



Oxy-fuel combustion based enhancement of the tri-reforming coupled methanol production process for CO₂ valorization

Abhishek Dwivedi^a, Ravindra Gudi^{a,*}, Pratim Biswas^b

^a Department of Chemical Engineering, Indian Institute of Technology, Powai, Mumbai, 400 076, India

^b Department of Energy, Environmental & Chemical Engineering, Washington University in St. Louis, St. Louis, MO, 63130, USA



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ABSTRACT

Capture and conversion of carbon dioxide from fossil fuel power generation systems is an important consideration. Tri-reforming of combustion exhausts (i.e. flue gas) with methane, which avoids the capture step, so as to produce synthesis gas for methanol production, has been proposed as a viable CO₂ valorization alternative for conventional air-combustion systems. However, the presence of nitrogen that is not a reactive component results in increased reactor sizes and decreased efficacy of the tri-reforming based process. In this paper, we explore the use of tri-reforming with an oxy-fuel combustion process, where the nitrogen content of the combustion exhaust gas is considerably reduced, and therefore a carbon dioxide enriched feed is utilized for the tri-reforming coupled methanol production process. Also, to support the oxy-fuel combustion process, we propose utilization of water electrolysis as an oxygen source, while also utilizing the generated hydrogen in the downstream methanol production. The main contributions of this paper are therefore (i) the proposition of combining oxy-fuel combustion with the tri-reforming coupled methanol production process to mitigate the above drawback, and (ii) utilization of water electrolysis as a source of oxygen and an evaluation of the impact of the generated hydrogen on the CO₂ valorization potential of the process. These two propositions have been implemented as process improvements on the conventional tri-reforming coupled methanol process. The resultant processes have been simulated using Aspen Plus V8.4, optimized and compared in this paper to justify their efficacy.

1. Introduction

Given the recent focus on greenhouse gas (GHG) mitigation with particular emphasis on CO₂ management, carbon capture and sequestration has already been receiving wide attention. Recently, research has also been gaining momentum in the area of CO₂ valorization [1,2]. However, most of the CO₂ valorization approaches, when applied to flue gases of fossil fuel based power plants, require a CO₂ capture based pre-treatment step. The amount of energy required in this pre-treatment step is as high as one-fifth of the total power output of a typical coal fired power plant [3]. However, the tri-reforming process does not require any pre-separation steps and thus is suitable for direct application on existing facilities such as power plants [4].

The tri-reforming process as proposed by Song [5] and Song [6], utilizes CO₂, H₂O and O₂ along with methane to convert a mixture of combustion exhaust gases and methane directly to synthesis gas. The process involves three major reactions (i) dry reforming of methane, (ii) steam reforming of methane, and (iii) partial oxidation of methane. The utilization of oxygen content of flue gas in the process leads to a number

of advantages such as (i) mitigation of carbon formation on the reforming catalyst resulting in increased catalyst life [3] and (ii) increase in energy efficiency of the process due to in-situ heat generation caused by exothermic POX reaction [3,7]. Minutillo and Perna [8] proposed utilization of tri-reformer generated synthesis gas in the downstream process to produce methanol. They also suggested recovery of heat from synthesis gas produced in the tri-reforming process to generate high pressure steam that can be utilized to improve efficiency of the overall process. Halmann and Steinfeld [9] utilized steam and air inputs along with methane to valorize coal fired power plant based flue gas to synthesis gas. They explored the possibilities of methanol, urea, ammonia and hydrogen production via tri-reformer synthesis gas and found them to be economically viable. Experimental studies have also been conducted on the tri-reforming process. Song and Pan [3] utilized Ni based catalysts to perform the tri-reforming process at atmospheric pressure and high temperature (800–850 °C) to obtain high methane and CO₂ conversions while generating synthesis gas in the optimal H₂/CO range of 1.5–2.0 and avoiding the menace of catalyst carbon formation. Another experimental study was conducted by Ren et al. [10]

* Corresponding author.

E-mail address: ravigudi@iitb.ac.in (R. Gudi).

which tested the tri-reforming process at higher pressures (up to 10 atm) and demonstrated that the results (CH₄/CO₂ conversions and synthesis gas H₂/CO ratio) were quite close to those obtained from thermodynamic equilibrium. Zhang et al. [11] designed and optimized a tri-reforming coupled methanol production process. Dwivedi et al. [12] introduced a steam input coupled water separation step (SWS) to the process as an improvement. Other co-reactants have also been attempted in research efforts for CO₂ valorization. Van-Dal and Bouallou [13] conducted a simulation study which involved direct hydrogenation of CO₂ (captured from flue gases generated by a typical coal fired power plant) by utilizing hydrogen generated from electrolysis of water via carbon free electricity.

A majority of the research on valorization of carbon dioxide has been on conventional air-combustion systems. However, the presence of large volumes of nitrogen in flue gas results in increased size of reactors and added cost of the overall valorization process [12]. Also, it reduces the efficacy of the tri-reforming coupled methanol production process in a number of ways, viz. (i) reduction of partial pressure of reacting components in the tri-reforming process and the downstream process which utilize the produced synthesis gas, (ii) higher recycle requirements in the process, (iii) increased reactor sizes that significantly contribute to already high capital costs of the process, especially for the tri-reforming process which is typically favoured at high temperature and lower pressure (Ex: 850 °C/1 atm), (iv) requirement of higher tri-reformer pressures to limit reactor size leading to decreased component conversions, lower syn-gas production, and resultant reduction in process efficacy [12,14], and (v) increased purge requirements that lead to increased emissions of valuable products. It is thus important to note that efficient CO₂ valorization applications may require a reduction in the nitrogen content of feed flue gas. On the other hand, oxy-fuel combustion process, is an alternative process which has a particular significance in carbon sequestration and other CO₂ capture based approaches. This is because, oxy-fuel combustion process utilizes enriched oxygen (in place of air) for fuel combustion [15,16]. This in turn brings about a significant reduction in the nitrogen content of the flue gas which leads to a number of advantages such as (i) reduction in flue gas volume and increase in CO₂ concentration which leads to easier CO₂ capture [17,18], (ii) decrease in flue gas volume also allows for easier removal of pollutants such as SO_x, NO_x, particulates [15], (iii) NO_x production is reduced [19], and (iv) increased fuel combustion efficiency [19]. Although oxy-combustion has been shown to help in lowering the CO₂ capture cost, this latter cost could still be quite significant for a capture and sequestration approach. Thus, it could be postulated that the nitrogen deficient, CO₂, oxygen and water containing oxy-fuel combustion based flue gas is more suited for valorization (rather than capture and sequestration) and is perhaps a suitable candidate for the tri-reforming process. Also, note that, though it has not been considered in this paper, coal water slurry containing petrochemicals (CWSPs) based on oil and coal processing wastes can be considered to be viable alternatives to coal, as they have been reported to contribute towards huge fuel cost savings [20] and in substantial reduction of SO_x/NO_x emissions [21]. Also, similar to the utilization of rapeseed oil in waste derived coal water slurry (CWS) to enhance its combustion and ignition characteristics [22], environmental, economic and energy performance of CWSPs can also be manipulated further using other plant based custom additives such as palm oil, olive oil et cetera [23].

In this paper, we analyze various alternate routes for CO₂ valorization by considering a judicious combination of the individual routes mentioned above. It is important to note that, in a typical coal fired power plant, utilization of oxy-fuel combustion process reduces the nitrogen content of the flue gas from 70.70% to 5.25% by volume (Table 1). Thus, in the quest for alternate and efficient valorization routes, we first propose coupling of the oxy-fuel combustion process with the tri-reforming + methanol production process. As discussed earlier, this also avoids the energy expenditure in the CO₂ capture step

Table 1
Flue gas compositions from a coal fired power plant operated in air-fuel combustion and oxy-fuel combustion (with 1% combustion air leakage) mode [17].

| Species | Volume % (Air-fuel combustion based power plant) (Yan [17]) | Mole % (Air-fuel combustion based power plant) (Used in simulation) | Volume % (Oxy-fuel combustion based power plant) (Yan [17]) | Mole % (Oxy-fuel combustion based power plant) (Used in simulation) |
|------------------|--|--|--|--|
| N ₂ | 70.70 | 70.70 | 5.2471 | 5.2471 |
| O ₂ | 4.29 | 4.29 | 3.0387 | 3.0387 |
| SO ₂ | 0.02 | 0.00 | 0.1376 | 0 |
| CO ₂ | 13.32 | 13.32 | 84.4560 | 84.456 |
| H ₂ O | 10.83 | 10.83 | 6.6511 | 6.6511 |
| Ar | 0.84 | 0.86 | 0.2415 | 0.4401 |
| CO | 0 | 0 | 0.1670 | 0.167 |
| NO _x | 0 | 0 | 0.0610 | 0 |

necessary for conventional CO₂ capture based valorization approaches. Further, we propose to generate the O₂ required for the oxy-combustion step through the water electrolysis step and look for routes to use the hydrogen generated in the same. Unlike, what has been suggested in the work of Van-Dal and Bouallou [13], we propose to divert the H₂ generated in the electrolysis, to the downstream methanol production step. It is noteworthy that the work of Van-Dal and Bouallou [13], used H₂ as a co-reactant with captured CO₂, and treated the O₂ as a revenue stream. We demonstrate the improvements of the resulting flowsheet in terms of two new metrics that measure the profit generating potential and the CO₂ valorization potential of the process.

The structure of the paper is as follows: Section 2 contains the process flowsheet description for the base case of conventional tri-reforming coupled with methanol production process. Section 3 introduces the methodologies adopted for the flowsheet modeling and the comparison cases for the suggested improvements. Section 4 introduces the two metrics viz. Gross Margin (GM) and Net Percentage of CO₂ Valorized (NPCV), and then presents the key improvements that result, and the discussions associated with these results. Section 5 concludes and summarizes the paper while exploring possible future work avenues in this direction.

2. Process flowsheet description

In this section we present the base case flowsheet for the tri-reforming coupled methanol production process:

Dwivedi et al. [12] developed the steam input coupled water separation step (SWS) enabled tri-reforming coupled methanol production process (Fig. 1). This process has been represented in this paper as process A, where air-fuel combustion based flue gas (Table 1) has been utilized as feed. The flowrate of the feed flue gas has been assumed to be 1000 kmol/h [11,12]. Note that, since SO_x and NO_x in the flue gas act as non-reacting inerts in the simulation, their content in the flue gas is replaced by equivalent amount of Argon for brevity (Table 1).

As shown in Fig. 1, air-fuel combustion based flue gas (at 150 °C), methane (at 25 °C) and steam (generated from water using heater HT) are mixed in mixer M1 and heated up to 850 °C, 1 atm in heater HT1 to be fed to the tri-reformer T-REFO. The generated synthesis gas (stream SYN-GAS) is cooled to 30 °C (in cooler CL1), compressed to 30 bar (in compressor COMP1) and cooled again to 25 °C (in cooler CL2) to be fed to the flash drum WSDRUM, to extract water from bottom stream WATEROUT, and to deliver the remnant synthesis gas to compressor COMP2, where it is further compressed to 50 bar, and fed to mixer M2. Mixer M2 has been utilized to mix the recycle stream (RECYCLE1) and syn-gas stream (SYN3) to generate stream 1 (at 50 bar) which is heated up to 220 °C, to be fed to the methanol production reactor R-METH. The methanol reactor product stream REAC-OUT (containing methanol, water and unconverted gases) is cooled to 25 °C to be fed to flash drum

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