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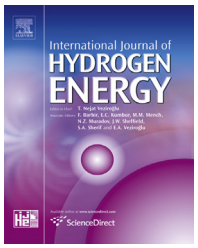

Experimental investigation on biogas reforming to hydrogen rich syngas production using solar energy

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ABSTRACT

In the present study catalytic reforming of biogas was investigated to produce hydrogen rich syngas using solar energy source. The main objective of this work is to upgrade the quality of biogas using solar thermal energy. A foam type Ni based Al_2O_3 catalyst reactor was designed and developed for the catalytic reforming of biogas. Since dry reforming reaction of biogas being endothermic reaction, a 16 m^2 solar concentrating collector was employed for supplying this heat. The performance of the reactor in terms of product gas composition at different temperatures using solar thermal energy was analysed. The results of the reforming reaction of biogas using solar energy have shown the conversion of both CH_4 and CO_2 into H_2 and CO. The experimental results were compared with thermodynamic chemical equilibrium analysis. The flame study of biogas and syngas was done with gas samples. The in situ production of hydrogen rich syngas can also address the issue of hydrogen storage. The hydrogen rich syngas can be used in I. C. engine, fuel cell and methanol production applications.

Introduction

The biogas can be produced from farm waste, animal manure, weeds and organic waste. Biogas mainly contains CH_4 and CO_2 and a small quantity of H_2S. The presence of CO_2 in biogas restricts its application as fuel in I.C. engines, gas turbines and fuel cells. However main content of biogas like CH_4 and CO_2 can be reformed to H_2 and CO in presence of catalyst to form syngas. The reforming reactions are of two types i.e endothermic which requires the external heat supply and another one exothermic in which heat is released during the reaction at the expense of the fuel. The production of hydrogen enrich gaseous fuel by the reforming of biogas can increase the share of renewable energy in the world. Lau C. S. et al. [1] demonstrated the upgradation of biogas to hydrogen enrich gaseous fuel using exhaust gas fuel reforming for use in transportation. By studying dry reforming and combined dry/oxidative reforming Lau C. S. et al. [2] observe that gas stream temperature and reactor space velocity are two important factors which will affect the process. In case of combined dry/oxidative process another factor which affect the performance is O_2/CH_4 ratio. Shyamsundar A. C et al. [3] investigated the effect of a major impurity (i.e., H_2S) on a commercial

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methane reforming catalyst during hydrogen production. The study found that even with the introduction of small amount of H_2S (0.5 mol%), the CH_4 and CO_2 conversions dropped to about 20% each as compared to 65% and 85%, respectively in the absence of H_2S. Stephen G. et al. [4] studied the syngas production capabilities of landfill (LF), corn cob (CC), whole stillage (WS), and combined cob and stillage (CS) biogas. Three cases were considered: Case 1 (Dry Reforming of Methane only), Case 2 (Dry reforming and partial oxidation) and Case 3 (Dry reforming and hydrogen oxidation). The thermo neutrality was observed in case 2 (Dry reforming and partial oxidation). Robert W. et al. [5] developed system for methane reforming using solar thermochemical reforming system to upgrade the heating content of natural gas. Fidalgo B. et al. [6] investigated microwave assisted CO_2 reforming of CH_4 over the carbon catalyst for studying energy consumption and conversions. Yuan J. O. et al. [7] conducted partial oxidation of methane (POM) in the presence of air ($2CH_4$:$1O_2$) at 750 °C for 6 h with NiM shown almost 100% conversion of CH_4 and CO_2. Yuan J. O. et al. [8] performed partial oxidation of methane (POM) and dry reforming of methane (DRM) coupled reactions ($1.5CH_4$: $1CO_2$: $0.25\ O_2$), to produce syngas (H_2/CO), at 750 °C for 7 h with the catalyst NiO–MgO–ZrO_2 including 20 wt.% nickel content showed the best activity and selectivity in the catalytic processes. Nader R. et al. [9] used Ni–Cu/Al_2O_3 nano catalysts toward syngas production from reforming of CH_4/CO_2 shown highest conversion of both CH_4 and CO_2 at 850 °C and gas hourly space velocity of 24 L/g hr. Bappy S. et al. [10] done experimentation on alumina based catalysts for the sulfur tolerance during the dry reforming of biogas. The result reveal that the catalysts formulation Ni/CaO–Al_2O_3 was suitable for feeds with H_2S and free of H_2S suitable for both methane-rich and/or lean feeds. Yuan J. O. et al. [11] analysed that on oxidative reforming of a model biogas ($CH_4/CO_2 = 1.5/1$) in presence of oxygen ($CH_4/CO_2/O_2 = 1.5/1/0.25$) at 750 °C for 6 h gave H_2/CO ratios in the reaction products formed on the best catalyst were 1:1. Arroyo J. et al. [12] investigated spark ignition engine fuelled with synthetic gas, gasoline, methane and biogas. Results showed that fractions of hydrogen in synthetic gases increased maximum pressures inside cylinder. Moreover, peak pressures were detected closer to top dead center than methane and biogas. In case of synthetic gases, high speeds and lean conditions resulted in higher indicated efficiencies than those obtained with gasoline. Changwei J. et al. [13] investigated effect of syngas addition on the performance of a gasoline engine at lean condition. The syngas addition helped improve the indicated thermal efficiency and shorten the combustion duration. HC, NO_x emissions and particle total number per cubic centimeter were reduced after the syngas addition at lean condition. Das L. M. et al. [14] investigated introduction of hydrogen in diesel engine. The performance improvement can be achieved by way of hydrogen substitution in a small horsepower diesel engine widely adopted in rural/agricultural sector of developing countries. Galvagno A. et al. [15] carried out investigation on biogas reforming processes using mathematical model, in Aspen Plus. The work deals with application of hydrogen rich syngas to fuel cell application. In the present work dry reforming reaction of biogas with varying proportion of CH_4 and CO_2 was investigated in the presence of Ni based Al_2O_3 catalyst. This reaction is endothermic which requires the external heating, which was given by a considerable size of solar concentrator in present case. A 16 m^2 solar concentrator was employed for producing the necessary heat input for the reaction. Dry reforming reaction is of particular interest for this work since both the main components of biogas (i.e. methane and carbon dioxide) are consumed to produce hydrogen and carbon monoxide, as shown in Eq. (1). However, the DRR is a slow reacting process and it is affected by the contact time between the reactor gas feed and the catalyst. The reaction is highly endothermic reaction.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (\Delta Hr = 260.62\ kJ/mol) \tag{1}$$

Materials and methods

Catalyst preparation

The catalyst plays a vital role in the conversion of biogas into syngas. In this work alumina based foam type catalysts were used. The catalysts were Ni coated using wet impregnation method. The alumina foam can sustain temperature as high as 1750 °C. The pretreated γ-alumina was added to the solution of Ni $(NO_3)_2.6H_2O$ in demineralised water and the mixture was dried in desiccators. Then through a programmed increase in temperature from 110 °C to 500 °C, the mixture was calcined at 500 °C over a period of time. The total porosity of alumina foam catalyst was 80% (vol %). Linear pore density of alumina foam was 27 pores per inch (ppi). Finally the prepared catalyst as shown in Fig. 1 was cut into required shape and placed in copper tube reactor which was used as receiver of the solar collector.

Experimental setup

Solar concentrating system

In this work a solar concentrating collector having 16 m^2 area was used with copper reactor. This collector is single point focus thermal heating system with sun tracking around the clock during the day. The temperature was measured with multiple k-type thermocouples placed inside the reactor. The accuracy of the temperature measuring device was ±1 °C. It is

Fig. 1 – Alumina foam type catalyst with Ni coating.