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Two-dimensional modeling of a plant-scale fixed-bed reactor for hydrogen production from methanol steam reforming

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ARTICLE INFO

Article history:

Received 26 January 2016

Received in revised form

12 July 2016

Accepted 15 July 2016

Available online xxx

Keywords:

Hydrogen production

Methanol steam reforming

Plant-scale fixed-bed reactor

Two-dimensional model

ABSTRACT

Methanol as hydrogen carrier can be reformed with steam over CuO/ZnO/Al₂O₃ catalysts. Two-dimensional pseudo-homogenous modeling and numerical simulation studies have been carried out for methanol steam reforming reactor integrating with global kinetics of methanol decomposition and methanol steam reforming. Hydrogen output and thermal behavior were investigated with respect to parameters such as mass flow rate and inlet mass fraction of methanol, external thermal oil inlet temperature and tube diameter. Good agreement was achieved between plant data and simulated data. The results show that temperature distribution changed more dramatically than concentration distribution along axial. Hydrogen production had a positive relationship with methanol mass flow rate, thermal oil inlet temperature. Thermal behavior along radial can be greatly affected by all discussed operating conditions. Large tube diameter was adverse to heat transfer leading to high temperature difference. These simulations can guide for manufacture operation and design of plant-scale reactor.

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Introduction

Hydrogen has an outstanding potential for being a key factor in driving the global energy system to a sustainable trajectory because of its high combustion heat and low emission. The so-called “hydrogen economy” as the most perspective scenario has been particularly concerned [1]. One of encountered obstacle about hydrogen economy development is that how to store and transport hydrogen safely on massive scale. Compared with different hydrogen carriers, methanol has high H/C ratio (4:1), equal to methane. Methanol can not only generate hydrogen through steam reforming at milder temperature (323–523 K) than most other fuels (>723 K) owing to

unnecessary of C–C bonds cleavage, but it is easily activated at low temperature unlike methane [2]. Methanol steam reforming can also dissolve the hydrogen of water molecule, which has less energy consumption than water direct electrolysis. Hence, methanol steam reforming (MSR) can regard as a key technology for hydrogen extraction from hydrogen carrier.

It is a desirable outcome that methanol steam reforming at low temperature has low CO concentration due to its favorable thermodynamics. Most investigations [2] have focused on Cu-based catalysts with the desired fast kinetics at low temperature. It is generally agreed that CuO/ZnO/Al₂O₃ catalysts for methanol synthesis or reforming catalysts regarded

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<http://dx.doi.org/10.1016/j.ijhydene.2016.07.117>

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copper as the active component [3]. High surface area from Alumina served to increase copper dispersion and decreased the susceptibility to sintering [4]. Clearly, ZnO as spacer and stabilizer can avoid direct contact of the Cu particles and prevent them from sintering [5]. Group VIII metals such as PdZn catalysts [6] were also studied for hydrogen production from methanol and these exhibited different performances with copper-based catalysts, which predominantly catalyzed methanol decomposition and produced more monoxide. Considering high cost of noble metal, CuO/ZnO/Al₂O₃ catalysts are widely used as commercial catalysts for methanol steam reforming.

There are different reactor types for methanol steam reforming to apply to different purposes. Micro-channel reactor with wall-coated catalysts has been focused by many researchers because of few heat transfer and mass transfer limitation, which is used for hydrogen source of fuel cells [7,8]. The micro-reactor's advantage disappears as system output increases owing to scale factor [9]. Membrane-based methanol reforming systems have been extensively demonstrated by several researches and development organizations [10–12]. Palladium-based membranes [13] have been adequately developed as a result of high product hydrogen purity and high methanol conversion. High cost of membrane reactors makes little chance to access to market. However, fixed-bed reactor as the simplest reactor type has enough knowledge to master the design of large-scale industrial plants [14]. Hence, fixed-bed reactor is still mainstream trend to manufacture massively for methanol steam reforming.

Considering the endothermic characteristic of methanol steam reforming, heat source need be provided to hold back reaction temperature drop. Slow reaction rates caused by low reaction temperature may decrease the conversion of methanol at reactor exit. Generally, pressurized water vapor, thermal oil and molten salt are used for supplying heat. Methanol steam reforming occurs at 513 K–573 K over CuO/ZnO/Al₂O₃ catalysts and thermal oil with advantage of high thermal capacity, low cost and convenient devices should be a better choice to provide heat for this reaction.

In past, the engineers carried out scale-up of industrial plants by means of experiments and experiences, which may consume a mountain of time and work. Researchers prefer to master the enlarging regulation through building mathematical model. One-dimensional pseudo homogeneous reactor model acquires enough detail to simulate normal operation of industrial plant. However, Yoon et al. [15] studied the limiting mechanisms in the methanol-steam reforming process theoretically and experimentally. Heat transfer could be main limiting mechanism when different reactor sizes were compared. Heat transfer resistance from exterior heat source gradually heightened as reactor diameter increased. One-dimensional model was assumed to be isothermal along radial and only specified or estimated different overall heat transfer coefficients along axial but reforming reactor displayed uneven thermal behavior along radial, indicating the drawback of one-dimensional model. Two-dimensional model had a more accurate description, compared to one-dimensional model

[16]. On purpose of a better prediction on scale-up process, two-dimensional model should be employed for multi-tubular fixed bed reactor with methanol steam reforming.

Two-dimensional mathematic model was established to demonstrate the behavior of a fixed-bed reactor for methanol steam reforming. Heat and mass distributions played crucial role in the performance of reforming reactor from the aspect of reactivity. Parametric study has been conducted with regards to parameters such as mass flow rate of methanol, inlet mass fraction of CH₃OH, external thermal oil temperature and tube diameter to figure out the thermal behavior and concentration variation.

Mathematical model

Process of methanol steam reforming

The process flow diagram of methanol steam reforming is depicted in Fig. 1. The mixed feeds of methanol and water were pumped into heat exchanger, then exchanged heat with the products from the reactor outlet. The thermal oil vaporized mixed feeds in vaporizer first then supplied heat for reactor. The feeds turned to products over commercial catalysts in reformer. The products were transferred to purifier and dry-based reforming gas was separated from water and methanol, which were circulated to mixed tank. The pressure swing adsorption unit (PSA) enriched product hydrogen to 99% purity and the exhaust gas was disposed by burner.

Description of reactor

The reactor for methanol steam reforming belonged to multi-tubular fixed-bed reactor. The thermal oil in shell side was used for providing heat source of reaction in shell side, which had heat exchange with tubular side in counter flow. The tubes were arranged in form of equilateral triangle. According to plant operation, the reactor structure data and operation conditions have been listed in Table 1.

Catalysts and characterization

The catalysts for methanol steam reforming used CuO/ZnO/Al₂O₃ cylinder catalysts with 5–6 mm × 5–6 mm. The bulk density of catalysts is 1050 kg/m³ and void fraction is 40%. The physic-chemical properties of CuO/ZnO/Al₂O₃ catalyst were characterized by several methods as follows:

X-ray diffraction (XRD) of CuO/ZnO/Al₂O₃ was recorded on a Rigaku D/Max 2550VB/PC (Rigaku, Tokyo, Japan, Cu K radiation). The textural properties of CuO/ZnO/Al₂O₃ were measured using a N₂ adsorption–desorption isotherm at 77 K through an ASAP 2020 instrument (Micromeritics, Atlanta, GA). Prior to the adsorption–desorption measurements, the samples were degassed at 473 K in a N₂ flow for 16 h to remove the moisture and other adsorbents. The reducibility of CuO/ZnO/Al₂O₃ was measured via H₂-TPR, using a TPR/TPD AutoChem II 2920 instrument (Micromeritics).

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