Energy Conversion and Management 171 (2018) 133–155

Contents lists available at ScienceDirect

Energy Conversion and Management

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

Review

# A review of recent developments in hydrogen production via biogas dry reforming

Yuchen Gao[a], Jianguo Jiang[a,b,c,*], Yuan Meng[a], Feng Yan[a], Aikelaimu Aihemaiti[a]

[a] School of Environment, Tsinghua University, Beijing 100084, China
[b] Key Laboratory for Solid Waste Management and Environment Safety, Ministry of Education of China, China
[c] Collaborative Innovation Center for Regional Environmental Quality, Tsinghua University, Beijing 100084, China

ARTICLE INFO

*Keywords:*
Biogas
Dry reforming
Renewable energy
Hydrogen production
Greenhouse gases

ABSTRACT

Biogas is a promising renewable energy resource. Among the existing biogas utilization technologies, dry reforming can convert two major greenhouse gases in biogas, methane and carbon dioxide, into syngas. In this review, we summarize the recent advances in biogas dry reforming toward hydrogen production, including the preparation of catalysts, the optimization of operation conditions, and the influence of impurities in biogas. The development of bimetallic catalysts and core-shell structure catalysts has become increasingly attractive due to their high catalytic activity and stability. Choosing active metals, supports, and promoters for catalysts is systematically discussed, and different catalyst synthesis methods are compared. Solid waste-derived catalysts have been developed as a new approach to obtain a high added value of solid waste and reduce the costs of catalyst preparation. The influences of reaction temperature, pressure, calcination conditions, reduction conditions, and gas hourly space velocity on dry reforming reactions are discussed in detail. In addition to conventional fixed bed and fluidized bed reactors, several newer reactors are introduced, including membrane reactors, microreactors, and solar thermal flow reactors. Impurities in biogas such as hydrogen sulfide, oxygen, and siloxanes have significant effects on dry reforming. These effects are summarized to improve overall understanding of biogas dry reforming and to provide guidelines for its industrial application in hydrogen energy generation.

## 1. Introduction

Climate change and energy depletion are the two most serious challenges of the modern era [1]. With industrialization and rapid population growth, energy consumption has increased quickly over the past years and will continue increasing in the future [2]. There is still a high dependence on traditional fossil fuels, including coal, petroleum, and natural gas, although these fuels cause serious greenhouse gas (GHG) emissions during combustion. They release additional carbon that had been sealed away from the ecosystem, which contributes greatly to global warming and climate change [3]. Table 1 demonstrates the GHG emissions of several major contributors and their global levels in 2014. Fig. 1shows the temporal evolution (from 1990 to 2014) of GHG emissions of the world and these contributors. The emission data are cited from the World Resources Institute. In 2014, global GHG emissions reached up to 45740.70 million tons carbon dioxide ($CO_2$) equivalent (Mt $CO_2$e) with the major component, $CO_2$, accounting for 75.87% [5]. China, the European Union (EU), and the United States (U.S.) top the list of global GHG emissions-producing countries, and their combined emissions amount to more than half of the global total. Notably, in the past 10 years, the energy sector has been the primary source of GHG emissions. Taking 2014 as an example, GHG emissions from the energy sector accounted for 78% of the world total [5]. As for the three aforementioned largest contributors, their proportions of GHG emissions from the energy field all exceed 80% [5]. On the other hand, because fossil fuels are non-renewable, they cannot satisfy the soaring energy demand over the long term. Therefore, the utilization of renewable energy is urgently needed to reduce GHGs. As of 2012, more than 100 countries have established policies and targets for renewable energy [4].

Biogas is a common source of renewable bioenergy. It is derived from different feedstocks, which are usually devided into three generations. The first-generation feedstocks mainly involve seeds, grains and sugars. The second-generation feedstocks refer to lignocellulosic biomass like crop residues and woody crops [203]. In recent years, algae emerges as a promising third-generation feedstock due to the high growth rate and carbohydrate content [204], which has obtained increasing attention. In general, raw biogas is mainly composed of methane ($CH_4$) (35–75%) and $CO_2$ (25–55%). There are other minor components including nitrogen ($N_2$), oxygen ($O_2$), hydrogen ($H_2$),

* Corresponding author at: School of Environment, Tsinghua University, Beijing 100084, China.
*E-mail address:* jianguoj@tsinghua.edu.cn (J. Jiang).

https://doi.org/10.1016/j.enconman.2018.05.083
Received 2 April 2018; Received in revised form 14 May 2018; Accepted 22 May 2018
0196-8904/ 

**Table 1**
Greenhouse gas (GHG) emissions of major contributors in 2014 (excluding land-use changes and forestry).

| Countries | Total GHG emissions (Mt $CO_2$e) | Total $CO_2$ | | Total $CH_4$ | | Total $N_2O$ | | Total F-gas | |
|---|---|---|---|---|---|---|---|---|---|
| | | Amount (Mt $CO_2$e) | Percent (%) | Amount (Mt $CO_2$e) | Percent (%) | Amount (Mt $CO_2$e) | Percent (%) | Amount (Mt $CO_2$e) | Percent (%) |
| China | 11911.71 | 10328.73 | 86.71 | 933.96 | 7.84 | 437.81 | 3.68 | 211.21 | 1.77 |
| United States | 6371.10 | 5234.24 | 82.16 | 652.47 | 10.24 | 277.80 | 4.36 | 206.59 | 3.24 |
| European Union | 4053.66 | 3246.99 | 80.10 | 417.96 | 10.31 | 297.74 | 7.34 | 90.97 | 2.24 |
| India | 3079.81 | 2158.18 | 70.08 | 609.91 | 19.80 | 262.02 | 8.51 | 49.70 | 1.61 |
| Russian Federation | 2137.82 | 1530.59 | 71.60 | 506.22 | 23.68 | 62.64 | 2.93 | 38.37 | 1.79 |
| Japan | 1314.59 | 1217.49 | 92.61 | 18.35 | 1.40 | 19.30 | 1.47 | 59.45 | 4.52 |
| World | 45740.70 | 34701.37 | 75.87 | 7200.37 | 15.74 | 2964.88 | 6.48 | 874.08 | 1.91 |

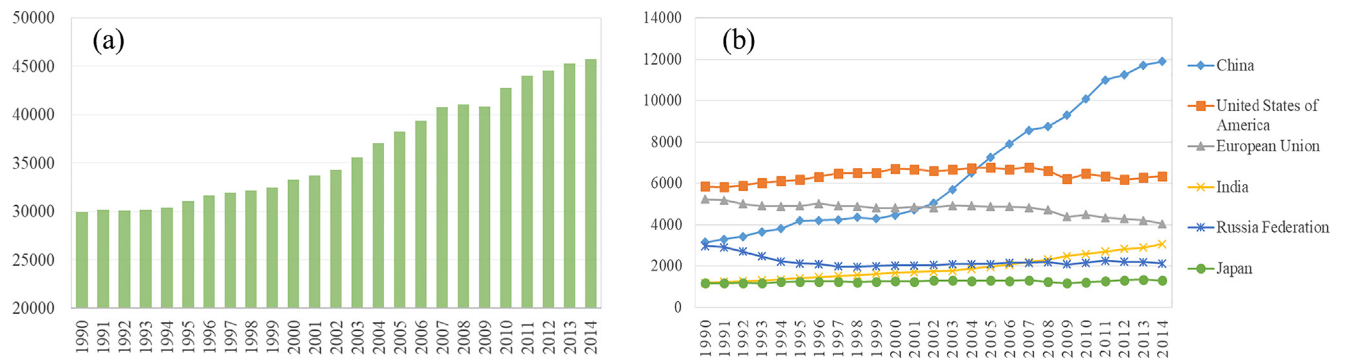


**Fig. 1.** Temporal evolution of GHG emissions in (a) world, (b) major contributors (Mt $CO_2$e).

**Table 2**
Properties and composition of biogas from different sources [6–10].

| Source | Sewage sludge digesters | Agricultural waste digesters | Landfills |
|---|---|---|---|
| Normal density (kg/N m$^3$) | 1.16 | 1.16 | 1.27 |
| Relative density | 0.9 | 0.9 | 1.1 |
| Wobbe Index (MJ/N m$^3$) | 26 | 27 | 18 |
| Dewpoint (°C) | 35 | 35 | 0–25 |
| Lower heating value (kW h/N m$^3$) | 6.0–7.5 | 5.0–7.5 | 4.4–5.5 |
| $CH_4$ (%) | 58–75 | 45–75 | 35–65 |
| $CO_2$ (%) | 20–40 | 25–55 | 15–40 |
| $N_2$ (%) | 0–8.1 | 0–5 | 1–25 |
| $O_2$ (%) | < 1 | 0.01–2 | 1–5 |
| $H_2$ (%) | traces | < 0.5 | 0 |
| $H_2S$ (ppm) | 0–62.9 | 10–180 | 0–427.5 |
| $H_2O$ (%) | n.r. | n.r. | 1–5 |
| CO (%) | < 0.2 | < 0.2 | < 0.2 |
| $NH_3$ (mg/N m$^3$) | traces | 0.01–2.50 | traces |
| Siloxanes (mg/N m$^3$) | 0.1–5.0 | traces | 0.1–5.0 |
| Benzene (mg/N m$^3$) | 0.1–0.3 | 0.1–1.1 | 0.6–35.6 |
| Toluene (mg/N m$^3$) | 2.8–11.8 | 0.2–7 | 1.7–287 |
| Total chlorine (mg/N m$^3$) | n.r. | 0–5 | 17.4–200 |

n.r., not reported.

hydrogen sulfide ($H_2S$), water vapor ($H_2O$), carbon monoxide (CO), ammonia ($NH_3$), siloxanes, and aromatics, as well as some dust particles. Table 2 illustrates the composition and physical properties of biogas from three different sources.

Interest in biogas production has increased in many countries since the 1970s, derived from the growing concerns about energy stock and environmental problems. China is the largest developing country and the second largest energy user, exceeded only by the U.S. [11]. China is also the largest producer and consumer of biogas. As a vast agricultural country, China produces more than 700 million tons of straw each year [12], which is an important contributor to rural biogas generation. With the encouragement of governmental policies and regulations, bioenergy has received increasing attention and undergone rapid development, and biogas is a crucial part of this revolution. Since the 1980s, the number of biogas installations in China has continuously increased. In 2008, government investment in the biogas sector reached USD 943.8 million per year. By the end of 2010, there were 40 billion domestic biogas plants and 15.4 billion m$^3$ of biogas were produced annually by these installations [13]. According to the *13th Five-year Plan for Renewable Energy Development* published in 2016, the biogas supply reached 19 billion m$^3$ in 2015 with an average annual growth rate of 6.3% compared to 2010, which could serve as a substitute for more than 11 million tons of standard coal per year. Biogas utilization is estimated to reach 44 billion m$^3$ in 2020, of which rural biogas utilization will account for 30 billion m$^3$. Other countries have also conducted substantial work on biogas production over the past decades. For example, total biogas production in Europe reached 10.9 metric tons in 2010, and some Asian countries, including India, had built 4.4 million domestic biogas installations by 2011 [13]. At the same time, increasing numbers of researchers have been studying the pathways of biogas utilization, including not only traditional ones such as heat and energy generation, but also new technologies such as conversion to hydrogen and liquid fuels. Another trend in recent years has been the development of biogas utilization from lower to higher end uses, to further develop the potential value of biogas and promote the industrialization and scaling of its utilization.

To clarify the general status of biogas utilization, we first present an overview of existing biogas utilization and purification technologies. Then we focus on biogas dry reforming, the next-generation technology. The developments and progress in biogas dry reforming technology, particularly during the past 5 years, are summarized and discussed in detail. The effects of impurities in biogas on the dry reforming reaction are also highlighted. Based on these discussions, we draw conclusions and present future perspectives of further research on biogas dry reforming.