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Hydrogen production from biogas reforming and the effect of H₂S on CH₄ conversion

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ARTICLE INFO

Article history:

Received 21 August 2014

Received in revised form

24 September 2014

Accepted 29 September 2014

Available online xxx

Keywords:

Biogas reforming

Hydrogen sulfide

Hydrogen selectivity

Catalytic poisoning

ABSTRACT

Biogas produced during anaerobic decomposition of plant and animal wastes consists of high concentrations of methane (CH₄), carbon dioxide (CO₂) and traces of hydrogen sulfide (H₂S). The primary focus of this research was on investigating the effect of a major impurity (i.e., H₂S) on a commercial methane reforming catalyst during hydrogen production. The effect of temperature on CH₄ and CO₂ conversions was studied at three temperatures (650, 750 and 850 °C) during catalytic biogas reforming. The experimental CH₄ and CO₂ conversions thus obtained were found to follow a trend similar to the simulated conversions predicted using ASPEN plus. The gas compositions at thermodynamic equilibrium were estimated as a function of temperature to understand the intermediate reactions taking place during biogas dry reforming. The exit gas concentrations as a function of temperature during catalytic reforming also followed a trend similar to that predicted by the model. Finally, catalytic reforming experiments were carried out using three different H₂S concentrations (0.5, 1.0 and 1.5 mol%). The study found that even with the introduction of small amount of H₂S (0.5 mol%), the CH₄ and CO₂ conversions dropped to about 20% each as compared to 65% and 85%, respectively in the absence of H₂S.

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Introduction

Growing energy demand due to population expansion has heightened the need for alternate energy sources. An ideal source of energy would be cheap, clean, renewable and sustainable in nature. One such energy source is biogas produced by anaerobic decomposition of plant and animal wastes typically consisting of 55–75% methane (CH₄), 25–44% carbon dioxide (CO₂) and 0.5–2% of hydrogen sulfide (H₂S) [1]. It is usually produced in landfills, sewage sludge and bio-waste

digesters [2]. Methane and CO₂ are the two main greenhouse gases, which upon release into earth's atmosphere, yield unfavorable results such as global warming. Methane and CO₂ contribute to 4–9% and 9–26% of the total greenhouse effect, respectively, and hence their emissions needs to be controlled [3]. The steady increase in the atmospheric CH₄ concentration (0.6–0.8% annually) has been a major concern [4]. Landfills are important sources for the emission of methane into the atmosphere and contribute to about 10% of total anthropogenic methane emitted [5]. About 2.6 million tons of CH₄ are captured annually from landfills across the U.S., 70% of which

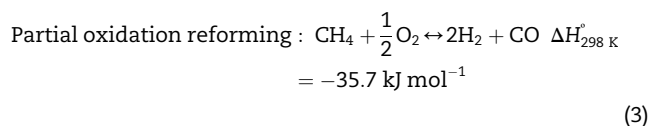
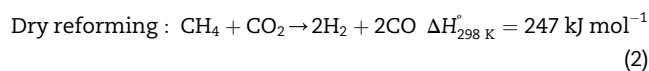
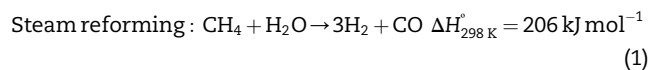
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<http://dx.doi.org/10.1016/j.ijhydene.2014.09.162>

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is converted to heat and electricity [6]. Steam reforming, dry reforming and partial oxidation (Equations (1)–(3), respectively) are three major techniques for conversion of CH₄ in biogas to H₂ and CO, which then can be used for the production of liquid fuels or used in the fuel cells [7,8].



Hydrogen has a very high energy content of 144 MJ/kg and burns clean without leaving ash [9]. Braga et al. conducted an economic and ecological analysis of H₂ production by steam reforming of biogas and reported the process was economically feasible and free from causing environmental impacts. The cost for H₂ production was estimated to be 0.27 US\$/kWh with a payback period of eight years and the ecological efficiency was 94.95% [10].

Although there are different reforming techniques, the focus of this work was on dry reforming of biogas for the conversion of both CH₄ and CO₂ to more useful syngas: H₂ and CO. Syngas can be converted to liquid hydrocarbons in the presence of Fe and Co catalysts via Fischer-Tropsch synthesis [11]. Dry reforming reaction is an endothermic reaction usually dominant at 750 °C–850 °C [7]. Many researchers have studied dry reforming of biogas. For example, Lau et al. studied the conversion of biogas to syngas using dry and oxidative reforming. They reported that oxidative reforming is dominant at low temperatures, while dry reforming is dominant at higher (>600 °C) temperatures [12]. Asencios et al. tested the performance of NiO–MgO–ZrO₂ catalyst on reforming model biogas at 750 °C and demonstrated that the addition of MgO to Ni/ZrO₂ improved CH₄ and CO₂ conversions [13]. A comparative study of fixed bed reactor and micro-reactor for H₂ production by biogas reforming using Ni, Rh–Ni promoted on alumina catalyst was done by Izquierdo et al. Furthermore, the importance of catalytic surface properties and morphology in driving the reforming reaction was emphasized by performing physicochemical catalyst characterizations like TPR, SEM, XPS, XRD, H₂ chemisorption, N₂ physisorption and ICP-AES [14]. Xu et al. investigated biogas reforming over Ni and Co/Al₂O₃–La₂O₃ catalyst in a fixed bed reactor using an inlet gas consisting of CH₄ and CO₂ having a molar ratio of one. They found that the addition of Co improved the performance of the Ni/Al La catalyst in terms of CH₄ and CO₂ conversions [15]. Lucrecio et al. investigated the effect of adding La on Ni–Rh/Al₂O₃ catalyst during reforming of model sulfur-free biogas. They observed that La reduced the carbon deposition by favoring gasification of carbon species [16]. Kohn et al. studied dry reforming of biogas in the presence of CH₃Cl using 4% Rh/Al₂O₃ catalyst in the temperature range 350–700 °C. They observed an increase in acidity of the catalyst due to the adsorption of chloride on its surface. The

study also reported that thermodynamically, the chloride adsorption is less favored at higher temperatures. However, the CH₄ concentration did not change and the only factor that was affected by CH₃Cl was H₂:CO ratio [17].

Although a number of studies have been conducted on biogas reforming, most of them have assumed a model gas mixture that does not contain H₂S. The work done by Appari et al. is an exception who proposed a detailed kinetic model capable of simulating the reforming of biogas even in the presence of H₂S over Ni based catalyst. They reported that operating at high temperatures (900 °C) mitigates sulfur adsorption, while lower temperature (700 °C) operation results in complete catalyst deactivation [18].

The goal of this study was to investigate the effect of temperature and H₂S concentration in biogas since many studies have neglected H₂S while conducting biogas reforming studies. The poisoning effect on the commercial catalyst was evaluated in terms of reduction in CH₄ and CO₂ conversions with the introduction of H₂S at three different concentrations.

Materials and methods

Materials

Dry reforming of biogas was carried out in a fixed-bed reactor as described elsewhere [7]. Reforming reactions were performed at temperatures from 650 °C to 850 °C and atmospheric pressure using a commercial CH₄ reforming catalyst (Reformax[®] 250). Experiments were conducted both in the presence and absence of H₂S. For runs performed in the absence of H₂S, the inlet gas consisted of a mixture of 59% CH₄, 2% N₂, and 39% CO₂ (all in mole percentage). For runs conducted in the presence of H₂S, the inlet gas composition had CH₄ and CO₂ in the molar ratio 1.5, H₂S concentrations were 0.5, 1.0 and 1.5% and the balance was N₂. The basis for selecting this mixture is to have an inlet stream with concentrations similar to the typical concentrations in biogas [18]. The flow rate of the model biogas was maintained at 60 cc/min using a rotameter (Omega, Stamford, Connecticut, USA). Experiments were conducted at three levels of temperature (650, 750 and 850 °C) in triplicates. The size of the commercial catalyst (Reformax[®] 250 – purchased from SudChemie, USA) used was between 707 μm and 420 μm; however its composition is proprietary. Hydrogen temperature programmed reduction (TPR) analysis was carried out using Autosorb-1Q (Quantachrome, Boynton Beach, Florida, USA) to measure the optimum temperature for catalyst reduction.

Experiments

An experimental setup used for this study is illustrated in Fig. 1, similar to the one used in the published document [7]. A known weight of the catalyst (0.20 g or 0.35 g) was loaded into the reactor, calcined and reduced *in-situ* at 800 °C with 60 cc/min of 5% H₂ in He for 2 h each time before an experiment was conducted. The residence time used for the experiments was 3.3×10^{-3} g_{cat} min/cc. Experiments were carried out for 5 h to test the stability of the catalyst under different experimental conditions. Exit gas composition was measured using a gas

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