



# Model-based analysis of CO<sub>2</sub> revalorization for di-methyl ether synthesis driven by solar catalytic reforming



Minh Tri Luu<sup>a</sup>, Dia Milani<sup>a</sup>, Manish Sharma<sup>a</sup>, Joseph Zeaiter<sup>b</sup>, Ali Abbas<sup>a,\*</sup>

<sup>a</sup> School of Chemical and Biomolecular Engineering, The University of Sydney, NSW 2006, Australia

<sup>b</sup> Department of Chemical and Petroleum Engineering, American University of Beirut, Lebanon

## HIGHLIGHTS

- Solar energy applied for synthesis of di-methyl ether via dry methane reforming.
- Concentrated solar energy at receiver reaction zone for syngas generation.
- H<sub>2</sub>/CO molar ratio of '1' is maintained via two alternative processing routes.
- Assessed three days of operation under different insolation levels.
- Improvements of 18.7%, 32.2% and 20% for methane, energy and CO<sub>2</sub> emission intensities.

## ARTICLE INFO

### Article history:

Received 14 December 2015

Received in revised form 28 February 2016

Accepted 28 April 2016

### Keywords:

Carbon dioxide utilization

Solar reforming

Dry methane reforming

Syngas

Di-methyl ether

Concentrated solar power

## ABSTRACT

The application of solar energy is investigated for the synthesis of di-methyl ether (DME) in a solar irradiated dry methane reformer (DMR). Solar radiations are concentrated onto a receiver and distributed to the reaction zone to provide necessary energy for syngas (CO and H<sub>2</sub>) generation. In order to maintain a H<sub>2</sub>/CO molar ratio of '1', as required in DME synthesis, the produced syngas is processed via two alternative routes: solar reformer coupled in parallel with a non-solar reformer (SoR-NSoR) and solar reformer integrated with a water-gas shift reactor (SoR-WGS). It is found that steam methane reforming (SMR) is the most suitable methodology when coupled with a solar reformer due to high H<sub>2</sub> content in the SMR syngas. Further performance analysis is conducted by simulating three days of operation under different insolation levels (high, medium and low irradiances). The simulation results showed that the SoR-WGS configuration produces the highest improvements of 18.7%, 32.2% and 20% in terms of methane, energy and CO<sub>2</sub> emission intensity respectively. This enhanced process performance originates from the exothermic nature of the WGS process which helps in controlling the overall syngas composition, whereas the SoR-NSoR requires fossil based thermal energy to drive the NSoR process to similar control targets. This promising improvement of all metrics in SoR-WGS may stimulate in-depth techno-economic feasibility of this unique solar integration for DME and other synthetic fuels production.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Hydrogen economy is regarded as a viable option for delivering high-quality energy services in a wide range of applications [1]. It

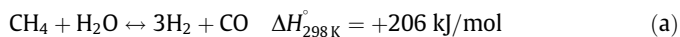
remains clean, safe and sustainable when process intensification and utilization of renewables are maintained [2]. Technically, hydrogen can be produced from a variety of gaseous, liquid, and solid feedstock including fossil fuels (i.e. natural gas, oil and coal) as well as renewables (i.e. biomass and water) [3]. However, hydrogen can only be considered as a clean fuel of the future when entirely produced from renewable or carbon-neutral energy sources such as sunlight, wind, hydropower or nuclear energy [4]. Most of the hydrogen produced worldwide is currently sourced from fossil fuels employing principal methods of steam methane reforming (SMR) (reaction (a)). Methane (CH<sub>4</sub>) is the primary component in natural gas (NG) generated in landfills or from coal

*Abbreviations:* CSP, concentrated solar power; DIVRR, directly irradiated volumetric receiver-reactor; DMR, dry methane reforming; DNI, direct normal irradiance; IIR, indirectly irradiated receiver; IIR reactor, indirectly irradiated reactor; SMR, steam methane reforming; SoP, solar penetration; SoR-NSoR, solar reformer integrated with non-solar reformer; SoR-WGS, solar reformer integrated with water-gas shift reactor.

\* Corresponding author.

E-mail address: [ali.abbas@sydney.edu.au](mailto:ali.abbas@sydney.edu.au) (A. Abbas).

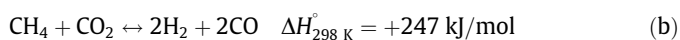
seam gas. The catalytic steam reforming of CH<sub>4</sub> (and other hydrocarbons) is estimated to provide approximately 95% of the world's industrial hydrogen production [5].



Depending on the feed composition and the adopted reforming method, the produced hydrogen (H<sub>2</sub>) and carbon monoxide (CO) are mixed at different ratios to produce synthetic gas (syngas). Other impurities and by-products such as CH<sub>4</sub>, H<sub>2</sub>O, CO<sub>2</sub>, H<sub>2</sub>S and inert gases may also be present. The produced hydrogen has to be separated from the syngas and purified in order to be used as a clean energy source. One practical solution, which is dependent on the syngas composition, is to extract excess H<sub>2</sub> (when available) in order to reach a specific H<sub>2</sub>/CO ratio desired for the production of synthetic liquid fuels such as methanol (MeOH) or di-methyl ether (DME). This practice satisfactorily addresses the sustainable production of hydrogen while diverting the carbon into chain liquid fuels. Reusing and recycling CO<sub>2</sub> in the process of synthetic fuel production would add value to these chemicals and reduce the uptake from the fossil-based natural resources [6] which is the principal of another conceptual framework known as “methanol economy” [7]. This concept can be further empowered by capturing large CO<sub>2</sub> emissions from power plants and other process industries to be converted and utilized as a feedstock for a wide variety of fuels and petrochemicals [8,9]. This approach is often known-as carbon capture and utilization (CCU).

### 1.1. Solar integrated di-methyl ether synthesis

Currently, the main environmental benefit of CCU is that it helps to reduce fossil fuel usage by utilizing CO<sub>2</sub> as a second carbon source [10]. The primary liquid fuels such as MeOH and DME are attractive hydrogen carriers and may constitute the building blocks for higher hydrocarbons synthesis. In fact, DME production might arguably be a preferred option attributed to its ability to accept syngas under various compositions [11], while MeOH requires a syngas composition with a predetermined H<sub>2</sub>/CO ratio. Production of DME based on CCU starts with the preparation of syngas in dry methane reforming reactor (DMR) (reaction (b)) followed by simultaneous MeOH synthesis and dehydration step in one separate reactor [7]. This route is known as DMR–DME which is emerging as a more sustainable DME synthesis process. This is because the DMR–DME route can utilize CO<sub>2</sub> as a second carbon feedstock, thus reducing the reliance on fossil fuel for carbon source. In addition, the syngas produced by the DMR unit has a molar ratio of 1 (i.e. H<sub>2</sub>/CO = 1) which is optimum for DME synthesis. The operation of DMR unit is conventionally driven by fossil fuels. Sourcing the required thermal energy from fossil fuels will undermine the sustainability of the DMR–DME route. It is estimated that the reformer duty (including the preheater and catalytic reactions) in DMR (reaction (b)) counts for approximately 55% of the total energy demand for the entire DME synthesis process [11,12].

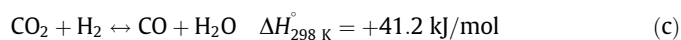


In order to further enhance the sustainability of the DMR–DME process, utilization of solar thermal energy for the DMR step becomes a subject of primary technological interest. As the reforming temperature range usually exceeds 800 °C, solar contribution is only achievable via sun-tracking concentrated solar power (CSP) collectors [13] (Fig. 1). If solar heat is effectively utilized for the preparation of syngas for DME synthesis, a considerable reduction of fossil fuel uptake will be achieved. In addition, the product syngas will contain solar energy embodied in the chemical form at approximately 26% for reaction (a) and 31% for reaction (b)

respectively (LHV basis and assuming water vapor) [14]. Overall, the integration of solar thermal and DMR–DME yields two desirable outcomes: (1) utilization of captured CO<sub>2</sub> as part of the carbon feedstock, (2) utilization of carbon-neutral solar energy. The former offers reduction in fossil fuel used as raw feed, while the latter reduces the thermal energy demanded from fossil fuel to drive the DMR step. Thus, the proposed approach for production of DME is more sustainable compared to conventional DME production (e.g. auto-thermal-reforming based) attributed to the reduction of fossil fuel consumption and CO<sub>2</sub> emission.

However, to the best of our knowledge, few studies have focused on the solar integrated DMR–DME process. Most solar DMR studies are at experimental and model validation levels [5,16–19]. As a result, literature studies often either focus on the solar-assisted DMR or DMR–DME respectively, but not the integration of the two parts [5,20–24]. Yu et al. [20] performed experimental study on DMR reaction in a tubular and semi-reactors heated by a solar dish system. In that study, Yu and co-authors found that increasing the direct normal irradiance (DNI) aids to enhance methane conversion. From the integration with DME synthesis perspective, this finding implies there will be unconverted methane in the syngas which should be recovered before the DME synthesis step. Vakili et al. [21] mathematically investigated a novel concept of energy saving by coupling the exothermic (DME synthesis) and endothermic (dehydrogenation of cyclohexane to benzene) reactions in one reactor. Further enhancement in the sustainability aspect of that study can be done by utilizing solar energy in the syngas preparation step (i.e. before the DME synthesis).

Studies about the integration aspect of the solar assisted DMR–DME process are vital for understanding and overcoming operational challenges, particularly for the transient nature of solar energy. For example, one typical requirement for optimum DME synthesis is the syngas should have a ratio of 1, i.e. H<sub>2</sub>/CO = 1 [25]. However, one of the intrinsic features of the DMR reaction is that it often fails to deliver that optimum ratio due to the acceleration of the reverse water-gas shift (RWGS) (reaction (c)) [5,19]. Thus, some of the produced H<sub>2</sub> is used to convert the excess CO<sub>2</sub> to CO, resulting in deficiency in H<sub>2</sub> in the syngas. From the syngas quality perspective, the presence of excess CO<sub>2</sub> is undesirable because it reduces the H<sub>2</sub>/CO ratio. On the other hand, if one considers the catalyst stability aspect of DMR system, excess CO<sub>2</sub> can help to suppress the solid-carbon formation [26] and endure catalyst life. Al-Ali et al. [19] performed experiments on solar cracking of methane using DMR in a contact bubble reactor containing suspended Ni/Al<sub>2</sub>O<sub>3</sub> catalysts and observed the opposite trends between solid-carbon formation and syngas ratio. Nikoo and Amin [27] performed thermodynamic analysis for DMR reaction and found that feeding excess CO<sub>2</sub> results in less solid carbon formation.



Another potential operational challenge is the intermittent nature of solar energy. It was found that fluctuations in DNI leads to variations in the conversion percentage of methane [20]. The aforementioned operational challenges leave uncertainties about how one could stabilize the operating performance of the integrated DME synthesis process when there are: (i) deficiency in H<sub>2</sub> in the syngas; (ii) fluctuation in methane conversion.

In this paper, we analyze the technical viability of solar integrated DMR–DME synthesis, by evaluating the environmental and process performance compared to a conventional process. Due to the solar DNI fluctuations, two process configurations are proposed in an attempt to control the operation of the syngas production step within the DME plant and to ensure an optimum

Download English Version:

<https://daneshyari.com/en/article/6682843>

Download Persian Version:

<https://daneshyari.com/article/6682843>

[Daneshyari.com](https://daneshyari.com)