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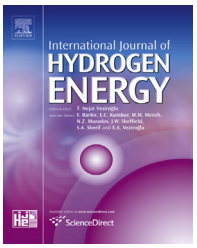

Process simulation and optimization of methanol production coupled to tri-reforming process

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ABSTRACT

Tri-reforming, as a new approach for the treatment of CO_2 in flue stack gases, has been studied in this work. To determine the optimum operating conditions for the production of syngas with target ratio and maximum CO_2 conversion, the effects of temperature (400–1200 °C), CH_4/Flue gas ratio (0.4–1.0) and pressure (1–5 atm), on the compositions of syngas were investigated. Also, the methanol production from syngas has been rigorously simulated. An optimum heat exchange network was obtained with the objective of minimizing both utility and capital costs, which were calculated by General Algebraic Modeling system (GAMS). Furthermore, an economic analysis was carried out to substantiate the potential profits based on the conceptual results from heat integration. Results showed that the tri-reforming process, when integrated with methanol synthesis, is an economical approach for the treatment and utilization of CO_2 in flue gases.

1. Introduction

CO_2 conversion and utilization is gaining significant attention worldwide not only because CO_2 has an impact on global climate change, but CO_2 also provides an important carbon source for potential fuels and chemicals [1–3]. Most of the CO_2 conversion and utilization technologies have been focused on pure CO_2 that is separated from industrial process waste streams. However, to separate CO_2 from other components in the waste stream requires substantial energy consumption [4,5]. Tri-reforming combines steam methane reforming, CO_2 dry reforming, and methane oxidation and has been proposed by some researchers as a promising method of reutilizing CO_2, without pre-purification [6]. Different from traditional CO_2 dry reforming, tri-reforming introduces H_2O and O_2 into the process, which greatly reduces the possibility of carbon formation on the catalyst. Carbon build-up, also known as coking, is the main reason for catalyst deactivation [7–9]. Furthermore, the H_2/CO ratio in the product stream from the tri-reforming process ranges from 1.5 to 2.0, which is desirable for the production of chemicals such as methanol, dimethyl ether, and other liquid hydrocarbons [10]. Therefore, tri-reforming could be an economically viable method to alleviate CO_2 emissions.

Some researchers have been focusing on the tri-reforming process as a method of flue gas treatment and CO_2 emission control; however, their attentions were limited to the syngas production without considering the impacts of the methanol synthesis, or other syngas conversion technologies, such as Fischer–Tropsch [11–14]. Thus, process simulation is required to test the effectiveness and profitability of this technology. Although the tri-reforming process uses methane as a co-reactant, current exploration technologies of natural gas make methane an affordable hydrogen-donor molecule.

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In this study, the methanol synthesis process via tri-reforming was investigated and rigorously simulated using Aspen Plus. On the basis of specific flue gas composition, the effects of reaction temperature, pressure, and CH_4/Flue gas ratios have been examined to determine the optimum conditions of the tri-reforming process to produce syngas, which is then converted to methanol. Additionally, heat integration with different objective functions was performed to optimize utility selection and energy costs. An economic analysis was also conducted after heat integration to evaluate the potential profits obtained through the integrated energy network. The purpose of this paper is to discuss the feasibility of the tri-reforming process as a CO_2 treatment approach and to shed some light on the industrial application of an integrated tri-reforming/methanol synthesis process. This paper focuses on operational optimization instead of optimal design, and the flowsheet is a tool used for evaluating different operating strategies. Capital costs usually include depreciation, labor costs, taxes, etc. and are not easily disclosed by vendors. While it is true that natural gas is available at high pressures (i.e. >1 MPa), this paper illustrates, which confluences with the current literature, that higher reactor pressures result in lower CH_4 and CO_2 conversions and higher coking of the catalyst [15–17]. The framework of modeling and optimization of the entire process is described in Fig. 1.

2. Methodology

Aspen Plus 7.3 has been used for this simulation. The equilibrium compositions have been calculated for a given operating condition and the mass and energy balances were solved in sequential modules for each unit. The RGibbs reactor was selected for tri-reforming reactions (R1–R9) while the REquil reactor was used for methanol production (R10–R12). For the RGibbs reactor, equilibrium compositions were calculated by minimizing the total Gibbs free energy summed over all the species regardless of the potential reactions. The total Gibbs free energy of a system is expressed by the summation over i species:

$$G^t = \sum_{i=1}^{N} n_i G_i^0 + R(T + 273.15) \sum_{i=1}^{N} n_i \ln \frac{f_i}{f_i^0}$$

where G_i^0 is the Gibbs free energy of the ith species under standard conditions; R is the molar gas constant; f_i^0 and f_i are fugacity of species i at standard and operating conditions, respectively. f_i is usually calculated through complex fugacity correlations dependent on pressure and temperature and etc. Therefore, the Gibbs free energy of N_2, which is a flue stack component, will have interplay with that of other species, and thus, influencing the ultimate equilibrium. Since there is a lack of kinetic data for tri-reforming reactions, the Gibbs reactor is a suitable choice for evaluating tri-reforming reactions [18]. With regard to methanol synthesis, the equilibrium reactor will take into consideration the effect of inert gas (N_2) on methanol production, as is also suggested in the literature [19,20]. For the REquil reactor, the product compositions were derived under the circumstance that all the reactions specified reached chemical equilibrium. Peng–Robinson equation of state was the thermal package adopted for this process simulation as seen in the literature [21–23]. In addition, the Peng–Robinson-Boston-Mathias (PR-BM) was also tested for the syngas reactions but had no appreciable differences. The involved reactions are listed as follows:

Tri-reforming reactions:

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \quad \Delta H = +247\ \text{kJ/mol} \tag{R1}$$

$$H_2O + CH_4 \rightarrow CO + 3H_2 \quad \Delta H = +206\ \text{kJ/mol} \tag{R2}$$

$$0.5O_2 + CH_4 \rightarrow CO + 2H_2 \quad \Delta H = -36\ \text{kJ/mol} \tag{R3}$$

$$2O_2 + CH_4 \rightarrow CO_2 + 2H_2O \quad \Delta H = -880\ \text{kJ/mol} \tag{R4}$$

$$CH_4 \rightarrow C + 2H_2 \quad \Delta H = +75\ \text{kJ/mol} \tag{R5}$$

$$2CO \rightarrow C + CO_2 \quad \Delta H = -172\ \text{kJ/mol} \tag{R6}$$

$$C + CO_2 \rightarrow 2CO \quad \Delta H = +172\ \text{kJ/mol} \tag{R7}$$

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H = +131\ \text{kJ/mol} \tag{R8}$$

$$C + O_2 \rightarrow CO_2 \quad \Delta H = -394\text{kJ/mol} \tag{R9}$$

Methanol production reactions:

$$2H_2 + CO \rightarrow CH_3OH \quad \Delta H = -91\ \text{kJ/mol} \tag{R10}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad \Delta H = -50\ \text{kJ/mol} \tag{R11}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H = -41\ \text{kJ/mol} \tag{R12}$$

For tri-reforming reactions (Fig. 2), the flue gas consists of four major components: carbon dioxide, water, oxygen and N_2

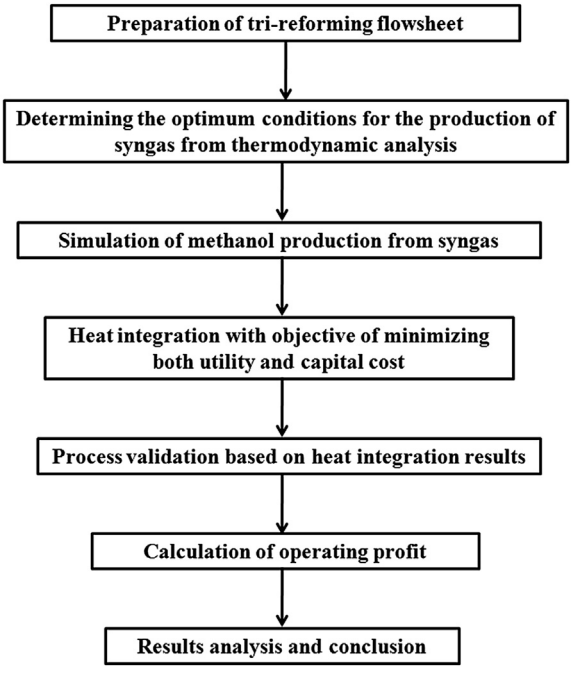

Fig. 1 – Framework of modeling and optimization of methanol production via tri-reforming process.