Modeling and analysis of a methanol synthesis process using a mixed reforming reactor: Perspective on methanol production and CO_2 utilization

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HIGHLIGHTS

- A methanol synthesis process using a mixed reforming reactor was modeled.
- Kinetic models for the mixed reforming and methanol synthesis were developed.
- Various effects of operating conditions on the MeOH production rate were evaluated.
- An analysis was conducted with respect to both the overall and local CO_2 conversions.
- A trade-off existed between the maximum MeOH production and the maximum CO_2 utilization.

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ABSTRACT

In this study, kinetic models were developed for the mixed reforming and synthesis of methanol (MeOH). The effectiveness of the reforming model in our previous work was proven in an experimental study using a bench-scale reactor, while the intrinsic rate model and effectiveness factors were developed to represent the MeOH synthesis. For a 10-ton-per-day production of MeOH, the rate model was used to determine the size of a reforming reactor so that the supplied heat could be used exclusively to engage the reaction (not for the heat-up of the reactant), while the MeOH reactor was specified using the reported values. The process model was then used to evaluate various effects of the following factors on the MeOH production rate: (1) reaction temperature, (2) CO_2 fraction in the feed, and (3) the recycle route of the unreacted gas either to the feed or to the MeOH reactor. Additionally, an analysis was conducted with respect to both the overall and local CO_2 conversions in each reactor, and it was shown that a trade-off existed between the maximum MeOH production rate and the maximum CO_2 utilization, regardless of the existence of a recycle stream.

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1. Introduction

Methanol (MeOH) can be either used as a solvent and fuel by itself or conveniently converted into useful products such as formaldehyde, amines, acetic acid, esters, and olefins [1]. MeOH is considered as an excellent alternative energy resource since its high octane number ensures good antiknock performance, in addition to high volatility, denser fuel–air charge and excellent lean burn properties [2]. In addition, it can be blended with gasoline, although it has half the volumetric energy density relative to gasoline or diesel [1]. Besides its direct use as fuel, methanol can be conveniently converted into ethylene or propylene in the MTO (methanol-to-olefins) process, and in turn, these olefins can be used to produce hydrocarbon fuels and their products [3]. Methanol is also used for supercritical treatment in the biodiesel fuel production [4–6], and is applied to the fuel cell system [7].

It is also a convenient medium for the storage and transport of CO and H_2 [8,9]. Recently, because of the increased interest in atmospheric pollution caused by the emission of significant

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amounts of greenhouse gases, particularly CO_2 [10], much attention has been focused on the development of processes for CO_2 utilization including MeOH synthesis by means of both CO and CO_2 hydrogenation [11–15]. In addition, if a MeOH production process is combined with the mixed (steam and CO_2) reforming of methane to produce syngas for MeOH synthesis, synergetic effects of CO_2 utilization are expected [16,17].

Much research work has been reported in the literature for the modeling and optimization of methanol synthesis processes. Holmgren et al. analyzed the energy balance of a commercial-scale MeOH process featuring a biomass gasification system [18]; in addition, the dynamic behavior and control of methanol synthesis fixed-bed reactors have been studied by many researchers [19,20]. Furthermore, the development of the methanol synthesis recycle-loop model has been described in detail, along with several case studies performed using steady-state and dynamic models for better understanding of the process behavior [21]. In addition to modeling and analysis, optimization methods have been extensively applied to the two processes including a genetic algorithm to obtain an optimal temperature profile and optimal two-stage cooling shell for the maximum production rate [22], and a repeated process estimation–optimization strategy has been applied to track the theoretical optimum profile of the selected control variable with the deactivation of the catalyst [23]. Optimal values of the inlet hydrogen mole fraction and the shell temperature have been investigated by employing methanol production rate as an objective function [24]; moreover, Luyben developed the economically optimum design of a methanol reactor and distillation column system to produce high-purity methanol from synthesis gas [25]. The syngas inlet temperature, steam drum pressure, and cooling water volumetric flow rate were optimized to maximize the methanol production in the reactor outlet [26]; Santangelo et al. presented an optimization procedure for increasing the methanol production in synthesis loops with quench reactors [27].

Recently, much effort has been directed to the reduction of CO_2 emissions to alleviate environmental phenomena such as global warming. In this sense, our previous work [17] reported the effects of operating conditions on the production rate of syngas and CO_2 conversion (utilization) for the mixed (steam + dry(CO_2)) reforming, where it was shown that a trade-off existed between the maximum syngas production and maximum CO_2 utilization. Based on these results, the mixed reforming reactor was incorporated into a MeOH synthesis process in the present work; here, the feed gas composed of CH_4, H_2O, and CO_2 was converted to syngas (CO + H_2 + CO_2) by a mixed reforming process, and the syngas was further converted to methanol by the hydrogenation of both CO and CO_2. This process includes both the consumption and production of CO_2, its consumption by dry reforming ($CH_4 + CO_2 \leftrightarrows 2CO + 2H_2$), and CO_2 hydrogenation to synthesize MeOH ($CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O$) vs. production by either steam reforming ($CH_4 + 2H_2O \leftrightarrows CO_2 + 4H_2$) or the water gas shift reaction ($CO + H_2O \leftrightarrows CO_2 + H_2$ (WGS)). Therefore, both an investigation of the effect of operating conditions on MeOH production and an analysis of the accompanying CO_2 emission were performed in this work.

2. Experimental

2.1. Bench-scale reforming reaction

The catalyst was prepared by a co-impregnation method using metal precursors of $Ni(NO_3)_2 \cdot 6H_2O$ (98%, Samchun) and $Ce(CH_3COO)_3 \cdot xH_2O$ (99.9%, Aldrich) with an aqueous solution. The weight ratio of Ni/Ce/support (Sasol Pural MG30 with a weight ratio of $MgO/Al_2O_3 = 3/7$) was fixed at 15/6/79 based on the metallic composition of Ni and Ce. The prepared catalyst was dried

overnight at 393 K and pelletized in the form of a cuboid with four holes. Then, it was subsequently calcined at 1123 K for 6 h in air. Thereafter, the catalyst cuboid was crushed in a mortar, and then sieved to collect the final catalyst pellets of ca. 5 mm in size.

The prepared catalyst pellets were charged to a tubular reactor that had an outer diameter of 42.7 mm and an inner diameter of 32.5 mm. The amount of catalyst pellets was 40 g, and 1220 g of α-Al_2O_3 balls of ca. 5 mm in diameter was additionally mixed well with the catalyst pellets as a diluent material in the catalyst bed. After inert α-Al_2O_3 balls were charged to a height of 80 mm for preheating, the height of the catalyst bed was ca. 745 mm. The wall temperature was measured at three points, which were regularly positioned as shown in Fig. 1. Prior to the activity test, the catalyst was pre-reduced at 1023 K for 3 h under a flow of 5 vol% H_2 balanced with N_2. The gas-hourly-space-velocity (GHSV) was 25,000 mL-CH_4/(g_{cat} h), and the pressure was 0.53 MPa. The tube wall temperature was maintained at 1201 K by operating three jacket-type electric furnaces that surrounded the tube in a series. The feed molar ratio was specified as $CH_4/H_2O/CO_2/N_2/H_2 = 4.07/6.37/1.75/1.00/1.07$. The product gases were analyzed using an online gas chromatography unit (Younglin ACME 6100) equipped with a thermal conductivity detector connected to a Porapak-Q packed column for CO_2 and a molecular sieve 5A packed column for H_2, N_2, CO, and CH_4.

2.2. MeOH synthesis

A commercial catalyst ($Cu/ZnO/Al_2O_3$, Süd-Chemie, MegaMax 700) was used for the kinetic experiment on the synthesis of MeOH. The pelletized catalyst (5 mm diameter, 3 mm height) was broken and sieved to produce three samples of uniform size: 0.15–0.25 mm, 0.75–0.85 mm, and 1.5–2.5 mm that were labeled as S1, S2, and S3, respectively. Additionally, the original catalyst pellet, denoted as S4, was also used without breaking and sieving it. The S1 catalyst was used for the kinetic investigation, while the other catalyst samples were used to evaluate the effect of particle size on the catalytic performance.

The kinetic data were collected using a continuous tubular-flow fixed-bed microreactor. The temperature within the reactor was controlled by adjusting the furnace temperature, and the flow rate was controlled using a mass flow controller. The pressure was precisely controlled by a back pressure regulator and monitored by a digital pressure sensor. The catalyst samples (0.4 g) were diluted with similar-sized and inert α-Al_2O_3 particles (1.2 g) and packed together into a stainless steel reactor (internal diameter = 7 mm). The catalyst was reduced under a flow of H_2 (100 mL/min), and the temperature was increased from room temperature to a predetermined point at a rate of 2 K/min and held constant for 3 h. After the reduction, the pressure was increased according to the operating conditions, and the H_2 gas was then replaced by the gas used in the synthesis of MeOH. The detailed conditions of temperature, pressure, and feed gas composition are listed in Table S1 in Supplementary data. The reaction products were analyzed using an on-line gas chromatograph (Young Lin), where a Carboxen 1000 column was installed to separate the CO, CO_2, H_2, and Ar gases that were detected with the thermal conductivity detector, and a HP-PLOT Q capillary column coupled to a flame ionization detector was used to separate and analyze all the hydrocarbons, including MeOH.

3. Results and discussion

3.1. Reaction rates

The reaction rates for the mixed reforming process over the pellet-type catalysts in this work were reported in our previous work