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Modeling and optimization of the mixed reforming of methane: Maximizing CO_2 utilization for non-equilibrated reaction

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HIGHLIGHTS

- Dry and mixed reforming of methane were conducted under non-equilibrium conditions.
- Kinetic model was developed with kinetic parameters estimated using experimental data.
- Effects of operating conditions on CO_2 conversion were evaluated using the model.
- A reactor with three sections was considered for optimization study.
- Optimization was performed to maximize CO_2 utilization using the genetic algorithm.

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ABSTRACT

In the present study, a reactor model for mixed reforming over Ni-based catalyst was developed to investigate non-equilibrium behavior and reactions. Kinetic parameters were estimated by fitting experimental data for CH_4 and CO_2 conversions and H_2/CO ratios under a variety of conditions, and the CO_2 consumption rate was shown to be significantly affected by operating conditions due to the different characteristics of each reaction: dry reforming (DRM), steam reforming for the production of CO (SRM1) and CO_2 (SRM2), and the water–gas shift (WGS) reaction. For optimization study, a reactor composed of three sections with different inert fractions and wall temperatures was considered, and optimization was conducted using various weighting factors on the CO productivity and the CO_2 consumption per unit CO productivity; when maximum CO_2 consumption per CO productivity was achieved, inert fraction of the first part of the reactor was lowered and wall temperature for the third part of the reactor was decreased, compared to maximum CO productivity case. Further analysis of instantaneous reaction rates showed that, in the case of maximum CO_2 consumption, one third of the later part of the reactor could be obviated, resulting in an increase in CO productivity per unit volume, that is, the efficiency of the reactor. As a result, the strategy in the present study was successfully applied in the design of a mixed reforming reaction process providing maximum CO_2 conversion as well as minimum CO_2 emissions while reducing energy costs.

1. Introduction

Synthesis gas (syngas), a mixture of hydrogen and carbon monoxide, has received significant research and industrial interest as a source of hydrogen, and has been used for highly selective syntheses of a wide range of chemicals and fuels. One of the most widely used methods for syngas production is the steam methane reforming (SMR) process [1]. However, the syngas generated by SMR has a higher H_2/CO ratio than that which is normally required for the production of fuels such as Fischer–Tropsch liquids [2]. Although the excess H_2 in syngas can be separated using a polymer membrane or a pressure swing adsorption unit [3], the additional units increase both capital and operating costs. As an alternative way to decrease H_2/CO ratios as well as to reduce the energy requirements, the endothermic SMR process can be coupled with the exothermic partial oxidation of methane (POM) [4]. POM has disadvantages in that it usually requires additional instrumentation such as air-separation units (ASU) to remove nitrogen from air; furthermore, SMR in conjunction with POM produces syngas with H_2/CO ratios higher than two [5]. The dry reforming of methane (DRM), which uses carbon

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Nomenclature

c_i	concentration of the species (mol/m^3)
C_p	heat capacity (J/(g K))
DRM	dry reforming reaction
D_e	effective diffusivity (cm^2/s)
D_t	tube diameter (m)
E_j	activation energy (J/mol)
f_i	partial fugacity of species i (Pa)
GHSV	gas hourly space velocity (mL-CH_4/(g_{cat} h))
$\triangle H$	heat of reaction (J/mol)
$k_{j\text{app}}$	apparent rate constant
K_i	adsorption equilibrium constant of species i
$K_{p,j}$	equilibrium reaction rate constant
L	length of reactor (m)
NR	number of reaction
$R_{i,j}$	reaction rate (mol/(g_{cat} h))
SRM	steam reforming reaction
u_s	gas velocity (m/h)
U	overall heat transfer coefficient (W/(m^2 K))
w	weighting factor
WGS	water–gas shift reaction

Greek letters

θ	inert reaction
ρ_B	bulk pellet density (kg/m^3)
ρ_g	bulk gas density (kg/m^3)

dioxide instead of steam, results in a H_2/CO ratio closer to unity [1]; thus, mixed reforming (incorporating both steam and dry conditions) is considered an ideal method to manipulate the H_2/CO ratio without incorporation of additional process units, such as those for the WGS reaction, prior to the reforming process unit [5]. By carrying out CO_2 reforming simultaneously with steam reforming, carbon deposition rate, which is very rapid in CO_2 reforming, is drastically reduced [6]. The information about the catalysts for the mixed reforming of methane can be referred to some previous studies [7–9].

Previous studies concerning optimization of the methane reforming process have focused on the optimization (i.e., maximization) of syngas production rates [10–12]. Hagh [10] maximized hydrogen yields at the highest possible steam-to-carbon ratio and inlet feed temperature while minimizing heat loss and reactor pressures in an autothermal reactor. Rajesh et al. [13] conducted a multi-objective optimization study to simultaneously minimize the methane feed rate and maximize the carbon monoxide flow rate in syngas to yield a fixed hydrogen production rate from the unit. Chattanathan et al. [14] maximized CH_4 conversion and minimized coke formation in the mixed reforming process. In addition to the strategies developed to improve the hydrogen yields and reduce CO_2 emissions using the mixed reforming process, the sorption enhanced steam methane reforming process has also been found as a promising method [15–17].

Most of previously reported studies related to the optimization of reforming processes have focused on productivity maximization. However, because of recent interest in the development of environmentally friendly processes, especially those with low CO_2 emissions, one of the aims in the present study is to suggest a reforming process with maximum CO_2 conversion, that is, to determine the optimal operating conditions for maximum CO_2 utilization in steam reforming combined with dry (CO_2) reforming. Previous approaches to process design have concentrated primarily on optimal equilibrium conditions, since high reaction rates guarantee that the reaction reaches equilibrium prior to exiting the unit. However, this approach is not environmentally or economically feasible with respect to the waste of catalytic materials and heating energy; thus, a further aim of the present study is to reduce CO_2 emissions in by investigating operations under non-equilibrium conditions in order to utilize the entire catalytic loading within the reactor and minimize energy costs.

2. Experimental

2.1. Catalyst preparation

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) in an aqueous solution. The weight ratio of Ni/Ce/support (Sasol Pural MG30 with weight ratio of MgO/Al_2O_3 = 3/7) was fixed at 12/4/84 based on the metallic composition of Ni and Ce metals. The prepared catalyst was dried overnight at 120 °C and pelletized. The pellets were subsequently calcined at 850 °C for 6 h in air. More details about catalyst preparation can be found in our previous work [8].

2.2. Test runs for kinetic studies

The fresh catalyst pellet was crushed into more suitably sized granules of 16–20 mesh. The prepared catalyst was charged in a micro fixed-bed reactor with an outer diameter of 12.7 mm. The amount of catalyst in the bed was 50 mg; 1 g of diluents (α-Al_2O_3 ball) was added to the bed. Prior to activity tests, the catalyst was pre-reduced at 750 °C for 3 h under a flow of 5 vol% H_2 balanced with N_2. The experimental conditions under investigation were as follows: gas hourly space velocities (GHSV) in the range of 90,000–250000 mL-CH_4/(g_{cat} h); temperatures between 700 and 900 °C; pressures of 0.5–1.2 MPa; CO_2/CH_4 ratios of 0.3–1.2. Table 1 shows the experimental conditions considered in the present study. In some cases, the value of GHSV was slightly different from the value of comparable experiments due to the replacement and re-calibration of the mass flow controller (MFC) during the tests. It is worth noting that, since syngas in the present study was assumed to originate from natural gas, H_2S with poisonous effects on nickel catalysts as well as fine particulates causing deactivation was not considered in the feed composition. In addition, CO_2 was assumed to be fed separately for various CO_2/CH_4 ratio in the feed, while gasification of woody biomass with oxygen results in CO_2/CH_4 ratio of 3–5 which is beyond the range used in the experiments. Product gases were analyzed by an online gas chromatograph (GC) (Younglin ACME 6100) equipped with a TCD connected to a carbosphere-packed column.

3. Results and discussion

3.1. Mathematical modeling

In our previous work [5], a kinetic model for the mixed reforming of methane over a Ni–CeO_2/$MgAl_2O_4$ catalyst (prepared by Korea Research Institute of Chemical Technolgoy) was developed by applying a Langmuir–Hinshelwood-type expression. The use of catalysts with different shape (pellet type) in the present study necessitated the modification of the kinetic parameters in the previous report by employing new experimental conditions with greatly increased space velocities for the non-equilibrium reaction.

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