-economic and environmental evaluation

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ARTICLE INFO

Keywords:
Carbon capture, utilization and storage (CCUS) technologies
Methanol synthesis
Renewable hydrogen
Techno-economic assessments

ABSTRACT

Carbon Capture, Utilization and Storage (CCUS) is a widely discussed method that can help reduce carbon emissions of energy intensive plants. The goal of this work is to evaluate from a techno-economic point of view such a plant that uses captured CO_2 and renewable H_2 obtained in a carbon-free way and produces methanol (MeOH). The paper presents (i) the impact of using a higher conversion rate (30%) than in previously reported works, (ii) the use of a gas turbine and (iii) the addition of organic Rankine cycles (ORC) for reducing the energy consumption. The CCUS plant uses $142.6*10^6$ kg of CO_2 annually, reduces the amount of CO_2 emitted by $140*10^6$ kg/year and produces $100*10^6$ kg/year of MeOH. H_2 is obtained on site, using a water-electrolyzing unit; this consumes 130 MW_e and generates the necessary H_2 for the process. The proposed MeOH production plant is designed and simulated in ChemCAD. Total purchased equipment cost and operational costs are estimated using the process flow modeling. Key performance indicators (KPI) are calculated using the mass and energy balances obtained. The calculated capital costs are similar to previously reported results in the literature. A rigorous mass and energy integration of the plant resulted in an energetically fully self-sufficient MeOH plant, not taking into account the water-hydrolyzing unit. Electricity price is the main contributor for operational costs, either this should be halved, MeOH prices should increase two times or CO_2 prices should increase to 0.255 €/kg to make the process economically viable.

1. Introduction

Lowering atmospheric CO_2 levels is the main scope of the present climate treaties (ex. Kyoto Protocol, Paris Agreement). The energy-intensive industrial applications (ex. energy sector, metallurgy, cement production) generate the most carbon, lowering the amount of emitted CO_2 by these plants is the first step towards meeting the goals, set at these climate agreements. For the European Union (EU) by the year 2020, the goal is to lower Greenhouse Gas (GHG) emissions by 20% compared to the amount of emitted GHG in the year 1990. Although this goal was achieved already in 2016 [1], on the long run further significant drops are planned in CO_2 emissions. Carbon Capture and Storage (CCS) is a group of technologies that captures the CO_2 from the flue gasses of high CO_2 emitters and stores it in geological formations. Although the technology is considered feasible, the main technological concern is the injection phase with regard to high CO_2 pressures and leakages. In time, by dissolution and mineral trapping, the storage of CO_2 becomes more and more secure [2].

Carbon recycling resulted in the group of technologies called CCUS. The processes use CO_2 to synthesize widely used chemicals such as methane, methanol (MeOH), formic acid or dimethyl ether (DME) etc [3–5]. Using it as an energy storage material is also applicable, examples being power to methane, power to methanol or power to syngas concepts [6–8]. Methanol, a simple chemical compound is widely used in the chemical industry as a starting material, as a reactant or as fuel. Formaldehyde, methyl-tert butyl ether and acetic acid are the main products obtained from it. Nearly 1/3 of the global methanol production is transformed into formaldehyde [9]. MeOH is also used as fuel, in high purity or in designated concentrations blended with diesel. Engines fuelled by pure MeOH have higher efficiencies [10]. This offers a potential for the transportation sector. The primary disadvantage of MeOH is its toxicity towards humans. DME, the chemical product resulted by dehydration of MeOH is much more preferred as a fuel being less toxic and having a higher energy content. The global MeOH

Abbreviations: CCC, cold composite curve; CCS, carbon capture and storage; CCUS, carbon capture, utilization and storage; CEPCI, chemical engineering plant cost index; DME, dimethyl ether; EPC, equipment purchase cost; FOC, fixed operation cost; GM, gross margin; HCC, hot composite curve; HEN, heat exchanger network; KPI, key performance indicators; LHW, lower heating value; MeOH, methanol; NPV, net present value; ORC, organic rankine cycle; REV, revenue of the plant; RMC, raw materials cost; TFCC, total fixed capital cost; UOU, utilities and offsite units; VOC, variable operational cost

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https://doi.org/10.1016/j.jcou.2018.02.007
Received 23 November 2017; Received in revised form 8 January 2018; Accepted 16 February 2018
2212-9820/

production has been on the rise in the past years; installed production grew by a rate of 10% each year, with the actual production growth-rate not falling far behind at 7%, reaching $60*10^9$ kg in the year 2012 [9]. With the growing MeOH demand beside the classical technology, a lot of effort has been put in this alternative technology that has the advantage of also reducing the amount of carbon emitted in the atmosphere. Several papers have been published in the past years with promising results, as presented in the next section.

Guido Collodi et al. presents a techno-economic evaluation of upgrading a MeOH plant that uses natural gas as feedstock with a CCUS unit to produce a surplus of MeOH from the generated CO_2. According to the work, with the CCUS unit in place specific carbon emissions would decrease by 90% while the costs only show a low increase in capital costs (+20%) and in operational costs (+5%) [11]. Lundgren et al. investigated the introduction of a CCUS unit to the SSAB steel plant located in Sweden. According to the findings at the investigated steel plant $100–280*10^6$ kg of MeOH could be produced annually from the flue gasses depending on the selected scenario. The benefits of the work besides an increase in energetic efficiency of the plant are lower carbon emissions [12].

W. Y. Cheah et al. emphasizes on the importance of bioconversion via photosynthesis. The review focuses on carbon sequestration by terrestrial plants, microalgae and microorganisms. Although from an environmental perspective the technologies presented here are more favorable then CCUS technologies, biochemical processes have a significantly lower efficiency rates due to the nature of biological systems [13]. Karakas et al. verified the techno-economic measures of a power-to-methanol technology in the case of a lignite-fired power plant. Results show, that the major contributor to the operational costs of the plant is the electricity price. Since this can vary from country to country, the proposed plant has a different profitability in Greece and Germany [6].

Bouallou et al. presents a CCUS plant that consists of CO_2 absorption unit that captures carbon from a coal power plants' flue gasses, a water hydrolyzing unit to produce H_2 and the MeOH synthesis and purification unit. Although it presents an entire CCUS plant, the work focuses on the CO_2 capture and MeOH synthesis part, using the kinetics of Vanden Busche and Froment [14]. A good heat integration and the introduction of ORCs leed to a higher energetic efficiency of the plant [15]. A. A. Kiss et al. presents a MeOH synthesis route focusing on the technological parameters. It uses H_2 from chlorine production, the wet H_2 stream being the strong point of the proposed technology. Beside the several sensitivity analysis performed to find the optimal operating conditions, the work also presents a detailed description of the kinetics used for the hydrogenation of CO_2 [16]. M. Pérez-Fortes et al. proposed a CCUS plant that uses the CO_2 generated by a pulverized coal power plant and produces MeOH. The techno-economic evaluation showed that although the proposed plant would reduce carbon emissions, the technology wouldn't be cost-effective in the present economic situation, H_2 price should decrease, MeOH price would have to increase 2 times or a high carbon tax would have to be introduced for the CCUS to be profitable [9].

In the present paper, the techno-economic indicators of a MeOH CCUS plant are evaluated, with the following key specifications: (i) 30% conversion rate for the CO_2 in the reactor and the addition of a (ii) gas turbine and (iii) several ORCs for reducing the ancillary energy consumption. Purified CO_2 is provided from the flue gasses of energy intensive plant, H_2 is obtained in a carbon-free way (water electrolysis run by electricity from renewable sources). The catalytic process uses $Cu/ZnO/Al_2O_3$, a commercially available catalyst and the kinetics found in the literature [17]. The plant is designed for an annual production of $100*10^6$ kg of MeOH, using ChemCAD process simulator. Although, a fully self-sufficient MeOH plant is obtained, that results in a much more energy efficient CCUS plant then previously reported, because of the high energy consumption for H_2 production, the plant is not financially viable.

2. Methanol production processes

The conventional MeOH production route is by the Fischer-Tropsch process where synthesis gas (or syngas, a mixture of H_2, CO and CO_2) reacts on the surface of the catalyst according to Eq. (1):

$$CO + 2H_2 \leftrightarrow CH_3OH \quad \Delta H_{298K} = -\ 90.77\ \text{kJ/mol} \tag{1}$$

The reaction is an equilibrium reaction; to shift the equilibrium towards the formation of MeOH high pressure (> 5 MPa) and medium to high, constant temperature has to be maintained. The main problem in this case is the heat generated, the reaction being highly exothermic. The excess heat has to be removed to avoid the formation of side products (ex: CO) and catalyst sintering. In the European industry, syngas is obtained two ways, by (i) steam reforming of natural gas and by (ii) partial oxidation (gasification) of residual oil, coal, lignite or other solid fuels. According to the findings of [9] in the European industry the feed-stock ratio is 3:7 natural gas to residual fuel oil and the price for 1000 kg of raw material is about 345 €. The associated emissions are 760 kg of CO_2 [9].

In the case when methanol is produced from CO_2 and H_2 the synthesis can go by two ways: first by a one-step reaction, Eq. (3) or by a two-step reaction, Eqs. (2) and (1):

$$CO_2 + H_2 \rightarrow CO + H_2O \quad \Delta H_{298K} = +\ 41.21\ \text{kJ/mol} \tag{2}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad \Delta H_{298K} = -\ 49.16\ \text{kJ/mol} \tag{3}$$

Both MeOH forming reactions are highly exothermic, hence the importance of heat removal from the reactor in this case, too. The formation of CO is an endothermic one, this reaction is favored as the temperature increases. CO_2 hydrogenation reaction can also be used for the synthesis of synthetic natural gas (SNG) or formic acid however the synthesis of MeOH is more developed with a plant running in Iceland [18]. When compared to SNG, the transportation and storage of liquid fuel is cheaper making MeOH more desirable. Feeding it into the national gas grid, can alleviate this problem [19]. A similar application can be used in the case of MeOH, by using it as a storage of electrical power [20,21] during low electricity consumption rates in the national grid and recovering the energy using fuel cells when there is a high demand. In the case of formic acid the lack of technological maturity posses a great disadvantage in applying the technology [4].

3. Simulation of methanol production process from captured CO_2 and renewable H_2

In this section, the main parameters of the process are presented for the production of high-purity MeOH from captured CO_2. The process was simulated in ChemCAD 6.3, using the UNIFAC K-value model, that was recommended for the selected components (H_2, CO, CO_2, MeOH, H_2O, DME) and operating conditions. In the case of the distillation column a Regular VLE model was chosen, as recommended by the program. W.J. Shen et al. [22] did a full investigation on the behavior of a system containing CO, CO_2, MeOH and H_2. According to his calculations, in the pressure range of 1 and 9 MPa the MeOH yield increases significantly, while the CO yield decreases. In the temperature range of 220 °C and 320 °C with the increase of the temperature MeOH yield drops, whereas the CO yield increases. Using his data, a trade-off has to be chosen between the two equilibrium data and operating costs, as high operating pressures lead to an increase in capital and operational costs.

Graaf et al. [23] compared several chemical equilibrium models for the CO-CO_2-H_2 system using an extensive literature survey consisting of more than 300 experimental data points. The obtained model, although more precise then previously reported ones is too complex. Hence, the equilibrium data used by A. A. Kiss et al. [16] was selected as the difference between the two models is very low.