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Hydrogen production from reforming of biogas: Review of technological advances and an Indian perspective

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ABSTRACT

This paper examines the benefits and potential of biogas generation and uses in India, with focus on advances made in hydrogen production by catalytic reforming technologies with steam, O_2, and CO_2 as the oxidants. Utilization of biomass by means of generating biogas is one of the easiest and cost effective methods of harnessing renewable energy. As India is an agricultural country, a tremendous amount of biomass and livestock waste is generated every year. Likewise the large population of India generates much food and municipal solid waste that is not being utilized for biogas generation. Fuel cells are one of the effective means of utilizing biogas, although the synthesis gas or hydrogen generated from biogas can also be used in internal combustion engines. Higher efficiency of fuel cells (45%) compared to internal combustion engines (30%) and even higher with co-generation systems (70%) make them highly desirable for biogas utilization for power generation. Investigations of hydrogen productionfor fuel cell use are in their infancy stage in India. Apart from a few scattered investigations not much work has been undertaken in the area of research. Large scale hydrogen production is achieved by steam reforming of hydrocarbons, in particular natural gas. Although the process is a proven technology it has come under considerable scrutiny due to its environmental impact and the energy intensive nature of the process. Several technical and scientific challenges have to be overcome for assimilation of the technology for hydrogen production from biogas and wide scale application in India. These challenges include development of less energy intensive features, highly active and poisons-resistant catalyst, and fuel cell development for utilization of biogas generated hydrogen.

1. Introduction

The energy sector at present is focused on generation of energy from traditional resources such as fossil fuels. Increased global energy demand and environmental concerns arising from release of greenhouse gases have contributed towards deployment of alternative energy generation options. Biomass as a renewable energy source, derived from biological material obtained from living organism i.e. plants or plant derived materials, is one of them.

The European Commission specified that there are large varieties of biomass available for potential conversion to energy such as agricultural by-products, forestry residue related industries, as well as the non-fossil, biodegradable parts of conventional industry and municipal solid waste (MSW) [1]. Biomass derived energy systems are suggested to become important contributors to sustainable energy systems and sustainable development in developed as well as developing countries in the near future [2]. According to the European Environmental Agency (EEA), 13% of the total energy consumption by 2020, would be provided by biomass [3].

Biomass can be the most suitable form of renewable energy source

Abbreviations: ACR, Autothermal Cyclic Reforming; AFC, alkaline fuel cell; ASU, Air separation unit; ATR, Autothermal reforming; ATRB, autothermal reforming of biogas; BNFC, Bio-nanostructured filamentous carbon; BOP, balance of plant; CHP, combined heat and power; COD, chemical oxygen demand; COPD, Chronic obstructive pulmonary disease; DR, Dry reforming; DRM, Dry reforming of CH4; EEA, European Environmental Agency; F-T, Fischer Tropsch; GE, General Electric; GHSV, Gas Hourly Space Velocity; GTL, Gas to liquid fuels; IISc, Indian Institute of Science; IITs, Indian Institutes of Technology; LAS, Lewis acid sites; MCFC, Molten carbonate fuel cell; MLD, Million litres per day; MSW, Municipal solid waste; MT, million tones; NPBD, National Project on Biogas Development; ODRB, Oxy dry reforming of biogas; OSC, Oxygen storage capacity; PAFC, Phosphoric acid fuel cell; PEMFC, Proton exchange membrane fuel cells; SDC, samaria doped ceria; SR, Steam reforming; SMR, Steam reforming of methane; SOFC, Solid oxide fuel cells; SRB, Steam reforming of biogas; WGS, Water gas shift reaction; WHSV, Weight hourly space velocity

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among various other renewable sources due to its many advantages. Biomass is produced abundantly in most part of the world. Continuous supply can be assured based on constant production. It is important to note that the annual production may vary, depending on the type of biomass grown. It is relatively cheaper to produce and some types of the biomass obtained as by-products are almost free. Biomass can also be directly used in some of the existing power generating infrastructure. Specially grown energy crops and other kinds of biomass can be co-fired with coal to generate electricity. The net calorific value from biomass ranges from about 8 MJ/kg for green wood, to 20 MJ/kg for dry plant matter to 55 MJ/kg for CH_4, as compared to 27 MJ/kg for coal [4].

The use of biomass can augment and complement that of fossil fuel. It will also help mitigate CO_2 emissions, as CO_2 produced from biomass and its utilization can be in part counter-balanced by the amount absorbed during its growth. India is one of the many countries that have ratified the UNFCCC Paris Agreement in 2016, thus committing to combat climate change. Cultivation and burning of *Miscanthus* (an energy crop) was predicted to reduce 9% of the total EU carbon emissions in 1990 [5]. The use of waste biomass will also help in moderating the CH_4 generated from decaying organic matter which otherwise can contribute towards green-house effect. By making use of the sugar cane bagasse for electricity production with sugar cane ethanol, it was reported that more than 100% reduction in GHG emissions is expected compared to gasoline/diesel [6].

Liquid fuels such as biodiesel and bio-ethanol can be produced from sugar containing biomass by fermentation processes. Next generation bio-fuels such as butanol can also be produced from similar biomass sources [7]. Complex fuels such as bio-oil can also be generated by pyrolysis of biomass [8]. Gaseous fuels like biogas and producer gas can be produced from biomass. For example, agricultural residue such as wheat straw or rice straw can be converted to biogas via anaerobic digestion, where biogas consists mainly of a mixture of CH_4 and CO_2. This in turn could help in reduction of in land filling and increase availability of land for other uses. Biogas can also be obtained through landfills, such a gas is known as 'landfill' gas. The typical composition of biogas and landfill gas in comparison to natural gas is shown in Table 1. The composition of biogas varies from site to site, depending on type of feedstock and also the type of anaerobic digesters used.

The composition of CH_4 in biogas and landfill gas is nearly similar, the former showing slightly higher composition. In comparison to natural gas both kinds of biogas exhibit lower CH_4 content thus lowering the calorific value of the gas. In contrast to natural gas, biogas shows presence of NH_3 and O_2. On the other hand higher hydrocarbons are absent in biogas/landfill gas. But both biogas and natural gas typically contain H_2S and N_2 as minor compounds. The major problems associated with combustion of biogas are presence of high amount of H_2S and of silicon compounds as they generate the SO_2 pollutant and silica particulates which damage combustion engine parts and heat exchanger surfaces. In reductive catalytic environments, the H_2S would also acts as catalyst poison. Anaerobically produced biogas exhibits higher H_2S content than landfill gas and natural gas. Similarly, more halogens are present in landfill derived biogas in comparison to the other two.

Table 1
Typical composition of biogas and landfill gas [9].

Component	Biogas composition			
	Unit	AD-biogas	Landfill biogas	Natural gas
CH_4	vol%	53–70	30–65	81–89
CO_2	vol%	30–50	25–47	0.67–1
N_2	vol%	2–6	< 1–17	0.28–14
O_2	vol%	0–5	< 1–3	0
H_2	vol%	NA	0–3	NA
Light hydrocarbons	vol%	NA	NA	3.5–9.4
H_2S	ppm	0–2000	30–500	0–2.9
NH_3	ppm	< 100	0–5	NA
Total chlorines	mg/Nm^3	< 0.25	0.–225	NA
Siloxanes	μg/g-dry	< 0.08–0.5	< 0.3–36	NA

Recently biogas has received considerable attention as an alternative energy source. Electricity can be generated via combustion of biogas in internal combustion engines (IC engine), but this requires an upgraded technology and infrastructure for removal of impurity that are present in biogas, which may reduce engine efficiency and create pollution due to incomplete combustion. Direct burning of biogas is quite a difficult process [11]. CH_4 is the main component in biogas which is combustible while other components are not involved in combustion process, though they absorb energy from combustion of CH_4. Presence of CO_2 decreases engine efficiency and increases emission of unburned hydrocarbons [10]. It also decreases burning velocity and reduces adiabatic temperature in the combustion process of biogas [11]. The presence of H_2S causes corrosion of engine parts, as H_2S is acidic in nature. In addition, the presence of moisture can cause starting problems. Therefore purification of biogas is necessary before combustion. To improve the combustion of the biogas, syngas can be added. The addition of syngas [11]. Addition of syngas (H_2+CO) to biogas would improve combustion process resulting in complete combustion and reducing emissions. It improves the combustion limitation of biogas such as lower flame speed, flammability limit Addition of syngas to CH_4 engine increases efficiency but fuel conversion decreases slightly. This occurs as a result of increase in fuel consumption rate [11]. Higher H_2containing syngas significantly reduces pollutant emissions from the engines. In the future, fuel cells may play an important role in power generation due to their superior efficiencies of conversion of chemical energy to work, in contrast to thermal engines. Currently fuel cells are expensive and certain limitations must be eliminated for successful commercialization. Internal combustion engines running on combination of biogas supplemented with syngas also derived from biogas could feature in the transition period till fuel cells become economically viable. The current review examines the potential of biogas in India The importance of biogas as source of hydrogen for current and future energy generation processes was explored. Currently there are no such reviews which examines the potential of hydrogen generation from biogas with respect to India. The current status of hydrogen production from biogas in India was analysed to determine the recent developments. The focus was to determine the right processes to produce hydrogen from biogas based on reactor type and process conditions. As catalyst is the most important part of the hydrogen production process, the use of various catalyst formulations in different biogas reforming processes was extensively examined. Factors affecting the performance of the catalyst i.e. preparation method, surface area, pore size, crystallite sizes and carbon formation were compared to determined the best formulation for biogas reforming technology implementation in India.

2. Biogas production and usage

Biogas production and utilization have several advantages. Fig. 1 shows current uses of biogas in India. It offers alternative fuel, high-quality fertilizer as a by-product, electricity, heat, complete waste recycling, greenhouse gas reduction and environmental protection from pollutants. Biogas systems convert organic household waste or manure into gas for cooking and lighting. These wastes like (rice, ugali), vegetables (tomatoes, cabbage), peels of potatoes and fruit, excreta can be converted to energy instead of disposing of them. Waste disposal and storage attracts insects and pests. Biogas helps in management of waste and contributes to improved hygiene in rural areas.

Table 2 shows the reductions in greenhouse gas emissions due to use of biogas as compared to fossil fuel. Biogas utilization has