Fuel Processing Technology 131 (2015) 7–13

Contents lists available at ScienceDirect

Fuel Processing Technology

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

A conceptual design by integrating dimethyl ether (DME) production with tri-reforming process for CO_2 emission reduction

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ARTICLE INFO

Article history:
Received 16 May 2014
Received in revised form 27 October 2014
Accepted 3 November 2014
Available online 21 November 2014

Keywords:
CO_2 treatment
Tri-reforming
Dimethyl ether
Heat integration

ABSTRACT

There has been considerable interest in the development of more efficient processes for conversion and utilization of CO_2. Tri-reforming, as a new approach for the treatment of CO_2 in flue stack gases, has been studied in this work. Tri-reforming process combines CO_2 reforming with steam methane reforming and methane oxidation to produce syngas (H_2 and CO) at a suitable ratio. To determine the optimum operating conditions for the production of syngas with a target ratio and maximized CO_2 conversion, the effects of various factors including reaction temperature, reactor pressure and CH_4 flow rate on the compositions of syngas obtained from tri-reforming process are investigated. Also, the production of dimethyl ether (DME) from syngas has been rigorously simulated. An optimum heat exchange network was obtained with the objective of minimizing utility cost, which was calculated by General algebraic modeling system (GAMS). Results show that tri-reforming coupled to DME synthesis is an economically feasible approach for the treatment and utilization of CO_2 in flue stack gases.

1. Introduction

Conversion and utilization of CO_2 have gained significant attention in recent years not only because it may have an impact on global climate change but also CO_2 can be an important carbon source for potential fuels and chemicals. An innovative process known as tri-reforming utilizes CO_2 from industrial flue gases as a co-reactant to produce syngas, as proposed by Song and Pan [1]. In the tri-reforming process, CO_2 reforming, steam reforming, and partial oxidation of methane are integrated into a single reactor. One of the benefits for this process is that the additions of O_2 and H_2O help reduce carbon deposition onto catalyst, which directly leads to catalyst deactivation [2]. Also, the H_2/CO ratio in synthesis gas (syngas) can be well controlled to enhance the downstream production of dimethyl ether (DME). Furthermore, the heat released by partial oxidation of methane compensates for the energy demand of the reforming reactions leading to a significant decrease for external energy sources. Accordingly, tri-reforming can be considered as an energy-efficient process for the treatment of CO_2 emissions [3–5].

Dimethyl ether is an alternative fuel that could potentially replace petroleum-based diesel fuel [6]. Since the combustion of DME does not generate harmful components such as NO_x, smoke or particulates, it is regarded as a clean energy source for the next generation of fuels. Dimethyl ether (DME) has been promoted as a diesel substitute since the mid-1990s [7]. To evaluate the exhaust emissions, compression ignition engine tests have been performed with DME and diesel. It was found that DME would generate fewer exhaust pollutants (NO_x, hydrocarbons, and carbon monoxide). Moreover, DME does not produce soot [6,8]. Apart from above merits, the global warming potential for DME has been modeled and the results indicate that DME has a global warming potential of 0.1 for a 500-year time horizon, which is much lower than diesel [9]. Another important aspect is that DME has the highest well-to-wheel efficiencies next to natural gas among all non-petroleum based fuels no matter what type of vehicle technologies are applied including conventional, hybrid, and fuel processor fuel cell [6]. As pointed out in the literature [10], the "single-step" conversion of syngas into DME is very attractive compared with the commercially available "two-step" process that includes conversion of syngas-to-methanol followed by methanol dehydration. The reasons not only lie in the fact that the "two-step" process has inherent productivity limitations due to the chemical equilibrium constraints in the syngas-to-methanol reactor but also that the "two-step" process needs a second dehydration reactor. In this study, the direct syngas-to-DME synthesis coupled to tri-reforming reactions was investigated and simulated using Aspen Plus 7.3 (AspenTech®). The traditional way to produce DME is through converting syngas to methanol through steam reforming reactions of methane and then methanol dehydration. However, steam reforming of methane has a big flaw in that significant quantities of CO_2 will be produced as a byproduct [5]. Since DME production also generates CO_2, tri-reforming can utilize the CO_2 byproducts stemming from these two processes to the greatest extent.

On the basis of the specific flue gas composition produced from coal-fired power plants, the interactions among CH_4 flow rate, reactor pressure, and reactor temperature were examined to determine the optimum conditions of the tri-reforming process to maximize the hydrogen yield, which is subsequently converted to DME. Furthermore, heat integration with the objective function of minimizing utility costs has been

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http://dx.doi.org/10.1016/j.fuproc.2014.11.006
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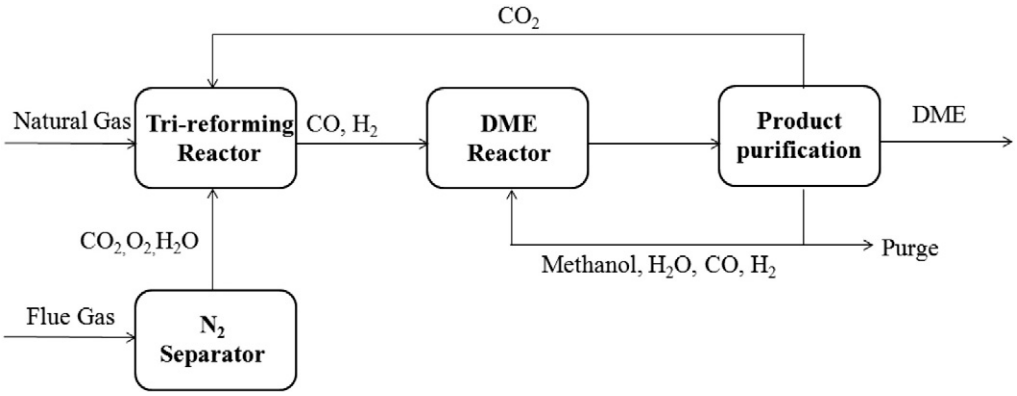

Fig. 1. Block diagram of DME production from tri-reforming reactions.

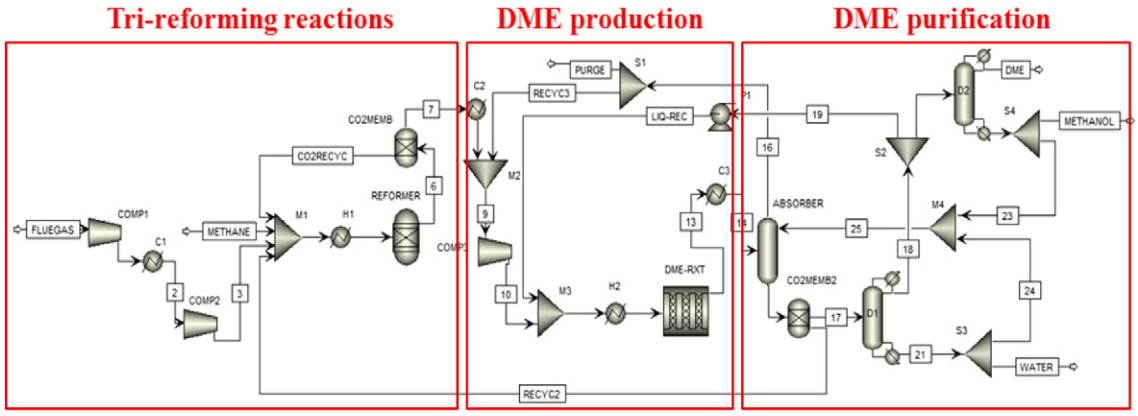

Fig. 2. Process flow diagram of DME production from tri-reforming process.

performed to optimize the heat exchange network (HEN). The production of DME via tri-reforming has two significant advantages: 1) CO_2 emission from flue gas of power plant is mitigated without extra CO_2 separation unit operations and 2) a viable carbon resource is converted into a useful chemical compound (DME). These results help to shed some light on the development of DME production coupled to tri-reforming process by utilizing CO_2 in the flue gas.

2. Process configuration

Fig. 1 shows the block diagram of DME production coupled to tri-reforming reactions. The detailed process flow sheet is shown in Fig. 2. The four major blocks in the proposed process are the N_2 separation unit, the tri-reforming reactor, the DME production, and the DME purification section.

2.1. N_2 separation unit

As with most gas-to-liquid processes, including Fischer Tropsch synthesis of long-chain hydrocarbons, syntheses of methanol and DME are all conducted at high-pressure conditions. It is practical to carry out tri-reforming reactions at elevated pressures corresponding to the downstream product synthesis from an economical point of view [11]. Thus, the flue gas is compressed to 20 bar to match the pressure of the tri-reforming reactor. Generally, coal-fired flue gas contains about 12.8% CO_2, 6.2% H_2O, 4.4% O_2, 73–74% N_2 and trace NO_x, SO_2, and CO, all on mole basis [12]. In this process, the flow rate of flue gas was chosen to be 1000 kmol/h. However, the large amount of N_2 contained in flue gas will result in decreased conversion and lead to higher toxic NO_x production. Hence, a N_2 separation unit, which was added to the process flow sheet but not modeled in detail in this study, was used to remove N_2 from the flue gas.

2.2. Tri-reforming reactor

Once N_2 has been removed, only H_2O, CO_2, and O_2 remain in the flue gas. Subsequently, the flue gas was mixed with high-pressure (20 bar) methane. A heater was used to increase the mixture temperature before entering into a Gibbs reactor. The Gibbs reactor was used to determine the product equilibrium compositions. The major reactions involved in tri-reforming are summarized in Table 1 [1,13]. The products were passed through a CO_2 membrane separator to separate CO_2 from the other components (CO, H_2, H_2O, and un-reacted CH_4) contained in syngas [14]. The separated CO_2 from the reactor effluent was then recycled back to the Gibbs reactor.

2.3. DME production

For DME production, a plug flow reactor (PFR) with Langmuir–Hinshelwood–Hougen–Watson (LHHW) kinetic mechanism was modeled for the DME synthesis reactor. The size of the PFR was calculated according to the catalyst loading and space velocity. Six potential reactions

Table 1
Reactions involved in tri-reforming reactor.

No.	Reaction equations
1	$CO_2 + CH_4 \rightarrow 2CO + 2H_2$
2	$H_2O + CH_4 \rightarrow CO + 3H_2$
3	$0.5O_2 + CH_4 \rightarrow CO + 2H_2$
4	$2O_2 + CH_4 \rightarrow CO_2 + 2H_2O$
5	$CH_4 \rightarrow C + 2H_2$
6	$2CO \rightarrow C + CO_2$
7	$C + CO_2 \rightarrow 2CO$
8	$C + H_2O \rightarrow CO + H_2$
9	$C + O_2 \rightarrow CO_2$