Applied Energy 204 (2017) 163–180

Contents lists available at ScienceDirect

Applied Energy

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

Plant-wide modeling and analysis of the shale gas to dimethyl ether (DME) process via direct and indirect synthesis routes

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HIGHLIGHTS

- Systems level modeling and analysis of the shale gas to DME process are undertaken.
- Both direct and indirect synthesis routes are investigated.
- A novel DME separation process is developed.
- Models of direct DME synthesis, ATR, and pre-reforming reactors are developed.
- Effects of the CO_2 recycle and H_2/CO ratio are evaluated.

ARTICLE INFO

Article history:
Received 24 April 2017
Received in revised form 25 June 2017
Accepted 28 June 2017

Keywords:
Shale gas
Dimethyl ether
Direct synthesis
Indirect synthesis
CO_2 capture

ABSTRACT

A plant-wide model of the shale gas to dimethyl ether (DME) process with integrated CO_2 capture via direct and indirect synthesis routes has been developed in Aspen Plus V8.4®. In this study, models of the pre-reforming reactor, autothermal reforming (ATR) reactor and DME synthesis reactors using kinetic data have been developed. For CO_2 capture, Rectisol and methyl diethanolamine (MDEA)/piperazine (PZ) technologies have been evaluated and results have been compared with the experimental data. A novel DME separation process has been developed and evaluated for efficient separation of DME, syngas, and CO_2. Binary interaction parameters for the vapor-liquid equilibrium (VLE) model of the methanol-DME-CO-CO_2-H_2O-H_2 system are regressed using the experimental data. Effects of the key parameters like CO_2 recycle ratio and H_2/CO ratio on the utility consumption in the syngas synthesis unit, acid gas removal (AGR) unit, DME synthesis unit and DME separation unit are studied. It is observed that the direct shale gas to DME production process operated with an optimal H_2/CO ratio of 1 has a higher DME yield and overall equivalent electrical efficiency than the indirect shale gas to DME production process.

1. Introduction

The shale gas boom in the United States has started replacing coal and petroleum as the energy source. Due to the increasing demand of transportation fuel and the volatile crude oil market, it is necessary to develop cleaner and more carbon efficient non-petroleum based transportation fuels [1]. In the recent years, use of dimethyl ether (DME) as an alternative liquid fuel is being strongly evaluated, because of its high cetane number (55–60) and potential to replace diesel. DME has properties similar to the liquefied petroleum gas (LPG) and can be used as a high quality household fuel [1]. Moreover, it is non-toxic, environmentally friendly (with about 95% less CO_2 emission than diesel) and an excellent refrigerant [1,2]. DME can be produced from a variety of fossil fuels, such as coal, biomass, and natural gas. Coal is the preferred feed for producing DME for most of the Asia-Pacific countries due to its abundance in those countries. However, in the United States, shale gas seems to be an attractive option for producing DME due to its low-cost and high availability [3].

Syngas composition can vary widely depending on the feedstock used. The syngas derived from coal has a much lower H_2/CO ratio (close to 1) compared to the syngas derived from natural gas or shale gas (usually >2) [4,5]. So, the feedstock has a strong impact on the process technology. Most of the papers in the area of DME synthesis from natural gas/coal have mainly focused on catalyst development, intrinsic kinetic studies, and on developing reactor technologies [1,6,7]. Systems level analysis of the DME synthesis processes from both technical and economic perspectives is lacking in the open literature not only for shale

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http://dx.doi.org/10.1016/j.apenergy.2017.06.085
0306-2619/

gas as the feed but also for coal/natural gas as the feed. Ohno et al. [8] have reported on the development of a 100 t/d natural gas to DME synthesis plant. In a study by Peng et al. [5], issues related to the direct DME synthesis process have been discussed. Studies on the DME synthesis processes from coal are also available in the open literature [9,10]. Han et al. [9] and Shim et al. [10] have developed kinetic models of the direct DME synthesis reactor. Chen et al. [11] have simulated the DME synthesis reactor by minimizing the Gibbs free energy. The authors have also performed pinch analysis to reduce energy consumption. Both one-dimensional model as well as three-dimensional CFD models of slurry and fixed bed direct DME synthesis reactors have been reported in the literature [12–14]. To the best of the authors' knowledge, systems level study on the direct DME synthesis process using shale gas as the feed is lacking in the current literature. The plant-wide process model of the shale gas to DME synthesis process developed in this work and the systems level study conducted using this process model can be instrumental in studying various design options and can be leveraged for techno-economic studies.

The first step in the shale gas to DME process is to produce syngas via autothermal reforming (ATR). Unlike natural gas, shale gas consists of not only CH_4 but also high amount of heavy hydrocarbons. Reaction rates of heavy hydrocarbons are typically faster than CH_4. In addition, they lead to coke formation which can significantly reduce the activity of a catalyst [15,16]. This issue can be avoided by integrating an adiabatic pre-reforming reactor before the ATR reactor to convert heavier hydrocarbons into CH_4 at relatively lower temperatures than the ATR reactor [17–19]. In addition to prevention of catalyst coking, the pre-reformer also offers several advantages such as an increase in production capacity by 10–20% and a reduction in the energy consumption in the primary reformer due to its operation at a lower steam to carbon ratio [17,20]. Existing literature in the area of pre-reforming of higher hydrocarbons has mainly focused on the development of catalysts and modeling of the reactor [15,21,22]. In some studies, both the pre-reformer and ATR reactors have been modeled as equilibrium reactors [23–25]. Modeling of micro-reactors for fuel cell applications where ATR reactions take place in presence of high steam to carbon ratio has been presented [26,27]. Some studies have also focused on one-dimensional modeling of the ATR reactor for estimating temperature profiles of different catalysts [28,29]. Considering the key roles a pre-reformer and ATR reactor play in the DME process, reactor models using kinetic data rather than the equilibrium models are desired especially when an economic analysis has to be undertaken.

Before sending the syngas produced from the ATR reactor to the DME synthesis unit, it has to be processed through an acid gas removal (AGR) unit for separation of impurities, mainly CO_2 from the syngas. The choice of AGR technology strongly depends on the partial pressure of CO_2 in the feed. Physical absorption is favored when the partial pressure of CO_2 in the feed is relatively high, while for low CO_2 partial pressure, chemical absorption such as amine based processes are preferred [30]. Final selection of the technology also depends on the impurities to be removed, capital costs, and energy requirements. There are several candidate technologies that can be evaluated. CO_2 removal by the Rectisol process has been considered by Ogawa et al. [31] for a similar application. In our study, Rectisol and methyl diethanolamine (MDEA)/piperazine (PZ) technologies are evaluated as the candidate physical and chemical absorption technologies, respectively.

DME can be synthesized from the clean syngas using the indirect or direct route. In the indirect synthesis route, syngas is first converted to methanol followed by dehydration of methanol in a separate reactor to produce DME. In the direct synthesis route, syngas is directly converted to DME in a single reactor where both methanol synthesis and dehydration reactions simultaneously take place over bi-functional catalysts such as $CuO/ZnO/Al_2O_3$ and γ-Al_2O_3. The indirect route is widely used commercially, but it has lower DME production rate due to the thermodynamic equilibrium limitation of CO conversion to methanol [32]. This problem can be overcome by the direct synthesis route leveraging the synergistic effect of the simultaneous conversion of methanol to DME which, in turn, increases syngas conversion and yield of DME [32]. In the direct synthesis route, the yield of DME is very sensitive to the H_2/CO ratio and CO_2 content in the feed stream. The maximum syngas conversion, i.e. the syngas conversion under equilibrium, is approximately 90% at the optimal operating condition [31]. The unconverted syngas is captured and recycled to the DME reactor along with the fresh syngas. Since the feed composition varies widely when recycle is considered, it is more appropriate to develop a reactor model using the reaction kinetic data for the direct DME synthesis reactor for rigorous techno-economic analysis of the system.

The H_2/CO ratio in the syngas derived from coal can be easily adjusted to 1 by feeding additional steam to the ATR reactor. However, when syngas is obtained from the hydrogen rich shale gas, this is not straightforward. The CO_2 recycles from the AGR unit and the DME separation unit have to be integrated to feed extra CO_2 to the ATR reactor to adjust the H_2/CO ratio to 1. Inclusion of the CO_2 recycle from the AGR and DME separation units results in additional complexity and more utility costs. Hence, it is important to evaluate the effect of CO_2 recycle on the H_2/CO ratio. Peng et al. [5], Ohno et al. [8], and Ogawa et al. [31] have considered the effect of CO_2 recycle to the ATR reactor, but a rigorous systems level analysis is still lacking.

Various approaches for DME separation have been proposed in the existing literature. In the study of Bhatt et al. [33], chilled methanol is used to separate unconverted syngas from CO_2. Then a series of flash separators and distillation columns is used to purify DME. In some pilot plants, chilled DME is used as a solvent to capture CO_2 and then physical or chemical absorption is considered to separate CO_2-DME from the unconverted syngas [8]. In the study of Han et al. [9], deionized water is used as a solvent to separate DME from the unconverted syngas and CO_2 [34]. The thermodynamic models used for DME separation technologies in the existing literature have binary interaction parameters that are estimated using UNIFAC-RQ or UNIFAC model [9,11]. As the DME separation unit has a large impact on the overall process technology and economics, it is important to estimate the binary interaction parameters using the experimental VLE data that can make the thermodynamic model more accurate. This, in turn, can increase the accuracy of the process model for DME, syngas, and CO_2 separation system.

To summarize, a detailed process model for the shale gas to DME process has been developed in this study. The focus is on configuration, technologies, operating conditions and energy consumption. In particular, following contributions have been made:

- Development of plant-wide models for the direct and indirect shale gas-to-DME production processes
- Regression and validation of the key kinetic parameters for the direct DME synthesis reactor
- Regression of the binary interaction parameters for the VLE model of the methanol-DME-CO-CO_2-H_2O-H_2 system
- Development of the reactor models using the kinetic data and validation of the kinetic models for the pre-reforming reactor, ATR reactor, methanol synthesis and methanol dehydration reactors for the indirect route
- Development of a novel configuration of the DME separation system considering the recycle system for CO_2 utilization
- Evaluation and comparison of Rectisol and MDEA/PZ technologies with varying H_2/CO ratio and CO_2 partial pressure