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Catalytic steam reforming of biogas – Effects of feed composition and operating conditions

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ABSTRACT

A study was conducted on the steam reforming of biogas mixtures over a 4 wt.% Rh/La–Al₂O₃ catalyst, where the effects of temperature (590–685 °C), steam (S/C molar ratio = 1.28–3.86), CO₂/CH₄ molar ratio (0.55–1.51), and the gas hourly space velocity (9810–27,000 hr⁻¹) on the conversions and product yields were evaluated. Within these ranges, temperature and steam had the most pronounced effect on methane and carbon dioxide conversions. The highest methane conversion observed was 99%. Low temperatures and high S/C resulted in a net CO₂ production. The water gas shift reaction appeared to have a stronger effect on the CO₂ conversion than the CO₂ reforming reaction. Experimental methane conversions were lower than the equilibrium predicted values. Lower temperature operations yielded a lower carbon balance suggesting the tendency to form carbonaceous species other than CO, CO₂, and CH₄. The presence of CO₂ in the biogas contributed to the CO yield (beyond that from CH₄ steam reforming) only above certain CO₂/CH₄ ratios.

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Introduction

Biogas is commonly referred to a gas produced by the biological breakdown of organic matter in the absence of oxygen, such as the anaerobic digestion or the fermentation of biodegradable materials of algal biomass, manure, municipal waste in landfills, sewage sludge in waste water treatment plants, rubbish dumps, septic tanks, green waste and energy crops, etc. This type of biogas comprises primarily methane and carbon dioxide [1]. Other components present include moisture, nitrogen, volatile organic compounds, and sulfur species – primarily hydrogen sulfide. The actual composition

of biogas varies depending on the anaerobic digestion process and the feedstock [2].

Biogas has been accepted to be a versatile renewable energy source and is receiving increased interest [3] because it can be used to replace fossil fuels for power and heat productions, and thus play an important role in minimizing global warming and climate change impacts. For biogas utilization, one widely studied subject is the biogas upgrading [4–6] through carbon-dioxide removal by physical separation technologies. This generates a methane-rich biogas (biomethane) as a natural gas substitute for various applications, including as a feedstock for producing chemicals and

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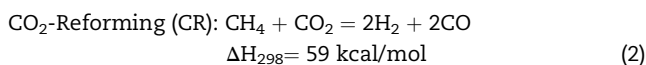
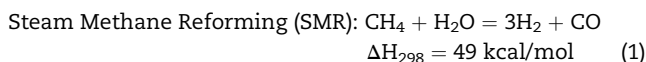
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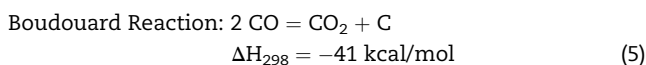
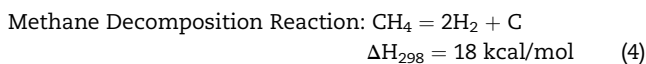
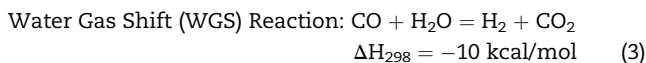
materials and its direct connection to pipe-line for network distribution. Biogas steam and oxidative reforming [7–10] have also received considerable research studies for either producing synthesis gas (a mixture of H₂ and CO) suitable for many industrial synthesis processes for fuels, such as gasoline, gasoil, kerosene, aldehydes, and alcohols [11,12] or producing hydrogen for fuel cell applications.

The methane in the biogas can be reformed by the steam methane reforming reaction and by the CO₂-reforming reaction.



Both of these reactions are highly endothermic and are favored by low pressures and high temperatures. The thermodynamics, catalyst selection and activity, reaction mechanisms, and kinetics of this CO₂-reforming reaction were reviewed in the literature [13].

In addition to these major reforming reactions, other potential side reactions include:



At the reformer temperatures, organic sulfur in the biogas can also react with hydrogen and carbon oxides to form H₂S and COS.

The CO₂-reforming of methane (reaction 2) offers some advantages over the steam reforming of methane (reaction 1). It produces a synthesis gas with a lower H₂/CO ratio (~1) that is a preferable feed gas and has higher energy efficiency for producing liquid fuels via the Fischer–Tropsch reaction [14]. The higher endothermicity of the reaction is attractive for conversion of solar or nuclear energy to chemical energy for storage in the form of CO and H₂. Catalyst deactivation during CO₂-reforming reaction has been a major obstacle in commercial implementation of this reaction. Coke formation is the primary reason for the catalyst deactivation [15–17] and it can be significantly inhibited by adding a small amount of steam [18]. Thus steam reforming of biogas to utilize the combined steam reforming and CO₂-reforming of methane can be a viable process for producing synthesis gas from biogas. Effendi et al. has studied the steam reforming of a clean model biogas in fluidized- and fixed-bed reactors [19,20].

Recent research has also centered on the development of catalysts for biogas reforming [21–23]. In our in-house studies,

a Rh supported on La-stabilized Al₂O₃ catalyst has been shown to have significantly higher activity and hydrogen selectivity for reforming reactions than other noble-metal catalysts [24]. This catalyst also showed good long-term stability than Rh on Y-ZrO₂, Gd-CeO₂, γ-Al₂O₃ and CaAl₁₂O₁₉, and was selected in our earlier work for the studies of autothermal reforming of natural gas [25] and steam reforming of ethanol [26]. Because of its good catalytic performance characteristic, this catalyst was selected in this study for steam reforming of biogas to produce a hydrogen-rich stream that can be used for upgrading biofuels.

Experimental

Catalyst: A Rh supported on La-stabilized Al₂O₃ catalyst was used in this study. Based on literature data and in-house experience [24], the La-stabilized alumina was selected as the support for Rh since (1) lanthanum as a basic oxide supports gasification of carbon in reforming reactions; (2) lanthanum forms a lanthanum aluminate (LaAlO_x) at the surface which has been shown to prevent the migration of Rh into the support. A 4 wt.% Rh/La–Al₂O₃ was prepared in house using the incipient wetness technique by adding a sufficient amount of solution containing rhodium nitrate (Rh(NO₃)₃–2H₂O, Alfa Aesar, Johnson Matthey Co.) to La–Al₂O₃ (3.1 wt.% La, HIQ X-160, 160 m²/g, Alcoa World Alumina) to yield a 4 wt.% loading of Rh. The 4 wt.% Rh/La–Al₂O₃ was then dried overnight at 100 °C and calcined by heating from room temperature to 700 °C at 5 °C/min heating rate, followed by holding at the temperature for 1 hr. The catalysts were crushed and sieved to particle sizes between 150 and 250 microns before being loaded into the reactor for experimental testing. The BET surface area of the calcined catalyst was 122 m²/g.

Biogas mixtures: A certified-grade cylinder mixture of methane and carbon dioxide was used as a biogas surrogate for experimental testing in this work. Table 1 shows four cylinder mixtures (Airgas USA, LLC) that were used for this study. As will be shown in the next section, the mixture was further mixed with controlled amounts of nitrogen (also served as a controlling inert for chemical analysis of the product gas) and steam to form a feed stream to the reactor.

Experimental apparatus: Fig. 1 shows the schematic of the micro-reactor process system installed in this work for studying the steam reforming of biogas mixtures (Table 1). A controlled amount of CH₄-CO₂ mixture is pre-mixed with a controlled amount of nitrogen and then flows directly to the steam generator (controlled at 120 °C), inside which a heater

Table 1 – Chemical composition of the biogas mixtures studied.

Biogas mixture	Chemical composition, %		CO ₂ /CH ₄ feed ratio
	CO ₂	CH ₄	
1	60.22	39.78	1.51
2	49.42	50.58	0.98
3	39.54	60.46	0.65
4	35.42	64.58	0.55

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