Chemical Engineering Journal 288 (2016) 671–679

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Warm plasma catalytic reforming of biogas in a heat-insulated reactor: Dramatic energy efficiency and catalyst auto-reduction

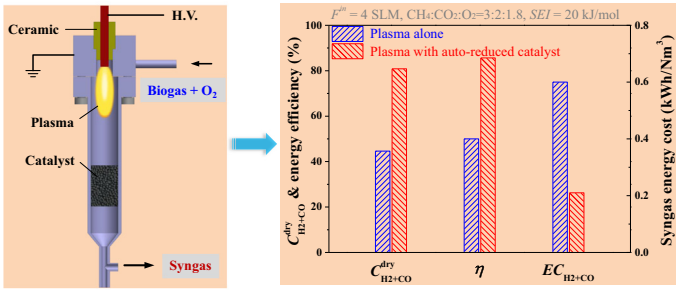
Kai Li, Jing-Lin Liu, Xiao-Song Li, Xiaobing Zhu *, Ai-Min Zhu *

Laboratory of Plasma Physical Chemistry, Dalian University of Technology, Dalian 116024, China
Center for Hydrogen Energy and Liquid Fuels, Dalian University of Technology, Dalian 116024, China

HIGHLIGHTS

- Highly efficient warm plasma catalytic reforming of biogas was reported.
- Ni-based catalyst could be auto-reduced in the heat-insulated reactor.
- Energy efficiency improved dramatically to 86%.
- Syngas energy cost reduced significantly to 0.21 kW h/N m^3.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 September 2015
Received in revised form 9 December 2015
Accepted 13 December 2015
Available online 18 December 2015

Keywords:
Plasma catalysis
Warm plasma
Ni catalyst
Biogas reforming
Syngas

ABSTRACT

Highly efficient warm plasma catalytic reforming of biogas in a compact and heat-insulated reactor using gliding arc discharge with a co-axial electrode configuration and Ni-based catalyst was reported. The effect of inlet flow rate at a special energy input (*SEI*) of 20 kJ/mol for the plasma alone was first investigated and the inlet flow rate was selected at 4 SLM. Then, it was found that the Ni-based catalyst could be auto-reduced by the outgoing gas from the warm plasma via comparing with the pre-reduced catalyst in the reforming reaction testing and characterizations of Brunauer–Emmett–Teller (BET) surface area, X-ray diffraction (XRD) and transmission electron microscopy (TEM). The effect of catalyst-bed position (*l*) was also examined. Feeding with the molar ratio of CH_4:CO_2:O_2 = 3:2:1.8, for the warm plasma with the auto-reduced $Ni/CeO_2/Al_2O_3$ catalyst located at *l* = 4 cm, dry-basis concentration of syngas rose substantially to 81% and energy efficiency improved dramatically to 86%. Syngas energy cost reduced significantly to 0.21 kW h/N m^3, which is nearly a threefold reduction compared with the plasma alone. The stability of the warm plasma catalytic reforming was preliminarily evaluated over time-on-stream (TOS) of 13.5 h.

1. Introduction

Biogas, typically consisting of 60% CH_4 and 40% CO_2, is a renewable, carbon-neutral and widely available resource for syngas (H_2 + CO) production via reforming [1,2]. Oxidative reforming (also called partial oxidation) of biogas with O_2 or air is of low energy cost due to its mild exothermicity and has attracted more attention. Conventional catalytic technique for oxidative reforming bears a drawback of hot-spot which results in catalyst sintering and subsequently deactivation [3,4].

An alternative technique is non-thermal plasma, in which reactant molecules collide with energetic electrons to produce radicals via excitation and dissociation pathways, followed by radical reactions to form final products. It has several merits, such as

* Corresponding authors at: Laboratory of Plasma Physical Chemistry, Dalian University of Technology, Dalian 116024, China. Tel./fax: +86 411 84706094.
E-mail addresses: xzhu@dlut.edu.cn (X. Zhu), amzhu@dlut.edu.cn (A.-M. Zhu).

http://dx.doi.org/10.1016/j.cej.2015.12.036
1385-8947/

compactness, feed flexibility, durability, and quick start. Non-thermal plasma can be categorized into two types, *i.e.* cold and warm plasmas [5]. Cold plasma, usually generated by corona or dielectric barrier discharges, suffers high energy cost of syngas (>10 kW h/N m^3) or low energy efficiency (<10%) in biogas reforming [6–10]. Warm plasma, normally produced by spark or gliding arc discharges, exhibits much higher energy efficiency than cold plasma for biogas reforming [11–16]. Using gliding arc discharge, Wu et al. [11] reported energy efficiency of 27% and syngas energy cost of 3.3 kW h/N m^3 with 36% of CH_4 conversion and 35% of CO_2 conversion at a molar ratio of CH_4:CO_2 = 1; Tu et al. [12] reported energy efficiency of 41% and syngas energy cost of 4.0 kW h/N m^3 with 13% of CH_4 conversion and 8% of CO_2 conversion at a molar ratio of CH_4:CO_2 = 0.43. In our previous work, using spark discharge, energy efficiency of 41% and syngas energy cost of 4.3 kW h/N m^3 with 76% of CH_4 conversion and 57% of CO_2 conversion at CH_4:CO_2:O_2 molar ratio of 3:2:1 was reported [14]. Subsequently, developed a rotating-electrode spark-shade plasma, energy efficiency of 54% and syngas energy cost of 1.2 kW h/N m^3 with 83% of CH_4 conversion and 35% of CO_2 conversion at CH_4:CO_2:O_2 molar ratio of 3:2:2 was reported [16].

Although the energy efficiency of warm plasma in biogas reforming is much higher than that of cold plasma, it should be further improved to meet the requirement of practical application. The exploration for the combination of warm plasma with catalyst in biogas reforming has been made. We [17] recently explored the spark-shade plasma with Ni-based catalyst kept at 800 °C by a tube furnace, assuming that the plasma could supply the heat energy for the subsequent catalytic reaction at 800 °C, and achieved energy efficiency of 70% and syngas energy cost of 1.0 kW h/N m^3 with 100% of CH_4 conversion and 35% of CO_2 conversion at CH_4:CO_2:O_2 molar ratio of 3:2:1.8. Rafiq et al. [18] investigated gliding arc discharge followed by Ni/Al_2O_3 catalyst in a heat-insulated reactor and reported energy efficiency of 59% and syngas energy cost of 0.8 kW h/N m^3 with 86% of CH_4 conversion and 4% of CO_2 conversion at CH_4:CO_2:O_2 molar ratio of 3:2:2. However, due to their gliding arc technique using two-dimensional (2D) flat electrode configuration, the complete stoichiometric burning of propane was required to increase the temperature during the start-up stage. Moreover, almost no CO_2 was converted and syngas energy cost should be further reduced.

In the present paper, we report warm plasma catalytic reforming of biogas in a compact and heat-insulated reactor using a three-dimensional (3D) co-axial electrode configuration for gliding arc discharge. It features dramatic energy efficiency, easy and fast start-up where any assistance do not need. Additionally, the Ni-based catalyst for biogas reforming is usually available in the oxide form and hence the catalyst pre-reduction prior to start-up is necessary. This work revealed the Ni-based catalyst could be auto-reduced during the start-up, which offers a simple technique without any activation or pre-reduction of catalyst for plasma catalytic reforming.

2. Experimental

2.1. Warm plasma catalytic reactor

The schematic diagram of the warm plasma catalytic reactor, which is made of stainless steel, was shown in Fig. 1(a). The cylinder with inner diameter of 20 mm was grounded. The high-voltage electrode with a ceramic electric insulator was located at the axis of the cylinder and powered by an AC high-voltage power supply (CTP-2000K, Nanjing Suman electronics Co., China) to generate gliding arc discharge. For heat insulation, ceramic fiber cotton was wrapped around the reactor (Fig. 1(b)). The simulated biogas (CH_4:CO_2 = 3:2) mixed with O_2 at a molar ratio of CH_4:CO_2:O_2 = 3:2:1.8 was used as the feed gas and introduced tangentially into the reactor from its top at room temperature. This experiment was conducted at atmosphere pressure and the gas flow rates were controlled by mass flow controllers.

The supported Ni/CeO_2/Al_2O_3 catalyst was packed into the cylinder and the temperature variation with axial distance from the catalyst-bed entrance was measured by a thermocouple. The catalyst-bed position was indicated by the distance (l) between the entrance of the catalyst bed and the top of the cylinder. It should be pointed out that, for heating the catalyst, the thermal energy only came from the warm plasma and there was not any extra heater.

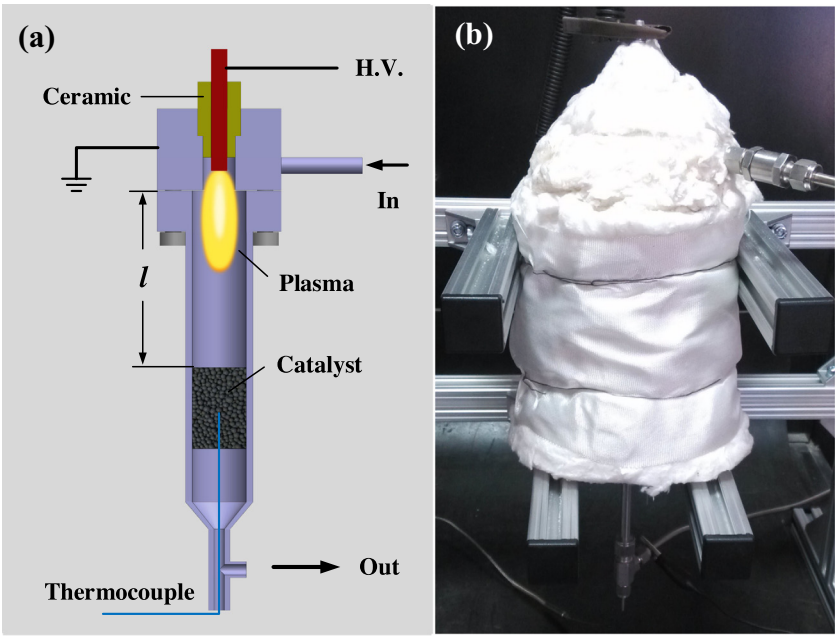


Fig. 1. (a) Schematic of the warm plasma catalytic reactor and (b) photo of the reactor with heat-insulation jacket.