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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 production for 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.

Key words- Hydrogen, biogas, fuel cells, autothermal and catalyst

1. Introduction

The energy sector is the most significant area focused at present on generation of traditional energy from fossil resources. 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[1].

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[1] Abbreviation: 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 CH_4, 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 and WHSV- Weight hourly space velocity.

. The European Commission specified that there are large varieties of biomass available for potential conversion to energy such as by-products, agricultural, forestry residue, related industries, as well as the non-fossil, biodegradable parts of industry and municipal solid waste (MSW) [1]. Biomass and biomass 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 among the various other renewable sources due to its many advantages. Biomass can be 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 it and some types of the biomass obtained as by-products are almost free. Biomass can also be directly used in 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 could augment and complement that of fossil fuel. It will also help mitigate CO_2 emissions, as CO_2 produced from biomass and its utilisation 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 moderate the CH_4 generated from decaying organic matter. By making use of the sugar cane bagasse for electricity production, more than 100 % reduction in GHG emissions compared to gasoline/diesel, was reported with sugar cane ethanol [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 these 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 in land filling and increase availability of land for other uses. Anaerobic digestion of biogas comprises of 4 different stages, namely, hydrolysis, acidogenesis, acetogenesis and methanogenesis. 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 similar, but the former shows slightly higher composition. In comparison to natural gas both kinds of biogas exhibit lower CH_4 content 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 act as a 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 land fill gas [9].

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. Although CH_4 is the main component in biogas that will be combusted, the other components are not involved in combustion process, but they absorb energy from combustion of CH_4. Presence of CO_2 decreases engine efficiency and increases emission of unburned hydrocarbon [10]. Also, the presence of CO_2 in the combustion process of biogas decreases burning velocity and reduces adiabatic temperature [11]. The presence of H_2S is responsible for corrosion of engine parts, as H_2S is acidic in nature. In addition, the presence of moisture can cause starting problems. As a result, purification of biogas is necessary before combustion. To improve the combustion of the biogas, syngas can be added. The addition of syngas will improve the combustion limitation of biogas such as lower flame speed, flammability limit [11]. Additions of syngas (H_2+CO) to biogas would improve combustion process resulting in complete combustion and reducing emissions. Addition of syngas to CH_4 engine increases efficiency but fuel conversion efficiency decreases slightly. This is a result from fuel consumption rate increases [11]. If syngas higher the concentration of H_2 resulted in higher reduction of the pollutant emissions. 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 barriers have to be overcome for successful commercialized. Internal combustion engines running on biogas supplemented with syngas derived from biogas could feature in a transition period till such time fuel cells become economically viable. The current review examines the potential of biogas in India and the methods for generating syngas or hydrogen from biogas are then reviewed with focus on catalyst formulations, reactor type and process reaction conditions.

2. Biogas production and usage

Biogas production and utilization have several advantages. Figure 1 shows current uses of biogas. 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.

Table 2 shows the reductions in greenhouse gas emissions due to biogas use as compared to fossil fuel. As seen from the table biogas utilization has tremendous potential to reduce greenhouse gas emissions. Wastes obtained from livestock, food waste and organic household waste has greatest potential of reduction.

Table 2: Reduction in greenhouse gas emissions as a result of biogas utilization 12].

The raw material used in biogas production is low cost and it also generates income making it an economically viable option for conversion of biomass. Biogas is also generated using animal waste, which is available in large quantities and is almost free. As livestock animals are commonly reared in rural areas in India, animal dung is produced and is easily obtainable. Burning dung is a common practice. One might argue that burning dung is cheaper than generating biogas. Table 3 compares and explains the advantages of generating biogas using animal dung. According to Table 3, burning dung is highly inefficient, with only 10 % of the energy obtained by combustion actually being utilized, in comparison to 55 % in the case of biogas. Similarly, burning dung does not generate any manure as by product compared to the biogas digester. Burning dung is a polluting process causing indoor pollution and thus increases the risk of illnesses such as chronic obstructive pulmonary disease (COPD), acute respiratory infections in children, increased infant and prenatal mortality, pulmonary tuberculosis, nasopharyngeal and laryngeal cancer, and cataract [13]. This is mainly due to carbonaceous aerosols being released during the burning of dung. Furthermore, these aerosols are responsible for warming and cooling the Earth's atmosphere [14]. In comparison, biogas is a cleaner fuel and combustion of biogas produces a smaller and less hazardous subset of pollutants in addition to CO_2. The biogas obtained from digestion of biomass is successfully utilized in some parts of India and this has resulted in enhancing the local ecology and relieving economic stress in rural communities[15].

Table 3: Comparison of direct burning of 1kg dung and its use as biogas[15].

The use of biogas helps reducing deforestation by minimizing use of firewood and also mitigates the use of synthetic fertilizers which affect the soil quality and carry a heavy carbon footprint. The use of biogas lowers GHG emissions in comparison to fossil fuels. bio-CNG's combustion generates ~8-22g CO_{2eq}/MJ which is 80% lower as compared to petroleum based fuels. Combustion of biogas does not produce harmful aromatic and polyaromatic hydrocarbons. The absence of these hydrocarbons prevents the net emission of soot and particulate matter from the combustion process. Soot formation during burning of natural gas or biogas, depends on the combustion conditions, the net emission of soot can be eliminated by gas combustion control, which is harder to achieve with liquid fuels. Filling stations of liquefied biogas are established in US, Europe and China. The production and utilization of biogas creates work opportunities for thousands of people. These jobs are blessings in rural areas, which are the targeted grounds for the use of biogas. In fact, biogas can easily be decentralized, making it easier to access by those living in remote areas or facing frequent power outages. One of the main advantages of biogas is easy setup and small scale plants require relatively little capital investment. The utilization of biogas helps farmers to become self-sufficient by using the livestock waste and surplus biomass available on the farm to generate power for domestic use.

The slurry obtained after digestion process is safe, organic, and nutrient-rich liquid fertilizer, which can be directly used to enhance agricultural productivity. The biogas slurry has great benefits to farmers. It can not only save money which otherwise is spent on the purchase of synthetic fertilizers, but it also help reducing environmental impacts. During the digestion process the elemental carbon to nitrogen ratio is reduced due to the removal of carbon from the substrate, increasing the fertilizing effect of the slurry. It is estimated that the application of biogas slurry may increase productivity as much as 25% when compared to applying manure directly to fields. Biogas slurry also has a pesticidal effect and can control certain pests without the harmful effect of synthetic pesticides. Experiments conducted at Tamil Nadu University, Coimbatore, India, have shown that biogas slurry can control nematode attack on tomatoes [16]. The severity of root-knot nematodemeloidogyne incognita attack on tomato reduced measurably using two levels of biogas slurry using 5% and 10% (w/w), added to soil. Both (3 fruits/plant) and fruit yield (35.2 g/plant) of tomato increased significantly with 10% (w/w) biogas slurry. The plants fertilized with biogas slurry put up more vegetative growth and tended to flower and fruit much earlier than the control. The nematode population in the soil and the severity of nematode attack also decreased.

Figure 1: Basic utilization of biogas.

3. Biogas potential and utilization in India

Currently, biogas has been mainly used as a cooking fuel and running stationary engines (Figure 1). The potential of biogas has not been completely realized and utilized yet. In order to promote the use of biogas for domestic purposes, the government of India has launched the National Project on Biogas Development (NPBD) in 1981. The number of biogas plants in India has increased from 1.23 million in 1990 to ~4.54 million in 2012, despite an estimated potential of 12.34 million digesters (Figure 2) [17]. The percentage of biogas plants installed with respect to its potential has increased from ~26% in 2002 to approximately 37% in 2012.

The family type (domestic scale) biogas plants resulted in an estimated 4 million tons (Mt) of fuel-wood per year, in addition to producing 1 Mt of enriched organic manure [15]. Cooking using biogas is faster in comparison to using charcoal or firewood. Biogas stoves do not take time to heat and cooking can begin once the stove is turned on.

Biomass such as fuel wood, animal dung, crop residue is widely used as a source of energy in developing countries. India is an agricultural country and large amount of biomass is produced as a result of agriculture activity. Agriculture is the backbone of India’s economy and accounts for 17% of India’s GDP while sustaining 60% of its population [18]. Agriculture activity is responsible for generation of large quantity of biomass. An estimated 686 Mt of gross biomass residue is generated from 26 crops every year in India. Table 4 show surplus crop yields and biomass potential of India. About 245 Mt of surplus biomass are generated annually, i.e. 34 % of the gross biomass is generated as surplus. In addition to biomass, livestock and poultry waste are other sources of biogas raw materials. According to 2013 census, 30.7 million livestock and 128 million poultry, there has been 33 and 48 % increase in the population of livestock and population, respectively. Table 5 shows the distribution of livestock and poultry in 2013-14. An estimated 298027 tonnes/day of manure was generated in India in 2013-14. Animal waste and decomposing biomass generates 55-65 vol % CH_4 which is directly released in atmosphere and has a greenhouse gas potential of 21 in comparison to 1 for CO_2.

Figure 2: Installed biogas plants in India [17].

In addition to agriculture farm waste, certain other kind of wastes generated by the agro- processing industry, vegetable market waste, roadside plantation waste are also important sources of biomass to be considered for biogas generation. Almost 200 Mt of household and agro processing wastes are generated annually in India and disposed in a dispersed manner [19]. As these wastes are produced at very low cost or no cost, they are under-utilized. In addition to the biomass and animal waste some of the industries also generate wastes which have great potential for conversion into biogas. Table 6 summarizes the potential for generation of biogas from wastewater in India. In India, distilleries produce about 6000 Mm^3 of wastewater (Table 6). Similarly a huge potential exits from the wastewater generation from other industries. The generation of biogas from wastewater streams can serve dual purpose. Firstly it will help in reduction of COD (chemical oxygen demand) of the effluent and secondly it would generate valuable energy. A biogas production potential in the range of 0.15–0.45 m^3 CH_4/kg of COD removed is possible. The discharge of these streams without treatment could cause serious environmental effects.

Sewage waste is similar to animal waste and can be converted to biogas. The increase in population has created a sharp rise in generation of sewage waste which remains unutilized. Table 7 summarizes the amount of waste water generated in Indian cities. An estimated 15,292 million litres per day (Mld) were generated and 66% i.e. 10,170 Mld were collected and treated [15]. The treatment of waste water will generate tremendous amount of sludge which has great potential for biogas generation. As a result the improper utilization of this abundantly available resource would result in serious environmental effects affecting quality of life in the country. Mammoth amount of household degradable waste containing waste paper, fruit vegetable peels and food waste are generated every year which can be effectively converted to biogas. India has a potential to generate 3000 MW of energy from MSW (Municipal Solid Waste)by 2020 [20]. MSW containing biodegradable waste and paper has lower calorific value. As a result, the conversion of MSW to biogas would be beneficial resulting from increased fuel quality by increased calorific value.

In addition to biomass generation, high amount of meat and poultry is consumed in the country. Indian poultry is the fifth largest production in the world, with egg production growing at the rate of 16% per year. There are three main phases in poultry industry namely production, development and processing which produce wastes such as egg shells, unhatched eggs, poultry droppings, and waste feed. The biogas potential of the poultry farms in India is estimated to be 438,227 m^3/day [15].The Indian meat industry is one of the largest in the world. In India about 4.42 Mt of meat are consumed per year which consists of beef, buffalo meat, mutton, goat meat, pork and poultry meat. Large amounts of water are consumed in the slaughterhouses while cleaning and washing of animals slaughtering and lairage. There are 3600 recognized slaughterhouses, 9 modern abattoirs and 171 meat processing units which slaughter over 121 million cattle’s (sheep, goat, pigs and poultry) and 36.9 million buffaloes, annually, for domestic consumption as well as for export purpose [21]. On average 15 litres of water are wasted in each slaughtering, about 630 million gallons water wasted every year in India. Based on the waste water utilization an estimated 1,494,225 m^3/day of biogas could be generated [15, 21]. The average Indian dairy's annual milk production was 20 Mt in the 1950s, which became 50 Mt in 1990 and 80 Mt by 2000, India now ranks as the world's number one milk producing country. A dairy consumes about 2-5 litres of water per litre of milk processed, used for washing and cleaning operations. Therefore, this industry poses a major threat to the environment, unless such effluents are subjected to proper treatment. It also provides a great opportunity and potential for biogas generation [22]. A total biogas generation potential from 342 dairy units in India is estimated to be 219,409 m^3/day[15].

Table 4: Gross and surplus biomass generated in India [18].

Table 5: Estimation of biogas generation from animal waste in India.

Table 6: Energy potential of waste water from India [19].

Table 7: Waste water generated in India [15].

4. Syngas/hydrogen production in India

The potential of biogas in India is not fully realized due to unavailability of large scale biogas plants. A compilation of various industries or institutes engaged in generating biogas for various applications is depicted in Table 8. Table 9 shows the recent large scale biogas generation projects implemented in India in the year 2014. From these tables, it can be seen that biogas generation and utilization are not even close to the estimated values. A vast potential exists for conversion and utilization of wastes to biogas. The implemented technologies have been useful for the industry to achieve energy saving in turn adding to profits. The implementation of the projects has been widely supported by MNRE and academic institutions like the Indian Institute of Science (IISc) and Indian Institutes of Technology (IITs).

Currently biogas is used in combined heat and power (CHP) for generation of heat and electricity. Biogas can be upgraded for injection in the natural gas grid when it becomes an option. In Germany and Sweden biogas is used as a transportation fuel. Apart from utilization as a fuel, biogas can be converted to synthesis gas (H_2+CO). Synthesis gas is a valuable commodity and is utilized in production of alcohols, alternative fuels and after separation of the H_2, ammonia based synthetic fertilisers, and petroleum refinery feedstock. Figure 2 represents the aspect of biogas conversion to synthesis gas and its uses. At this moment there are no installation in India using biogas to convert to syngas.

4.1 Syngas/hydrogen utilization in fuel cells:

One of the widely studied methods of utilization of H_2 and syngas is fuel cells [23, 24]. Technically, fuel cells can be described as electrochemical energy conversion devices that convert H_2 and O_2 into H_2O and in the process produce electricity [25]. Their mode of operation is similar to that of a battery. Unlike a battery, a fuel cell does not store energy and instead converts chemical energy to electrical energy, without the intermediate conversion steps into heat and then mechanical power, which are required in combustion based power generation technologies [26]. Efficiency exhibited by fuel cells is twice that observed in internal combustion engines and turbines, making them one of the promising energy conversion devices [27]. They can be used in association with other devices such as turbines, further increasing their efficiency up to ~70% [28]. PEMFC (proton exchange membrane fuel cells) and solid oxide fuel cells (SOFC) are the two most promising types of fuel cells. The PEMFC has a polymer based electrolyte such as Nafion which provides excellent resistance to gas crossover. The PEMFC's low operating temperature allows rapid start-up and, with the absence of corrosive cell constituents, the use of the exotic materials required in other fuel cell types, both in stack construction and in the BoP (balance of plant) is not required [24]. Other advantages compared to alkaline fuel cell (AFC), molten carbonate fuel cell (MCFC) and phosphoric acid fuel cell (PAFC) include significantly reduced corrosion problems due to the limited operating temperature, and the use of a solid electrolyte.

Moreover, PEMFCs are smaller and lighter than other fuel cells, making them ideal in the cases where size and mobility is key parameter for the application. The high power density of these fuel cells makes them ideal for applications in laptops, automotive power, computers and mobile phones. In recent years some of the major drawbacks such as life of the fuel cell and cost of the power generated are being resolved, but further cost improvements are necessary in order to compete with the mature internal combustion technologies [29]. One of the key aspects of PEMFC, which need addressing, is its intolerance to impurities in fuel and oxidant, as these affect the performance and expedite degradation. PEMFC fuel cells are extremely vulnerable to carbon monoxide in the fuel, which poisons the platinum catalysts.

On the other hand, SOFC's are versatile fuel cells with high electrical efficiency of 55% [30]. As a result of their high operating temperatures, SOFCs can be effectively combined with other new energy technologies such as micro turbines to enable the development of electricity generation products with ~70% efficiency [28]. They can also be used in combined heat and power systems (CHP) to provide electricity and heat for applications in cold areas of the world. SOFCs are made from commonly available ceramic materials and have no moving parts or corrosive liquid electrolytes. Therefore they should lead to highly reliable electricity generation systems which require low maintenance [31]. The manufacturing process for SOFCs is based on well-known equipment that is widely available and well proven in the manufacture of electronic ceramic components. SOFCs do not require expensive catalysts for their operation. SOFCs are heavier than PEMFCs and thus are more suitable for stationary power generation. Biogas is successfully utilized for generating H_2 for fuel cell use [9]. The advantages of using biogas for fuel cells use are quite a few.

1. Available in large amount. As biogas is generated from renewable biomass and livestock waste. Cost of production of these resources is very low or almost free.
2. The fuel cost generated from biogas for fuel cells would be low in turn reducing the cost of power generated using fuel cells.
3. Higher electrical efficiency of fuel cells in comparison to internal combustion engine would result in higher power generation with the same input of fuel.
4. Biogas contains CO_2, which reduces its calorific value; in turn lowering the amount of power generated using internal combustion engines. Removal of CO_2 for power generation using fuel cells is not required. In fact the presence of CO_2 is beneficial for the operation of the fuel cell i.e. SOFC’s[32].
5. Carbon dioxide generated from use of biogas in fuel cell will be in part counter balanced by the biomass used for biogas generation.
6. Small scale generation is possible.
7. No moving parts in fuel cells result in silent operation.
8. Scalable.
9. Simpler purification system.
10. Hybridization with other technologies such as solar and wind power and heat pumps have great market potential.
11. Remote power generation is possible.

12. Few commercially available technologies for using biogas using fuel cells. Commercial scale 2.8 MW fuel cell power plant running on biogas generated from waste water is constructed and operated by fuel cell energy in California, US.

To summarise, biogas can be effectively used in fuel cells. In case of utilisation of biogas for cells no separation of CO_2 is required. Carbon dioxide is useful in the H_2 rich gas (syngas) production process. Fuel cells (SOFC) are able to utilise biogas directly and produce stable power [33]. In case of failure of the fuel cell, the whole process is shut down for maintenance, which is a major drawback of this process. Carbon formed during the H_2 production by the internal reforming process deposits on the anode's surface, affecting the life of the fuel cell. In case of PEMFC, an external generation of H_2 is required. This option can be adopted to supply H_2 from both SOFC and PEMFC fuel cells.

Figure 3: Schematic of synthesis gas utilization derived from biogas.

Table 8: Conversion of different waste biomass to energy in India and reported benefits[19].

Table 9: Biogas implemented projects in India in the year 2014.

5. Syngas/hydrogen production

5.1 Reforming processes for syngas/hydrogen production:

On industrial scale for the last 10 decades, H_2 is mainly produced by processes of steam reforming of methane (SMR) [31]. The H_2 produced by SMR is mainly used for utilization in refineries and fertilizer plants. It is used in hydro treating, (hydrocracking, hydrogenation, hydrodesulphurization, hydrodemetallisation and hydrodenitrogenation) in the refineries for producing clean fuels like gasoline, diesel and many other products. In fertilizer plants it is used for the manufacture of ammonia, methanol and many other derived chemicals like urea, nitric acid and ammonium nitrate. Most industrial steam reformers use Ni catalysts on a ceramic support, operating in the temperatures ranging from 700-1000 ^{o}C in the pressure range of 15-30 atm [34, 35].

The main disadvantage of steam reforming (SR) is the endothermic nature of the reaction; i.e. it consumes a large amount of heat to shift the equilibrium towards the right to yield H_2 and CO (reaction 5.1). Further harsh conditions required during SR result in formation of carbon on catalyst surface and sintering of the active metals.

$$\text{Steam Reforming }(\text{SR})\text{:}C_nH_m\text{+}nH_2O\xrightleftharpoons{\text{Ni cat}}n\text{CO+}(n\text{+}\frac{m}{2})H_2,\ \Delta H\ \square\ 0 \qquad (5.1)$$

Partial oxidation is another reforming process used for H_2 generation. The reaction (5.2) is mildly exothermic and uses air or oxygen gas as a source of oxygen to produce H_2 and CO.

$$\text{Partial Oxidation }(\text{PO}): C_nH_m+\frac{n}{2}O_2\longrightarrow n\text{CO}+\frac{m}{2}H_2,\ \Delta H\prec 0 \qquad (5.2)$$

One of the important aspects to be considered during the process is the molar O_2/C ratio. Higher O_2/C ratio would result in complete combustion of the fuel (5.3) which is a highly exothermic reaction causing reaction temperature increase, which can form hot-spots in the reactor bed and form coke on the catalyst surface [9]. Another important drawback of the process is lower H_2 yield.

$$\text{Oxidation }(\text{Ox}):\ C_nH_m+(n+\frac{m}{4})O_2\xrightarrow{\text{Nicat}}n\text{CO}_2+\frac{m}{2}H_2O,\ \Delta H\ \square\ 0 \qquad (5.3)$$

To mitigate the problem of lower H_2 yield in case of partial oxidation (5.2) and endothermic SR(5.1), a combination of both the process called autothermal reforming (ATR) has been developed. The term ‘Autothermal’ in the context of reforming means a process that does not rely on external provision of heat, it is self-sufficient by balancing the heat requirement of the endothermic reactions by those of exothermic reactions, thus avoiding thermodynamic irreversibilities caused by heat transfer across the reactor boundaries. This combination is considered as one of the most attractive options for on-board reforming of complex hydrocarbons like kerosene and diesel [36, 37]. Its main characteristics are: low energy requirement due to the complementary SR and PO reactions, high Gas Hourly Space Velocity (GHSV) at least one order of magnitude relative to traditional SR, and preset H_2/CO ratio easily regulated by inlet reactant ratios and CO_2 recycling [38].

Harsh temperature and pressure conditions during SR requires costly reactor materials and installation. In order to overcome these drawbacks the development of compact ATR reformers is investigated. In an ATR reformer the PO reaction occurs in a thermal zone generating the heat for SR to take place in the catalytic zone, with down flow of steam. The heat generated from the PO mitigates the requirement of external heating. The startup and shut down of an ATR reformer is quite fast and can produce large amount of H_2 with lower O_2 consumption compared to PO reaction, by manipulating the inlet $CH_4/O_2/H_2O$ to get the desired H_2/CO ratio [9]. ATR reformers can use biogas containing CO_2 to adjust the H_2/CO ratio in the product. The major problems associated with ATR reforming is formation of soot in the combustion zone of the reformer, which is controlled by adding steam to the feed, but this increases capital and operating costs of the reformer.

There are two types of ATR reformers. The first type of ATR reformer is compact and just contains a catalyst bed in which SR and combustion occurs on it simultaneously. The first type of ATR reformers is desirable for fuel cell applications because of compact size. In the second type, there are two separate chambers or sections. In the first section non-catalytic PO occurs using a burner. The second chamber where catalytic SR occurs is placed downstream of the PO chamber (Figure 4). This type of ATR reformer is well suited for conversion of gas to liquid fuels (GTL) applications. The major problems arising in the second type of ATR reformers is formation of soot in the non-catalytic PO chamber which depends on factors such as composition, temperature, pressure and especially burner design. Soot precursors may be formed in the combustion chamber during operation. It is essential that the burner, catalyst and reactor are designed in such a way that the catalyst bed destroys the soot precursors avoiding soot accumulation. The process can be applied in H_2 production from various fuels including natural gas, diesel, coal and renewable feed-stocks.

ATR plants based on oxygen-blown ATR at low H_2O/C ratios are the preferred option for large-scale and economic production of synthetic gas for GTL plants [39]. Finally, ANL has favored catalytic ATR developing new catalysts for the reforming and shift reactors. It is suggested that ATR systems can be very productive, fast starting and compact.

Figure 4:ATR reformer applied in GTL applications [40].

One of the disadvantages of air-fed ATR is dilution of the reformer outlet with the inert N_2 from the air reactant. Further, the oxidation of fuel used to generate the exothermic heat reduces the H_2 yield. To counteract these problems, Autothermal Cyclic Reforming (ACR) process was designed by the U.S. based company General Electric (GE). The process operates in a three-step cycle that involves SR of fuel on Ni catalyst (reforming), heating the reactor through the oxidation Ni catalyst (air regeneration) and the reduction of the catalyst to its original state (fuel regeneration) [41]. ACR has common features to chemical looping reforming, which can operate in packed bed configuration with alternating flows that result in reactive conditions change from oxidative to reducing/reforming with time in the packed bed reactor, essentially in semi-batch operation, or via fluidized beds fed with steady gas flows and interconnected to allow recirculating material beds, where the conditions in each reactor remain the same with time, permitting continuous flow operation.

Typically, SMR reformers require higher combustion-operating temperatures to augment heat transfer and heat transfer area by means of smaller diameter structures. Use of high grade stainless steels with higher mass is required increasing the construction cost of the reformers. Comparatively ATR reformers would require lower material cost and lesser heat transfer area thereby decreasing construction costs.

Along with the above mentioned processes H_2 can be produced by reacting the fuel i.e. hydrocarbon with CO_2 as the source of oxygen, producing H_2 and CO. As a result of large negative enthalpy of CO_2, the process is highly endothermic process in comparison to other process like SR. The process is generally referred as dry reforming (DR) due to absence of steam reactant, although it can be generated as a by-product or intermediate. Dry reforming of CH_4 (DRM) has been widely investigated to produce H_2 and CO for Fischer Tropsch (F-T) synthesis [42-44].

$$\text{Dry Reforming }\left(\text{DR}\right)\text{: } C_nH_m + nCO_2 \xrightleftharpoons{\Delta H>>0} 2nCO + \frac{m}{2}\ H_2 \tag{5.4}$$

$$\text{Dry reforming of methane }\left(\text{DRM}\right)\text{: } CH_4 + CO_2 \xrightleftharpoons{\Delta H>>0} 2CO + 2H_2 \tag{5.5}$$

The highly endothermic nature of the process mandates the use of an external heat source similar to SMR. The process is slow, requiring long residence time and hence slower transient responses [42]. Likewise, the process is prone to carbon deposition by CO disproportionation (5.6, also called the Boudouard reaction) and CH_4 decomposition reactions (5.7)

$$\text{Boudouard}\left(\text{Boud}\right)(2CO \xrightleftharpoons{\Delta H_o=-171.5kJ/mol} CO_2 + C) \tag{5.6}$$

$$\text{Methane decomp}\left(\text{MED}\right)(CH_4 \xrightleftharpoons{\Delta H_o=-90.1kJ/mol} 2H_2 + C) \tag{5.7}$$

These reactions result in the formation of carbon deposits especially over Ni based catalysts, resulting in blockage of catalyst pores destroying catalyst particles and disrupting and blocking the reactor. These two side reactions which occur and generate the carbon deposits, eventually would negate the catalyst's activity and would block the reactor. According to Liu et al. [45] activity of CO disproportionation reaction (5.6) is reduced at and above 700°C, the operating temperature of dry reforming reaction. On the other hand CH_4 decomposition forms highly reactive C_α, which can be further gasified by reactions with H_2O (reaction 5.8) by, CO_2 (rev 5.6) or H_2 (rev 5.6), where 'rev' means reverse reaction.

$$\text{Coke gasification } (\text{GS})\ C+H_2O \xrightleftharpoons{\Delta H_o=139\text{kJ/mol}} CO+H_2 \tag{5.8}$$

However, some are converted to the less reactive C_β which may encapsulate on the surface or may dissolve in or encapsulate the Ni crystallite based on kinetic balance of various reactions. The dissolution of carbon in Ni is a key step for growth of carbon whiskers, which can destroy the catalyst or block the reactor [42].

$$\text{Coke oxidation } (CO_x)\ C+\frac{1}{2}O_2 \xrightarrow{\Delta H_o=-110.5\text{kJ/mol}} CO \tag{5.9}$$

$$\text{Coke oxidation } (CO_x)\ C+O_2 \xrightarrow{\Delta H_o=-395.6\text{kJ/mol}} CO_2 \tag{5.10}$$

Reactions (5.6-5.8) are not limited to dry reforming process, they also occur in other reforming processes. In addition, to the oxidation reactions (5.3 and 5.4), carbon oxidation reactions (5.9-5.10) occur in PO and ATR reforming processes. Pressure, temperature, reactant ratio, reactor and catalyst type are the important factors determining the extent of the reactions in the reactor.

Apart from all the above side reactions (5.6-5.10), water gas shift reaction (WGS) given by reaction (5.10) is the most important side reaction. The catalyst promoting WGS reaction (5.10) is highly favorable as it reduces CO from the product thus increasing H_2 yield and selectivity. The reaction also limits the operating temperature of the reactor. Since very high temperature 800 °C or above promote RWGS (rev 5.11), consuming H_2 and CO_2, producing CO and H_2O, in turn decreasing H_2 yield. WGS is one of the important reactions occurring during H_2 production. It determines the amount of CO in the H_2 rich gas produced, to be fed to fuel cells that are sensitive to CO levels.

Similarly the extent of WGS reaction determines the H_2 yield obtained during the reforming process.

$$\text{Water Gas Shift }(\text{WGS}):n\times(CO + H_2O \xrightleftharpoons{\Delta H_o = -41 kJ/mol} CO_2 + H_2) \tag{5.11}$$

5.2 Catalyst formulations used in reforming processes:

Catalyst is one of the important parameter to be considered in H_2 production from hydrocarbons or oxygenated hydrocarbons. The type of catalyst used determines the yield and selectivity of H_2 produced as well as selectivity to by-products. The nature of the catalyst determines the life and activity of the catalyst. In case of H_2 production process, life of catalyst is affected by carbon formation resulting in lower H_2 yield and selectivity and shorter life. Table 10 summarises carbon formation in some catalytic evaluations of H_2 production from biogas. It is important to note that the amount of carbon alone does not affect the activity of the catalyst, while type of carbon formed during the greatly influences catalyst deactivation. The type of metal loaded on catalyst and temperature of process, determines the type and amount of carbon formed on the catalyst. Maximum amount of C was produced over Ni/Al_2O_3 catalyst at 600 °C in comparison to 800 and 900 °C for Co and Fe supported on Al_2O_3[46]. Fishbone-like bio-nanostructured filamentous carbon (BNFC) was observed at 600 °C over Ni/Al_2O_3 catalyst compared to chain-like BNFC obtained with the Fe/Al_2O_3 catalyst at 900 °C. Encapsulating carbon was reported be formed at evident at higher temperatures 800-900 °C.

Similarly H_2 production processes operate at high temperatures, and prolonged exposure to high temperature results in decreased catalyst surface area (a type of sintering), which in turn affects the performance of the catalyst. Table 11 summarises the surface areas of various catalyst used in H_2 production. It can be clearly seen that the surface area of the catalyst is lower after the testing of the catalyst. Also catalysts prepared using different supports result in formation of material with different surface areas. Usually higher surface area results in better catalytic activity of the catalyst caused by higher dispersion of the active metal on the support [47]. Also, the pore structure of the support andthe metal–support interaction significantly affect the catalytic activity and coking resistance of the catalyst. Catalyst with well-developed pores exhibited higher catalytic activity. Strong interaction between metal and the support increases the resistance to sintering and coking, imparting higher stability to the catalyst [48]. A summary of different pore sizes obtained in various catalysts used in H_2 production from biogas is provided in Table 12. It is obvious that different supports used in catalyst preparation resulted in varied size pores and pore volumes.

The activity of the catalyst is related to the metal surface area (active sites). This implies that higher metallic dispersion results in higher catalytic activity. The main objective of catalyst preparation is producing high surface area materials with defined microstructure. Although the name ‘catalyst supports’ suggests chemically inert mechanical support, they are often involved in chemical reaction and play an important role in the performance of the catalyst. The methods of catalyst preparation also influence the effectiveness of the catalyst. Catalyst of a given chemical composition prepared by one method can behave differently when prepared using a different method. The method of preparation often defines the size of support and active metal which often help in minimising carbon deposits. Catalyst prepared by soverthmal method of preparation resulted in formation of smaller metal particles (5 nm) in comparison to 30 nm obtained by hydrothermal method. The prepared catalyst used in H_2 production by DRB resulted in higher CH_4 conversion and H_2 yield. Catalyst pore volume and pore size is affected by catalyst preparation methods [49]. Metal surface area and dispersion was affected by different catalyst preparation methods, in turn affecting the carbon formation and catalyst activity. Smaller metallic particles resulted in higher catalytic activity as a result of number of unsaturated metallic surface atoms [50]. The catalyst stability was ascribed to lower carbon formation as a result of smaller metallic particles. Smaller metallic crystals were shown to have a larger filamentous carbon saturation concentration level compared to larger metallic crystals [51]. This was reported to result in a smaller driving force for carbon diffusion and thus a higher resistance to coke formation for the catalyst prepared by hydrotalcite method. On the other hand smaller Ni crystallites were shown to be less effective in ATR of isooctane which resulted in lower catalytic activity as a result of oxidation of metallic Ni to form NiO [52].

Table 10: Carbon formation in H_2 production form biogas.

Ceria exhibits superior catalytic activity for WGS (R-5.10)[61]. It is also well known to promote metal activity and dispersion, justifying several investigations of various catalytic formulations for H_2 production. Like K_2O, addition of CaO modified the basic nature of the SiO_2 support and active phase particle size [62]. As carbon formation occurs mainly when the metal clusters are greater than a critical value, smaller particle size of the active phase results in lower carbon formation. Addition of CaO changes the nature of carbon formed over Ni/Al_2O_3 catalyst in SRE [63]. Addition of CaO results in the formation of crystalline carbon which is more easily gasified, leaving more active Ni particles exposed for reaction. Addition of CaO into $Ni/\gamma\text{-}Al_2O_3$ favored the formation of Ni species in lower interaction with the support, thus requiring a lower activation temperature [64]. Also, catalysts containing CaO did not undergo oxidation of Ni species during the SR, leading to a more stable catalytic system. Formation of perovskite $CaZrO_3$ by addition of 0.55 mol ratio of CaO/ZrO_2 to Al_2O_3 enhanced the activity of the catalyst[63, 65][[64], Lertwittayanon, Atong et al. [63]. The presence of this phase resulted in formation of oxygen vacancies and increased water adsorption creating favorable conditions for carbon gasification and, then, WGS.

The nature of catalyst support e.g. acidic or basic plays an important role in preventing carbon deposition. Addition of K_2O to Ni/Al_2O_3 catalyst, neutralizes acidic sites of Al_2O_3 and reduces the possibility of coke formation [66]. Carbon gasification reaction is enhanced by addition of K affecting carbon deposited on the catalyst surface [67]. It also increases the adsorption of steam on the catalyst surface [68] affecting H_2 production. Likewise addition of CeO_2 to catalyst support has a significant influence on carbon formation and catalyst activity. The property of the material responsible for reduction in carbon formation, is its oxygen storage capacity (OSC) by means of redox shift between Ce^{3+} and Ce^{4+} under oxidizing and reduction environments [69].

Table 11: Surface area properties for various catalysts utilized in H_2 production.

Table 12: Pore sizes of catalysts tested in H_2 production.

The promotion of these reactions kept the Ni surface clean, leading to increase in H_2 yield. The increase in the amount of $CaZrO_3$ phase significantly improved carbon gasification. On the other hand addition of La_2O_3 to Ni/Al_2O_3 in SR catalyst resulted in the formation of smaller particles of the catalytically inactive $NiAl_2O_4$phase by serving as promoter, decreasing the reducibility of the catalyst [76]. Addition of certain amount of La_2O_3 to the catalyst resulted in the formation of the smallest Ni particles which achieved the best catalytic performance and the strongest resistance toward carbon deposition and sintering. The addition of La_2O_3 to Ni/Al_2O_3increased metallic surface area, preventing the oxidation of Ni species and also increased stability of the support [77]. Addition of La_2O_3 to Ni/Al_2O_3 catalyst promoted the stabilization of the catalyst and was related to the enhancement of gasification of carbon residues from catalyst surface [78]. Impregnation of Ni/Al_2O_3 with B affected the performance of the catalyst by reducing the Ni particle size [79]. Ni et al. [80] reported better resistance to coking for the catalyst containing 5 wt% B_2O_3 than the un-promoted one, as a result of lower (weaker) Lewis acid sites ('LAS') and the more basic O-H groups formed on the borated Al_2O_3. Another effect of boron regarding the inhibition of carbon deposition on Ni catalysts has also been proposed. According to Xu and Sayes[81] and [82] boron atoms preferentially adsorb in the octahedral sites of the first subsurface layer of the Ni lattice, blocking effectively carbon diffusion into the bulk and retaining carbon atoms/groups of atoms on the surface available for gasification. Furthermore, boron is also expected to provoke a decrease of the on-surface carbon binding energy [82].

Like CaO and K_2O, Y_2O_3 addition to Rh/Al_2O_3 increased the basicity of Al_2O_3 leading to highest H_2 yield and formation of less stable, easily oxidisable coke [83]. The addition of Ni to Rh/Y-Al catalyst also modified the support by formation of $NiAl_2O_4$ phase at the support surface. The presence of this structure maintains the basic properties responsible for the high SR activity.

Similarly dispersed Ni remains at the support surface. The presence of Ni reinforced the amount of weak LAS, thus preventing the catalyst deactivation by carbonaceous deposits. Secondly, the addition of Ni modified the metallic phase by increasing the rhodium accessibility and stabilizing the rhodium particles. The presence of the $NiAl_2O_4$ at the support surface prevented the loss of rhodium by diffusion in the support bulk. Lastly, the presence of Ni^0 at the support surface was responsible for the higher H_2 yield observed in the presence of the bimetallic catalyst compared to the monometallic Rh-Y-Al, which may be due to the activity of Ni for SMR and/or for SRE. Addition of Y to Ni/Al_2O_3 increased reducibility of the catalyst in addition to the reduction in metal particle size and carbon deposition [84]. The interaction between Ni and the support was enhanced resulting in stronger interaction between Ni and support improving Ni particle dispersion and reducing Ni sintering [85]. Addition of MgO resulted in the formation of $Mg\text{-}Al_2O_4$, which reduced the acidity of Al_2O_3, and strong interaction $Ni–MgAl_2O_4$ favored Ni dispersion, imparting high activity to the catalyst [86].

Although traditionally H_2 production using SR process employs Ni based catalyst, noble metals like Rh, Pt and Pd are also used. The cost of noble metal based catalyst make Ni catalyst economically viable and the preferred metal for SR catalyst. Ni/Al_2O_3 is the widely used catalyst employed in SR reactions. One of the main disadvantages of Ni catalyst is susceptibility to deactivation by coke formation. The growth of Ni particle size and the oxidation of active Ni to nickel aluminate ($NiAl_2O_4$) are the other important reasons leading to the deactivation of $Ni/\alpha\text{-}A1_2O_3$ catalysts. Doping Al_2O_3 with the rare earth oxides restrain the growth of Ni particle and suppress the formation of $NiAl_2O_4$ through their interaction with Ni greatly improving the stability of Ni catalysts. Heavy rare earth oxides are more effective than light ones [87].

One of the approaches to reduce carbon accumulations is preparation of bimetallic catalyst using alkali metals like K and other metals like Sn [88], and Bi [89] to the catalyst. According to Trimm [88], carbide formation is an essential intermediate route to coke formation, formed by interaction of 2p carbon electrons with 3d Ni electrons. Addition of penta-valent p metals (such as Ge, Sn and

Pb or As, Sb or Bi) interacts with Ni 3d electrons, thereby reducing the chance of NiC formation in turn affecting carbon accumulation. Pengpanich et al [90] found addition of Sn to NiO disrupted the active site ensembles responsible for coking. Solubility of carbon in Ni particles responsible for NiC formation is also reduced by addition to Sn to Ni catalyst. Addition of MnO_x to Ni/Al_2O_3 was reported to have co-catalytic function with high redox property [91]. It was suggested that the MnO_x species are present on the surface of the Ni particles, the oxygen atoms derived from MnO_x species can be supplied to the Ni species promoting the reaction between carbonaceous species on Ni and oxygen species. This resulted in high reforming activity of the catalyst. Addition of Mo to Ni/Al_2O_3 increased conversion of LPG resulting in higher H_2 yields and showed superior performance in resisting catalyst coking as well as Ni sintering and Ni oxidation to inactive phases [92].

5.3 Current Research

5.3.1 Autothermal and Steam reforming:

Hydrogen production via SR of biogas is (SRB) is considered as a feasible alternative to SMR with similar efficiency. An economics analysis showed that H_2 can be produced at the rate of 0.27US$/kWh with a payback period of 8 years with an ecological efficiency of 94.95%, even without considering the cycle of CO_2 [93]. A brief assessment of H_2 production process using biogas has been presented by Alves et al [9] and Yang et al [94]. The authors examined and discussed various H_2 production processes. Although the various catalyst formulations were discussed the effect of H_2S and other contaminants were not explored. Similarly several other authors have examined H_2 production via dry reforming (DRB, i.e. the very endothermic reaction of CH_4 with the CO_2 from the biogas in absence of steam reactant to produce syngas, using reaction 5.4) [70, 95-97] or oxy-dry reforming (ODRB, i.e. DRB in the presence of O_2) [98]. Table 13 summarizes the performance of catalytic SRB and autothermal reforming of biogas (ATRB) evaluations. As seen in the table, noble metals provide higher conversion at lower temperatures in comparison to Ni, which provided higher conversion at higher temperatures.

One of the main challenges in developing catalysts for H_2 production form biogas is preventing carbon deposition on the active phase in order to increase its useful life. In addition, it includes improving the resistance of the catalyst to sulphur poisoning and developing high surface area catalyst to promote activity.

Hydrogen production using 4 wt% Rh/La-Al_2O_3 catalyst in SBR was evaluated by Ahmed et al. [99]. The performance of the catalyst was analyzed for temperatures 590-685°C, with steam to carbon molar ratio (S/C)1.28-3.86, CO_2/CH_4 molar ratio 0.55-1.51, and using gas hourly space velocities (GHSV) in the 9,810-27,000 h^{-1} range. Highest CH_4 conversion and lowest CO_2 conversion were observed at 650°C (Table 13) at S/C of 1.32 and GHSV of 9810 h^{-1}. The lower conversion of CO_2 was as a result of lower reaction temperature resulting in higher WGS reaction (5.11) contribution and lower DRM reaction (5.4). Variation of GHSV had marginal effect on the performance of the process. On the other hand increasing S/C had a positive impact on CH_4 conversion, increasing H_2 yield (Table 13). This was as result of prompted SMR (5.1) and WGS (5.11) reactions, contributing to lower CO_2 conversion [100]. The use of Ni based catalyst in SBR resulted in decrease in conversion of CH_4 and CO_2. Effendi et al [101] compared the performance of a fixed bed reactor with a fluidized bed reactor for SBR at 750 °C and H_2O/CH_4 ratio 2.2, using a 11.5 wt % Ni/Al_2O_3 catalyst with a GHSV of 18,000 h^{-1}. The fluidized bed was reported to provide 5-15% better performance in comparison to the fixed bed reactor. Highest feed gas to steam ratio was reported to induce poor fluidization in the reactor resulting in severe carbon formation, which was reduced by increasing the steam feed. Formation of cold spots in the catalyst bed used in the fixed bed reactor was responsible for its poor performance. Izquierdo et al.[102] evaluated the effect of different support compositions on the performance of Ni and bimetallic Rh-Ni catalysts in SBR reforming at 800°C with CH_4/CO_2 ratio of 1.5 and WHSV of 131.8 g_{gas}/g_{cat} h. A CH_4 conversion of 99.5 and CO_2 conversion of 67.5% were observed at S/C of 1 over a 13 wt % Ni/Ce-Zr-Al_2O_3 catalyst with 3 and 4 wt% Ce and Zr respectively. Similar to Ahmed at al.[99], increasing S/C was beneficial for CH_4 conversion but was detrimental for CO_2 conversion as result of inhibition of DRM (5.4) and promotion of WGS (5.11) over 4 wt% Rh/La-Al_2O_3. In spite of higher CH_4 and CO_2 conversion, the catalyst exhibited lower H_2 yield compared to Ni/Ce-Al_2O_3 and Ni/Zr-Al_2O_3 catalysts.

Presence of H_2S in biogas affects the activity and stability of the catalyst. Sulphur from H_2S reacts with active metal sites limiting the access of the reactants to the active sites and reducing activity of the catalyst. Further, formation of the stable metal-adsorbate bonds can lead to non-selective side reactions. The inhibition of the highly endothermic reforming reactions like SR (5.1) and DRM(5.4) causes the reactor temperature to rise considerably in turn increasing the risk of catalyst deactivation as a result of overheating by hot-spot formation close to the entrance section [103].

Although H_2S acts as a poisonous gas for metallic-based catalysts, presence of certain amount of H_2S in the feed enhances the reforming activity of the catalyst [100]. According to Laosiripojana et al [100], exposure of certain amount of H_2S to 5 wt % Ni/CeO_2 catalyst resulted in the formation of Ce–O–S phases (Ce $(SO_4)_2$, Ce_2 $(SO_4)_3$, and Ce_2O_2S) during the SBR. The formation of Ce $(SO_4)_2$ was reported to promote the oxygen storage capacity (OSC), the lattice oxygen mobility, and eventually the reforming activity, whereas the formation of Ce_2O_2S conversely reduces both properties and lowering the reforming rate. Addition of H_2S to SOFC running on CH_4 had a surprisingly positive effect on fuel cell activity and increased carbon resistance. The addition of H_2S into pure fuel streams enhanced the performance by converting the anodes from pure metal to metal sulfides, suggesting metal-sulfides are interesting anode materials for SOFC's with fuels contaminated by sulfur species [104].

In contrast, 15 wt% Ni/Al_2O_3 catalyst suffered from severe sulphur poisoning, 98% loss of the catalyst activity was reported by Appari et al [72] in SBR. The loss in activity due to sulphur coverage over catalyst surface is temperature dependent and independent of the H_2S concentration. Catalyst poisoning at low temperature 700 °C is not recoverable just by removal of H_2S from the feed stream. In contrast, catalyst activity at high temperature 800 °C was easily reversed just by removal of H_2S from the feed stream. Similar observation was made by Ashrafi et al.[105]. A complete deactivation of the catalyst activity was recorded at 700 °C which recovered with increase in temperature to 800 °C. The extent of catalyst regeneration by H_2S removal increases with an increasing temperature. For small scale biogas applications where high efficiency sulphur removal can be expensive, operating reformers with biogas feed with higher H_2S content at higher temperatures, could be economically advantageous. High temperature operation of reformers lead to a wide variety of problems like formation of hot spots, reduction in catalyst surface area, sintering of active metal crystallites etc. These factors could result in loss of activity and life of the catalyst. Chang et al. [106] have performed steam reforming of Biogas in honeycomb reactor using 5 wt% NiO/CeO_2 catalyst at 800°C. Methane conversion obtained is not at par with available literature, however the reactor configuration used is of commercial interest. Angeli et al.[107] have performed experiments at relatively lower temperature (400-550°C) in the presence of Ni and Rh on La_2O_3-ZrO_2. Methane conversion increases with temperature whereas for both metals i.e. Ni and Rh, performance with CeZrLa support was better than with ZrLa. Effect of organic pollutants in the Biogas stream on the performance of catalyst and its deactivation has been studied by Chiodo et al. [108]. It was observed that in moderate concentration the performance of Ni based catalyst was hampered and coke deposition was promoted. Roy et al. [109] have studied steam biogas reforming in the presence of metal foam coated Ru and Ni catalyst on various supports. The metal foam support was shown to achieve better performance than alumina.

Although SR (5.1) followed by WGS (5.11) is the prominent commercial technology, its small scale applications are restricted due to the endothermic nature of the reaction requiring high temperature operation. It also requires an external heat source to drive the endothermic SR(5.1) reaction. Industrially the SMR is carried out in very long tubes filled with catalyst. Even though high pressure has a negative effect on the reforming reactions, it is performed at high temperature and pressure to increase the productivity of the process. SR(5.1) has restriction for adoption in H_2 generation from unseparated biogas due to its negative effect on CO_2 conversion, with higher S/C promoting higher CH_4 conversion and higher WGS (5.11) activity producing more CO_2 than consumed [99].

To date, the number of investigations in autothermal reforming of biogas (ATRB) is limited. ATRB of model biogas was performed by Arkai et al [110, 111] by means of a 30 wt% Ni/Al_2O_3

catalyst. The effect of O_2/C and S/C at constant temperature was studied and the optimum values of O_2/C ratios of 0.45−0.55 and S/C ratios of 1.5−2.5 at 750°C, leading to 90% CH_4 conversion were reported. An important factor influencing the activity of the catalyst was identified. Redox cycles were recorded between Ni, NiO and Ni_2O_3 during the ATR of biogas[112]. The reduction reaction of the Ni oxides proceeded poorly while the oxidation reaction of the Ni components proceeded sufficiently under these conditions. More steam in the reactor during ATRB resulted in oxidation of Ni to Ni_2O_3 under steam rich condition (S/C of 3) and O_2/C of 0.5, reducing the activity of the catalyst. ATR reforming of model biogas over Ni/CeO_2 catalyst was investigated by Vita et al [113]. Lower value of S/C of 0.3 and O_2/C of 0.1 was reported to provide 99.6 and 90.5 % CH_4 and CO_2 conversions respectively, with a 17.6 wt% Ni catalyst at 850 °C (Table 13). The catalytic performance was evaluated for 150 h with slight evidence of deactivation. The stable activity of the catalyst was maintained as a result of higher NiO dispersion of the metal on the catalyst surface, limiting the aggregation of the Ni particles, in addition to the presence of Ni-Ce solid solution.

The same 13 wt% Ni/Ce-Zr-Al_2O_3 catalyst used in SRB [102], Izquierdo et al [114] examined ATRB with S/C of 1 and O_2/C of 0.25 at 800 °C and WHSV (weight hourly space velocity) of 161h^{-1} (Table 13). Addition of O_2 resulted in slightly improved CH_4 conversion in comparison to [102]. In comparison, CO_2 conversion in [102] was higher due to lower WHSV of 131 h^{-1} for the SR experiments, as compared to 161 h^{-1} in ATR [114]. The other explanation for lower CO_2 conversion could be the inhibition of reverse WGS (Rev 5.11) in ATR compared to SBR. Bimetallic Rh-Ni/Ce-Al_2O_3 catalyst showed the highest H_2 yield under ATR conditions among the catalysts examined. Table 13 summarizes the performance of various catalysts in SRB and ATRB. It can be clearly seen that Ni based catalyst are active in both the processes. In comparison to CH_4 conversion, CO_2 conversion was lower in most of the applications, although some investigations have also reported very high CO_2 conversion. Higher CH_4 and CO_2 conversion has reported to exhibit high H_2 yield.

Table 13: Catalyst performance summary evaluated in SRB and ATRB.

5.3.2 Dry and Oxy-dry reforming

Apart from SRB and ATRB reforming, several investigations involving dry reforming and oxy dry reforming of biogas (DRB and ODRB) have been reported [59, 68, 74, 98, 115]. Table 14 summarizes the performance of various catalysts in DRB and ODRB. As seen from the table various catalysts provide a wide variety of results. The major advantage of this process is utilization of two greenhouse gases. Although the process uses CO_2 for reaction, the endothermic nature of the reaction (5.4) requires external burning of fuel to provide heat, which in turn generates CO_2 emissions. Reducing the energy requirement of the process, by driving the endothermic reforming reaction with partial combustion of CH_4, CO, H_2 and C, has been researched [68, 116, 117]. Due to the lack of steam-carbon reaction during the DR (5.4) process, formation of coke occurs over catalyst active sites and support, which is responsible for clogging the reactor and destroying it. Development of carbon tolerant and thermally stable catalysts has directed the research in H_2 production via DR. Noble metals like Pt, Rh and Ru are very well suited for DR reaction(5.4) [9, 118, 119]. But the availability and cost of these materials make them expensive and undesirable for industrial scale or even small scale applications. Depending on the cost and availability of the materials, use of Ni based catalyst has been evaluated. The higher temperature requirement of the DR reaction and the high carbon content in its reactants makes these materials prone to deactivation by sintering and carbon deposition respectively. Preparation of bimetallic catalysts like Ni-Co [59, 120, 121], Ni-B [79] and Ni-K [122, 123] in DRB is evaluated.

DRB over 13wt%Ni/Ce-Zr-Al_2O_3 catalyst was reported to exhibit a CH_4 conversion of 64.5 and 85.6 % CO_2 conversion resulting in a H_2 yield of 57.5 % (Table 14). The absence of steam during the process resulted in higher CO_2 conversion via DRB [114] as compared to SBR [102].

Introduction of O_2 in DRB resulted in 96.3 and 87.4% CH_4 and CO_2 conversions respectively with O_2/CH_4 of 0.125 at 800°C, with beneficial 33.5% increase in H_2 yield (91% of stoichiometric max). This suggests promotion of PO (5.2) by addition of O_2 augmenting H_2 yield [102]. The authors compared different processes at different reactor residence time, making it difficult to understand the effects of processes parameters on the behavior of the process.

Xu et al [56] reported higher performance of Ni-Co/La_2O_3-Al_2O_3 catalyst in comparison to Ni/Ce-Zr-Al_2O_3 for DRB. Typical Ni, Co and La loading utilized were 7, 3 and 6 wt%. The average conversion of 94.5 and 97.0%, for CH_4 and CO_2, respectively, with a selectivity to H_2 of 92.7% was (Table 14) observed at 800 °C with CH_4/CO_2 of 1 for a period of 500 h with minimum 1.9 wt % (Table 11) carbon deposited on the catalyst surface. The authors reported the benefits of adding Co to the Ni/La_2O_3-Al_2O_3 catalyst used for DRB [55]. The reduction of Ni and/or Co present in the catalyst occurred around 500°C, resulting in the formation of active sites for the catalytic reaction. The active sites were reported to be formed in the reductive atmosphere of H_2 and CO during the process. A similar observation was made by Arbag et al [124]. According to the authors the content of Co played an important role in the performance of the catalyst. Higher amount of Co i.e. 5 wt % resulted in the formation of $CoAl_2O_4$, which was difficult to reduce, thus affecting the catalytic activity. In comparison, bimetallic 2.5 wt% Ni - 2.5 wt% Co onAl_2O_3 showed better performance. , with CH_4 conversion improving with Ni-Co metals loading. This suggests limited contribution of DR reaction to CH_4 conversion.

Likewise, addition of La_2O_3 to Al_2O_3 resulted in the formation of $La_2O_2CO_3$[125]. The formation of $La_2O_2CO_3$ was reported to establish equilibrium on the surface of Ni crystallites gradually. The interfacial area between Ni and oxy-carbonate particles provided active sites formation of Ni, forming active sites over the catalyst. Li et al [126] prepared nano rod shaped La_2O_3 support from sol gel synthesized $La_2O_2CO_3$. The support was shown to have medium-strength basic sites, facilitating increase in adsorption and activation of CO_2, promoting higher CO_2 conversion over 5 wt % Ni/La_2O_3. The nano rod shaped La_2O_3 promoted dispersion of Ni particles on the catalyst surface, positively affecting the catalytic activity. Catalytic activity was reported to take place in the Ni-$La_2O_2CO_3$ inter-phase, while oxy-carbonate species participate directly reacting with carbon deposited on the metal, recovering nickel activity [127].The $La_2O_2CO_3$ species are considered as an oxygen dynamic tampon. C-C compounds are removed by oxidation reactions to produce CO. The stable behaviour was attributed to equilibrium achieved between carbon species formation on nickel crystallites and removing rate of C-C oxidation reactions.

Instead of conventional pre-reduction of $NiO\text{-}Co_2O_3/Al_2O_3$ catalyst with H_2, a different pretreatment method to improve the performance of the catalyst was designed by Zhao et al [57]. The catalyst was pre-reduced in H_2 followed by treatment with CO_2 resulting in the formation of $Ni\ (HCO_3)_2$, which decomposed to release oxygen that reacted with carbon deposited over the Ni crystallites during DRB. As a result the activity of the catalyst was maintained, in turn significantly affecting the performance of the catalyst (Table14). The H_2-reduced and CO_2-pretreated catalyst offered much more stable performance for 24h. On the contrary, H_2-reduced and CO_2-untreated catalyst showed a long adjustment period, suggesting gradual formation of active sites during the process. An increase of conversion in CH_4 from 87 to 95% and in CO_2 from 95 to 99% was observed for catalyst with pretreatment time from 0 to 1 h. Formation of carboxyl species was detected by the authors during the CO_2 pretreatment process, resulting from the formation of bicarbonate of Ni. This bicarbonate of Ni was reported to decompose providing oxygen species. These oxygen species would gasify the carbon deposited on Ni crystallites protecting active sites in turn rendering high activity [75]. According to the authors, 0.5 h of catalyst pre-treatment resulted in strongest resistance to coking, and catalyst pretreated for 1 h exhibited the greatest resistance to sintering, suggesting the optimum pre-treatment period of 0.5-1 h [57].

In a different evaluation at lower temperature (600 °C), the activity of $Ni\text{-}Co/Al_2O_3$ catalyst was significantly affected. Mere 25 % CH_4 conversion was observed over 11.25 wt% Ni and 3.75 wt% Co supported on Al_2O_3 catalyst (Table 14) [59]. An enhancement in activity of the $Ni\text{-}Co/Al_2O_3$ catalyst in comparison to [59], was observed by Saha et al [115] at 900 ^{o}C with 5 wt% Co and 15 wt% Ni, supported on $MgO\text{-}Al_2O_3$. The authors reported a 57.1% CH_4 conversion with 97% selectivity to H_2 (Table 14). The addition of Co to Ni/Al_2O_3 catalyst was reported to play an important role in the performance of the catalyst. The order of Co addition plays a crucial role in determining the activity of the catalyst. Addition of Co before Ni impregnation on to the support was beneficial to the activity of the catalyst by acting as sacrificial element, promoting the activity of the catalyst. On the other hand addition of Co after Ni impregnation reduced the activity by blocking some of the active sites of Ni, affecting the performance of the process.

Catalyst preparation methods also play a key role in their performance. Goula et al [128]examined the performance of Ni supported on alumina prepared by wet impregnation, incipient wetness method and equilibrium deposition technique. It was proven that the synthesis method, affects the catalyst's reducibility, as well as the nickel species' particle size. The equilibrium deposition method showed higher Ni dispersion due to smaller particle size, in comparison to the other two methods, affecting the catalytic activity. On the other hand, conventional impregnation resulted in uncontrolled precipitation on catalysts surface during drying, affecting the dispersion of the active phase.

In recent years ZrO_2 has been evaluated as catalytic support [129] and partial substitution in supports for catalytic reactions [130], due to its several advantages, including high ionic conductivity and thermal stability, the latter being very important for reforming reactions. Asencios et al [73] examined the performance of 20 wt% Ni supported on MgO-ZrO_2 catalyst. Among the catalysts Ni/MgO was reported to provide highest activity (Table 14) with the activity decreasing with reduced MgO content. The Ni/ZrO_2 catalyst preferentially catalyzed the PO reaction (5.2), while the catalysts with higher MgO content showed a strong preference for the DR reaction (5.4). A 20 wt% MgO-ZrO_2 catalyst reported best activity in terms of all high CH_4 conversion; lower carbon formation and low reverse WGS (rev5.11) in addition to higher H_2/CO.

In order to develop a C resistant catalyst, Juan-Juan et al [123] investigated the use of K addition to 10 wt% Ni/Al_2O_3utilized in DRB. The addition of certain amount of K (0.2 wt % K_2O) to the catalyst had a positive effect on the activity of the catalyst. Due to K addition, interaction between NiO and Al_2O_3 was modified, resulting in increased NiO reducibility. Potassium migrates from the support to the Ni surface and neutralizes a fraction of the active sites, thereby increasing the gasification of the coke during the process without modification of its structure. Potassium does not modify the size nor the structure of the Ni particles. These factors resulted in very low coke deposition and a high catalytic activity (more than 90% reduction in coke deposition and less than 10% decrease in the catalytic activity). Similar observation of K addition to 10 wt% Ni/MgO–ZrO_2 was made by Nagaraja at al [122], who reported an optimum K content of 0.5 wt.% to the catalyst. Snoeck et al [131] have reported that one of the important benefits of K addition to a Ni-containing catalyst is a decrease of the value of the lumped forward rate coefficient for CH_4 decomposition and the presence of higher surface oxygen coverage. The reduction in number of active sites available for CH_4 decomposition resulted in lower CH_4 decomposition rate. The alkalized catalyst was responsible for WGS (5.11) reaction.

Doping Al_2O_3 with CeO_2 was also beneficial in increasing CH_4 and CO_2 conversion in DRB. But the catalyst provided inferior H_2 yield in comparison to [114]. CH_4 and CO_2 conversions of ~95 % was reported by Bereketidou and Goula [60] in DRB over 8 wt% Ni/Ce-Al catalyst at 850 °C with a CH_4/CO_2 ratio of 1.5. At the experimental conditions a H_2 yields of 50 and 66% were observed with 8 wt% Ni/10 wt% CeO_2-Al_2O_3 and 8 wt% Ni/20 wt% CeO_2-Al_2O_3 catalysts, respectively (Table 14). In spite of higher conversions (CH_4 and CO_2) reported by Bereketidou and Goula [60] using 8 wt% Ni/10 wt% CeO_2-Al_2O_3 catalyst, the H_2 yield was similar to that observed by Izquierdo et al [114] using 13 wt % Ni/ 3 wt % CeO_2-Al_2O_3 catalyst. The addition of CeO_2 to Al_2O_3 helped to improve the stability of the catalyst stability. The same catalyst exhibited a 40 % reduction in CH_4 conversion Charisiou et al [132] with increased flows and operating temperature. The performance was shown to be hampered by increased reactant flows, although catalyst stability of the CeO_2 doped catalyst was better compared to bare Al_2O_3.

Like cobalt, the order of Cerium addition to Ni/SBA was reported to enhance the activity of the catalyst in DRB. The beneficial effect of CeO_2 addition (<10 wt %) to Al_2O_3 in DRB was ascribed to the redox property of CeO_2. The reaction between the lattice oxygen and CH_4 as well as CO during the process prevents carbon that would have formed via CH_4 decomposition reaction (5.6) and Boudouard reaction (5.7), imparting high catalytic activity. However, very high CeO_2 content (>10 wt%) caused Ni oxidation retarding catalytic activity [133]. The order of impregnation of active Ni and Ce was reported to influence the activity of the catalyst. Impregnation of Ce before Ni onto the support resulted in smaller Ni crystallites and higher reducibility, in turn promoting the activity of the catalyst. Contrarily, the impregnation of Ce after Ni caused additional plugging of the pores and formation of larger NiO particles, thus hindering the accessibility of the reactants to the active sites and lowering the activity [134]. The improved catalytic behavior by CeO_2 addition was as a result of higher dispersion of nano-sized Ni species and inhibited the carbon formation. Further addition of CeO_2 in the SBA promoted formation of the smaller size Ni crystallites [135].

Apart from Al_2O_3 supported catalyst, the use of the supports like samaria doped ceria (SDC) in DRB of biogas was evaluated by Zmiciz et al.[136]. They reported CH_4 and CO_2 conversions over 95% resulting in 80% H_2 yield at 800 °C with CH_4/CO_2 ratio of 1 (Table 14), using 9 wt% Ni/SDC catalyst. The long term evaluation of the catalyst at 800 °C with CH_4/CO_2 ratio of 1 showed reduction in CO_2 conversion with time, accompanied by presence of graphite type carbon confirmed by XRD. Increasing CH_4/CO_2 ratio had a positive impact on CH_4 conversion, which reached 100% at CH_4/CO_2 ratio of 2.3.

Catalysts prepared by hydrotalcite-like precursors containing Mg (Ni,Al)O were evaluated for DRB at 750 °C with CH_4/CO_2 ratio of 1 (Table 14) [70]. The performance of the catalyst was in comparison to the others (Table 14). Addition of La to the catalyst was shown to impart higher catalytic activity in comparison to the undoped catalyst. Increasing La content from 1 to 2 wt% decreased catalytic activity but increased stability of the catalyst without carbon formation.

To mitigate the main drawback of carbon formation during DRB, addition of H_2O and O_2 to the process was investigated by Pino et al [74] over Ni/La-Ce-O catalyst. A catalyst with lower Ni content $Ce_{0.70}La_{0.20}Ni_{0.10}O_{2-\delta}$ was reported to show very high activity at 800 °C with CH_4:CO_2:H_2O:O_2 molar ratios of 1:0.66:0.66:0.10. The application Ni supported on sol-gel synthesized Al_2O_3 for ODRB was investigated by Asencios et al [116]. Supports were synthesized using various pH values and aging temperatures. A 20 wt% Ni supported on Al_2O_3 synthesized using pH 7 and 80 °C showed the highest activity and stable performance for 6 h. Conversions of 70 and 80% for CH_4 and CO_2 (Table 14) were observed respectively during the catalytic evaluation performed at 750 °C, with a feed consisting of model biogas and oxygen, with molar ratios

CH_4:CO_2:O_2 of 1.5:1:0.25, fed at the rate of 107.5 mol/min. The activity of the catalyst was attributed to low acidity of the support resulting in lower coke deposition on the catalyst. The lower acidity of the support caused easy reaction of CO_2 on basic centers of Al_2O_3 with acid-base interaction favoring this reaction.

Table 14: Catalyst performance summary investigated in DRB and ODRB.

5.4 Summary

Hydrogen production from biogas is relatively very new in India and very few investigations have been reported. Development of small scale reformers to convert biogas to H_2 rich gas is essential. The reformate product (H_2+CO) could widely be utilised for power generation and even for other important applications in energy conversion and the chemical industry. For successful utilization of H_2 energy technology, development of fuel cells is also a key piece of the puzzle which would require time. For immediate application, synthesis gas (H_2+CO) can be used directly for power generation using internal combustion engines. In comparison, direct utilization of biogas in combustion applications is unfavorable due to the large CO_2 content reducing its calorific value as compared to synthesis gas.

Hydrogen production from biogas can be achieved via various methods like steam reforming, partial oxidation, dry reforming, and autothermal reforming. Table 15 compares the advantages and disadvantages of the various reforming processes. One of the key aspects of H_2 production from biogas is development of carbon resistant and sulphur tolerant catalysts. Hydrogen production via SMR is widely studied and commercially operated. But the major problem associated with SRB is the presence of CO_2 which would affect the performance of the catalyst. As water gas shift is an important reaction taking place during SR process, its promotion has been shown to have negative effect on CO_2 conversion [99]. The lower CO_2 conversion as a result of higher water gas shift activity would alter the composition of the reformate by changing the H_2/CO ratio and affecting its quality. Also, the presence CO_2 in the feed could catalyze carbon forming reactions reducing catalyst activity and performance. The removal of CO_2 from biogas could solve several problems but removal methods are costlier for small sale operations. The presence CO_2 would also be useful in reduction of hot-spots formed in the reactor due to high temperature operation.

In addition the widely studied dry reforming process results in lower H_2 yield and catalyst deactivation by carbon formation. Both the processes dry and steam reforming are endothermic, with dry reforming more so. They require an external heat source for their energy supply. Other attempts have been focused on investigating the effects of O_2 addition (ODRB) to improve the performance of the process by carbon removal by oxidation with O_2. Some interesting investigations are reported [116]. But the addition of O_2 was too small to affect the overall energy balance of the process. The O_2 addition was intended to reduce the carbon formation rather than provide energy for the process. Hydrogen production investigations using ATRB are very few [110-112] and limited and suggest further work has to be performed. Effect of H_2S on catalytic activity of the ATR catalyst has to be evaluated and assessed. Similarly the effect of the ATR process on CO_2 conversion was not investigated in the investigations and has to be evaluated. The process performance was measured in terms of CH_4 conversion and molar gas composition which does not provide a full explanation of process performance. The performance of the process must be measured in terms of H_2 and CO yield and efficiencies needs to be evaluated by comparison with equivalent chemical equilibrium conditions. The conditions of S/C, O_2/C and temperature were reported, but whether real autothermality, i.e. no reliance on heat provided externally, was achieved or not, was not reported in any of the investigations. Detailed energy balances and experiments would need to be performed accordingly to ensure actual autothermal operation of the reformer. One of the drawbacks of ATR reformer is reduction of H_2 yield resulting in lower H_2/CO ratio. As a result the autothermal cyclic reforming (ACR) processes have been developed.

As mentioned earlier, ATR reduces H_2 yield due to combustion of fuel or H_2 produced during the process. Hydrogen yield can be increased by using the ACR process. Hydrogen yield can be increased by using ACR. In addition the process has a benefit of lower energy requirement by maintaining autothermal conditions. One type of ACR has been under great deal of development since last decade. This process, also called chemical looping reforming, is based on the transfer of oxygen from air to the fuel by means of a solid oxygen carrier avoiding direct contact between fuel and air. In the ACR process the air to fuel ratio is kept low to prevent the complete oxidation of the fuel to CO_2 and H_2O. Figure 4 shows the scheme of a typical ACR process. A N_2 free gas stream concentrated in H_2 and CO is obtained at the outlet of the fuel reactor. Moreover, the air separation unit (ASU) required in the conventional auto-thermal reforming for CO_2 capture is avoided here. Recently ACR has been reported as an promising approach to produce H_2 for fuel cells applications [137]. This approach allows to maintain autothermal conditions in the reformer and at the same time provides high quality reformate similar to SR reformers. The power and voltage with a PEMFC stack fed H_2 produced from ACR reformers was close to the values achieved when SR fuel processors are used. Experimental investigations of ACR using biogas needs to be assessed and evaluated for potential future applications.

Figure 5: Schematic of ACR reforming system.

The process has a benefit of lower energy requirement by maintaining autothermal conditions over the redox cycle. Recently ACR has been reported as a promising approach to produce H_2 for fuel cells applications [137]. This approach allows to maintain net autothermal conditions in the reformer and at the same time provides high quality reformate similar to SR reformers. The power and voltage with a PEMFC stack fed with H_2 produced from ACR reformers was close to the values achieved when SR fuel processors are used. Experimental investigations of ACR using biogas need to be assessed and evaluated for potential future applications.

Table 15: Comparison of various reforming technologies for H_2 production form biogas adopted from [9, 147, 148].

6. Conclusion and recommendation

6.1 Conclusion

By 2050 renewable energy resources are projected to contribute to 50% of the world energy demand. In order to keep with the global trend, India will also have to adapt to the changing circumstances and will have to adopt new and renewable energy resources. Looking at the forecast, biogas has potential to become an integral part of the renewable energies circle. India being an agricultural country, a tremendous amount of agricultural and livestock waste is available. Likewise, the rise in population has resulted in growth in food and agriculture processing industry, bringing about large amount of waste being produced which remain unprocessed, and causing environmental concerns as well as spreading diseases. It is an important and valuable resource for India. It has diverse applications and has great potential for generating environment friendly and suitable bio-fuels using surplus biomass, livestock waste along with industrial and domestic waste water. It possesses potential to address the pressing economic issues like depletion of fossil fuels, management of renewable energy resource, emission of GHG and replacement of chemical fertilizers which have arrived over the past few years.

Hydrogen energy in addition to solar, hydro and biomass would be one of the key renewable energy sources essential for India to maintain its high GDP. The technology is new, and considerable work in the field is required for the adoption in India. The utilization of biogas for H_2 generation would have a prominent impact on the successful implementation of H_2 energy technology for India. It will help minimize the environmental effects along with increasing the affordability for wide scale application.

6.2 Recommendation:

Wide scale use of the hydrogen energy technology for sustainable distributed power generation for remote and local areas has to be undertaken. Biogas has great potential to provide a cost effective and environment-friendly means for generating H_2 in India. The development of an energy efficient H_2 production process from biogas has to be developed and evaluated. autothermal reforming (ATR) and autothermal cyclic reforming (ACR), i.e. chemical looping reforming (CLR) seem to provide alternative means to generate sustainable and environment friendly H_2 production due to their lack of reliance on heat provided externally. Stable and active catalyst need to be developed for the processes. Catalyst formulations based on CeO_2 are promising candidates to produce sulphur and carbon tolerant catalyst. Development of nano sized Ni based material to improve the stability and activity of the catalyst using a variety of catalyst preparation methods have to be prepared and tested. A detailed system efficiency analysis needs to be performed to determine the extent of autothermal condition achievement for the processes. Bimetallic catalyst based on La, Co, B along with K and Sn can be prepared to improve the processes' performance. Similarly, use of micro-reactor systems for these processes can be investigated to reduce the cost and increase the affordability of the system.

The developed technology could also be used for cost reduction of other bio-fuel producing processes, having potential of biogas generation as byproduct. For example productions of ethanol and biodiesel have potential for biogas generation. The spent wash obtained from distillery waste is usually converted to biogas. Likewise the oil cake obtained from crushing of non-edible oil seeds in vegetable oil feedstock for biodiesel production can be targeted for biogas production. Under the new Clean India scheme "Swachh Bharat Abhiyan" will be greatly benefited by the implementation of the idea by utilizing waste and generating clean power, in addition to providing environmental friendly fertilizer, resulting in cleaner cities and villages and meeting the day today power requirements.

7. References:

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Figures

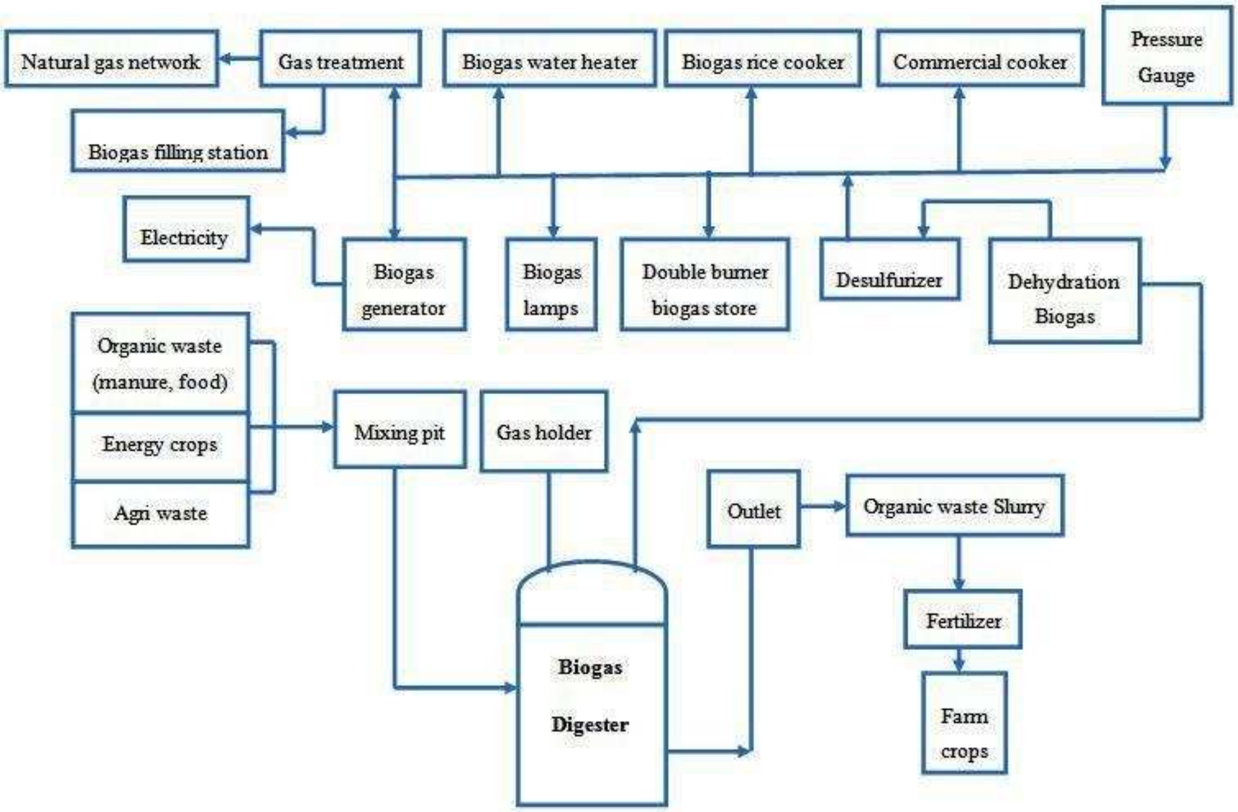

Figure 6: Basic utilization of biogas.

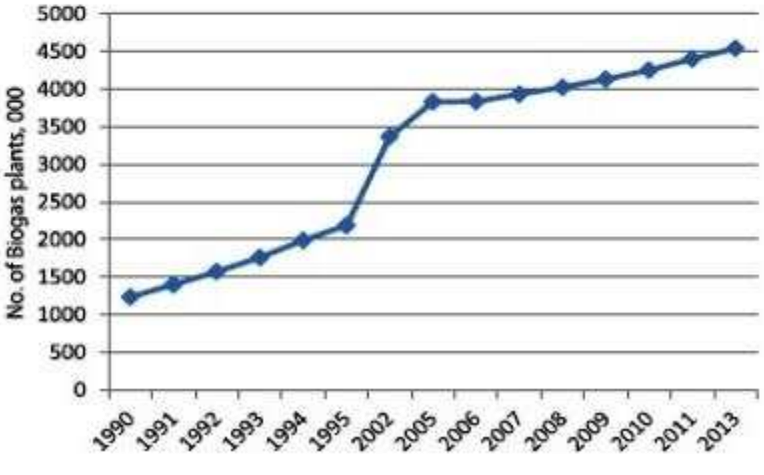

Figure 7: Installed biogas plants in India [17].

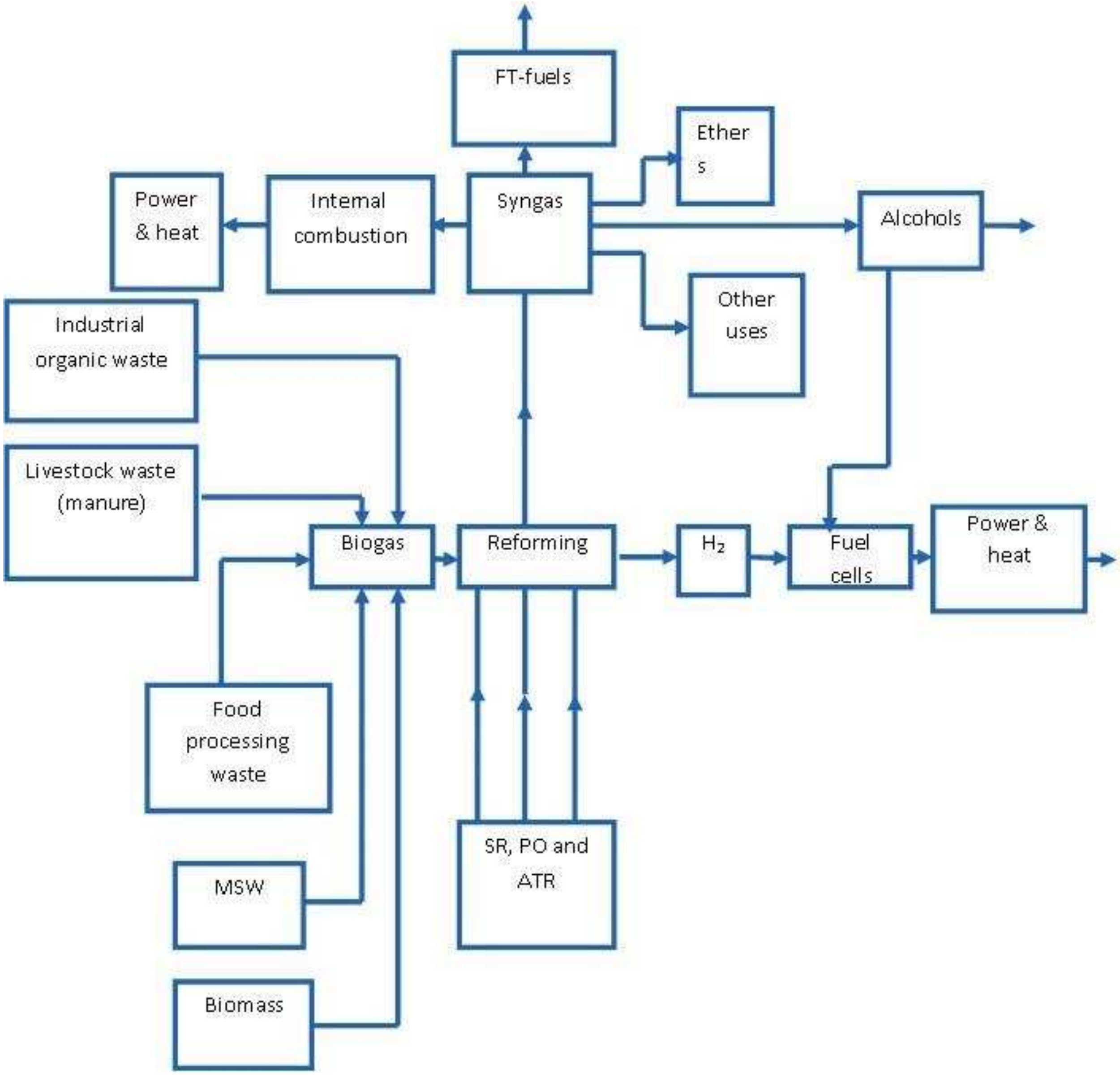

Figure 8: Schematic of synthesis gas utilization derived from biogas.

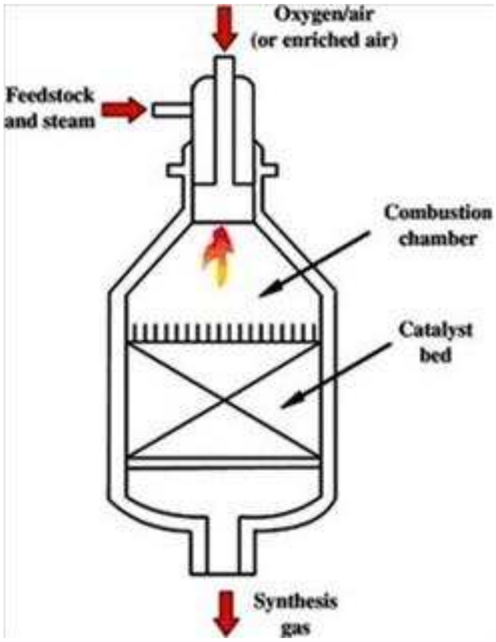

Figure 9:ATR reformer applied in GTL applications [40]

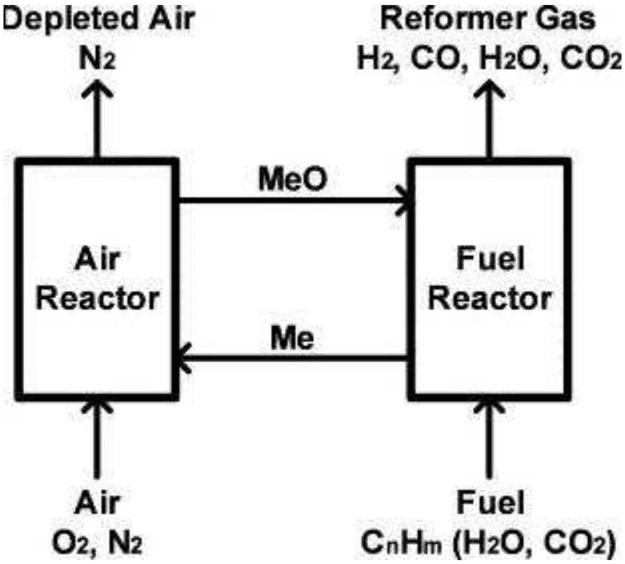

Figure 10: Schematic of ACR reforming system.

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

		Biogas composition		
Component	**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

Table 2: Reduction in greenhouse gas emissions as a result of biogas utilization [12].

Substrate	(%)
Grass	86
Sugar beet (Incl. Tops)	85
Maize	75
Manure	148
Waste from food industry	119
Organic household waste	103

Table 3: Comparison of direct burning of 1kg of dung and its use as biogas [15].

Parameters	Burning dung	Bio-gas
Gross energy	10,460 kcal	4713 kcal
Device efficiency	10%	55%
Useful energy	1046 kcal	2592 kcal
Manure	Not generated	10 kg of air dried

Table 4: Gross and surplus biomass generated in India [18]. A kt is a kilo tonne.

State	Area (kha)	Crop production kt/year	Biomass generation (kt/year)	Biomass surplus (kt/year)
Andhra Pradesh	2540.2	3232.0	8301.7	1172.8
Assam	2633.1	6075.7	6896.3	1398.4
Bihar	5833.1	13817.8	20441.8	4286.2
Chhattisgarh	3815.5	6142.8	10123.7	1907.8
Goa	156.3	554.7	827.2	129.9
Gujarat	6512.9	20627.0	24164.4	7505.5
Haryana	4890.2	13520.0	26160.9	9796.1
Himachal Pradesh	710.3	1329.2	2668.2	988.3
Jammu and Kashmir	368.7	648.7	1198.7	237.7
Jharkhand	1299.8	1509.0	2191.2	567.7
Karnataka	7277.3	38638.5	23766.8	6400.6
Kerala	2041.7	9749.7	9420.5	5702.0
Madhya Pradesh	9937.0	14166.9	26499.6	8033.3
Maharashtra	15278.3	51343.3	36804.4	11803.9

Table 5: Estimation of bio-gas generation from animal waste in India.

Animal	**Population (million)**	**Waste (kg day^{-1}head^{-1})**	**Estimated fresh waste tonnes/day**	**Gas Yield m^3/kg of dry matter**
Cattle	11.189	20	223780	0.34
Buffalo	2.009	25	50225	0.24
Sheep	7.991	0.6	4794.6	0.37
Goat	9.275	0.6	5565	0.37
Pigs	0.284	3	852	0.39
Poultry	128.1	0.1	12810.8	0.46
Total	242.32		298027.4	

Table 6: Energy potential of waste water from India [19].

Industry	Wastewater Produced (Mm^3)	COD of wastewater (kg/m^3)	Energy value of CH_4 at 20% conversion of wastewater to energy, TJ [ab]	Energy value of CH_4 at 90% conversion of wastewater to energy, TJ[b]
Distillery	6000	118.00	5,947.20	9,558.00
Steel plants	10,40,000	0.60	5,241.60	8,424.00
Paper and pulp	7,200	5.91	357.44	574.45
Sugar industry	230	2.50	4.83	7.76
Cotton	1,550	0.60	7.81	12.56
Fertilizers	52	2.00	0.87	1.40
Refineries	15	0.30	0.04	0.06
Dairy	206	2.24	3.88	6.23
Pharmaceuticals	56	0.39	0.18	0.29
Coffee	1.3	2.80	0.03	0.05
Edible oil	1,425	4.60	55.06	88.49
Total	10,56,730		11,618.94	18,673.30

a-The IPCC default value of 20% is considered as the fraction of wastewater treated in anaerobic systems. For distillery 56% is considered based on literature. b- It is assumed that with advent of efficient waste treatment mechanisms and innovations in reactors, up to 90% of wastewater can be treated in an anaerobic system. Energy values are calculated with a conversion factor of 0.05 MJ/m^3 CH_4, with CH_4 producing capacity of 0.30 m^3 CH_4/kg COD.

Table 7: Waste water generated in India [15].

Name of the zone	City classification	Wastewater generated (Mld)	Wastewater collected (Mld)
South	Very large	669.53	
	Large	58.22	
	Medium	640.42	
	Small	1532	
		2911	1812
North	Very large	1935	
	Large	394	
	Medium	948.26	
	Small	2250	
		5578	3932
Western	Very large	978	
	Large	437	
	Medium	780.525	
	Small	1269	
		3469	2275
Eastern	Very large	55	
	Large	297	
	Medium	631	
	Small	2461	
		3434	2151

Table 8: Conversion of different waste biomass to energy in India and reported benefits [19].

S.N.	Name of the industry/agency	Feedstock/waste	Conversion route	Applications	Reported benefits/savings
1.	Sakthi Sugars, Maharashtra	Sugarcane bagasse	Biomethanation	Heating	Reported IRR = 32% Biogas substituted for almost 87% of fuel oil consumption

2.	K.M. Sugar Mills, Uttar Pradesh	Do	Do	Power plant (capacity 1 MW)	12,000 m^3 biogas produced from 400 KL of spent wash per day
3.	Pravar Nagar, Sugar factory at Maharashtra	Sugar factory press mud (75% organic matter; 29% solid content; 65% is volatile	Biogas (having 60% methane)	Domestic fuel for cooking	Four biogas plants each having 85 m^3 capacity each are setup with MNRE's financial assistance. Meeting cooking needs of 196 households for 4 h/day
4.	Demo plants by an NGO Appropriate Technology Institute (ARTI)	Sugarcane leaves left after harvesting	Oven and rotary kiln conversion to char and briquetting biogas	Fuel for various applications	Plant output 100 kg char per day. Earning of Rs. 75,000 in 25 weeks of harvesting season
5.	ASTRA, IISc	Leafy biomass	biogas	Fuel	It is claimed that 2/3 of the families of estimated 100 million rural household could be provided if we use only 10% of around 1130 million ton leafy biomass waste available in India
6.	Al-Kabeer Exports Pvt. Ltd. Medak (Andhra Pradesh)	Slaughter house waste (liquid and solid)	Two stage digestion process for biogas production	Fuel	3000-4000 m^3 gas is produced, which saves furnace oil consumption worth Rs. 4 million per annum

7.	Western Hatcheries Ltd.	Poultry waste	UASB reactor for biogas production	Power plant (capacity 1.2 MW)	60 m3 biogas is produced per day from 200 TPD poultry waste processing plant at Namakhal
8.	MSW to energy & resources in singupa town in Bellary District by Technology Informatics design Endeavour (TIDE) &IISc	Organic fraction of municipal waste	Plug flow biogas reactor	Not known	Data collected shows that 1 kg waste gives 50-601 of biogas. C/N ratio of compost is found to be 11.4
9.	Coffee Board and Ministry of commerce	Coffee pulping waste	Bioreactor for biogas conversion	Power generation	About 80 m3 of biogas is produced from each ton of coffee parchment. The technology has been successfully has been successfully demonstrated at 13 locations
10.	Transport House, KSRTC, Bangalore	Canteen waste (rice straw, bagasse, paper shreds, garden cuttings, lawn mowing, vegetable peels, uneaten rice, plate and washings, fruit and vegetable rejects)	Biomethanation	Fuel for food warming	The KSRTC plant can handle 25 kg of canteen rejects per day along with leaf litter, which produces 1.5 m3 of biogas

Table 9: Bio-gas implemented projects in India in the year 2014.

SR. No.	State	Implementing Agency	No. of Proposals received	Plant capacity m^3	Proposed Power Generation Capacity(kW)	Total CFA including administrative Charges (Rs in Cr.)	Date of receipt	Status
1	Karnataka	BDTC, Bangalore	14	4700	472	1.83	17.01.2014	Sanctioned (F. No. -25-32/2012-BE 09.06.2014
2	Uttar Pradesh	UPNEDA, Lucknow	16	1630	216	0.83	16.07.2014	Sanctioned (F. No. -25-1/2014-15/Bp 10.09.2014)
3	Punjab	PEDA Chandigarh	22	3535	343	1.44	01.09.2014	Sanctioned (F. No. -25-5/14-15-BE 05.11.2014)
4	Andhra Pradesh and Telengana	NREDCAP, Hyderabad	7	855	90	0.39	30.8.2014	Sanctioned (F. No. -25-4/14-15/BPP 03.11.2014)
5	Madhya Pradesh	MPUVN, Bhopal	1	85	10	0.04	24.09.2014	Under process* (File with IFD)

Table 9 continues on next page

SR. No.	State	Implementing Agency	No. of Proposals received	Plant capacity m^3	Proposed Power Generation Capacity(kW)	Total CFA including administrative Charges (Rs in Cr.)	Date Of receipt	Status
6	Andhra Pradesh & Telengana	NREDCAP, Hyderabad	2	1560	187	0.58	08.10.2014	Under process* (File with IFD)
7	Uttar Pradesh	UPNEDA, Lucknow	10	1155	134	0.57	10.09.2014 & 17.11.2014	Under process* (File with IFD)
8	Punjab	BDTC, PAU, Ludhiana	1	200	24	0.09	18.11.2014	Under process* (File with IFD)
9	Nagaland	DNRE, Nagaland, Kohima	1	85	3	0.01	12.09.2014	Incomplete documents* (Letter issued on 28.11.2014)
10	Maharashtra	MEDA, Pune	6	1550	186	0.70	23.10.2014 & 28.10.2014	Incomplete documents* (Letter issued on 28.11.2014)

Table 10: Carbon formation in H_2 production from bio-gas.

Catalyst	**Condition**				**Deposited**	**Author**
	Temp (°C)	**S/C**	**O_2/CH_4**	**CH_4CO_2**	**Carbon**	
Refomax	750	-	-	1.5	15.21%[a]	[53]
Pd(7)-Rh(1)/$CeZrO_2$-Al_2O_3	700	2.00	-	-	14.62%[b]	[54]
NiO/Al_2O_3-Ni/Al=67:33	600	-	-	1.5	8.79[c]	[46]
10NiO/6wt%La_2O_3-Al_2O_3	800	-	-	1	6.74%[d]	[55]
7NiO-3wt%CoO_2/ 6 wt% La_2O_3-Al_2O_3	800	-	-	1	6.53%[e]	[56]
7NiO-3wt%CoO_2/ 6 wt % La_2O_3-Al_2O [f]	850	-	-	1	3.15[f]	[57]
$Ni_{0.4}Ce_{0.8}O_2$	600	-	-	-	1.2%	[58]
75%NiO-25%CoO_2/Al_2O_3	600	-	-	1	0.20[g]	[59]
8wt%NiO/Al_2O_3	860	-	-	1.5	0.180[h]	[60]

a- The experiment was performed using GHSV of 300 cm^{3}/(g$_{cat}$ min)

b- The coke deposited was measured in terms of % of feed. The experiment was performed of GHSV of 10000/h

c- The value is provided rate of carbon deposited measured in terms of (g$_{carbon}$/g$_{catalyst}$)

d- The experiment was performed using GHSV of 6000 cm^{3}/(g$_{cat}$.h)

e- Catalyst tested for 100 h in stainless steel reactor & The experiment was performed using GHSV of 6000 cm^{3}/ (g$_{cat}$.h)

f- Carbon amount was measured as percentage of the used catalyst and the experiment was performed using GHSV of 6000 cm^{3}/(g$_{cat}$.h). The catalyst was reduced for 2 h in pure H_2 at a flow rate of 30 ml min^{-1} at 700 ˚C

g- The value is provided rate of carbon deposited measured in terms of g$_{carbon}$/g$_{catalyst}$. The total metal loading for the catalyst was 15wt%.

h- The experiment was performed using GHSV of 1200/h. Amount of Coke was measured in the form of g$_{carbon}$/g$_{catalyst}$ Amount of Carbon deposition was measured in the form of g$_{carbon}$/c$_{atalyst}$

Table 11: Surface area properties for various catalysts utilized in H_2 production from biogas.

Formulation	Catalyst	Support	Crystallite size	Reference
10 wt% NiO/6wt %La_2O_3-Al_2O_3	252.7^a	-	5.3	[55]
7wt %NiO-3wt% CoO_2/6wt %La_2O_3-Al_2O_3	252.2^a		4.7	
	203^a	-		[70]
HT2-750^h	162^c		4.19^a	
LaHT2-750^h	166^a		4.18^a	
	142^c			
0.5 wt% PtO_2/Al_2O_3	163^d	188	-	[71]
	159^e			
	152^a			
8wt% NiO/Al_2O_3	163^a	281	14	[60]
8wt% NiO/10wt% CeO_2-Al_2O_3	136^a		13	
8wt%NiO/20wt%CeO_2-Al_2O_3	126^a			
15 wt% NiO/γ-Al_2O_3	151^a	206	11.34^a	[72]
	106^c		12.09^b	
	86^b			

1.31 wt%-Pd(7)-Rh(1) / $CeZrO_2$	143.2^{a} 130^{b}	-		[54]
$Ni_{0.1}Ce_{0.95}O_2$	128^{a}	-	7.36^{a} 17.1^{b}	[58]
$Ni_{0.26}Ce_{0.87}O_2$	105^{a}		7.35^{a} 13.4^{b}	
20 wt% NiO/ZrO_2	34^{a}	-	14^{a}	[73]
20 wt% NiO–4wt%MgO–ZrO_2	23^{a}		16.1^{a}	
$Ce_{0.25}La_{0.50}Ni_{0.25}O_{2-\delta}$	3.8^{a}	--	18.3^{f} 9.8^{g}	[74]
$Ce_{0.40}La_{0.40}Ni_{0.20}O_{2-\delta}$	2.9^{a}		26.9^{f} 6.8^{g}	
7wt %NiO-3wt% CoO_2/6wt %La_2O_3-Al_2O_3^{h}		-	16.5	[75]
7wt %NiO-3wt% CoO_2/6wt %La_2O_3-Al_2O_3^{i}			15.3	

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a- Fresh catalyst
b- Used catalyst
c- Reduced catalyst
d- Catalyst activity preformed at 900°C and reduced at 900°C.
e- Catalyst examined at 900°C without reduction.
f- CeO_2 crystallite size.
g- Ni crystallite size.

Table 12: Pore sizes of catalysts tested in H_2production from biogas.

Material	**Support**		**Catalyst**		**Reference**
	Pore size (nm)	**Pore volume (cm^3/g)**	**Pore size (nm)**	**Pore volume (cm^3/g)**	
15 wt% NiO/γ-Al_2O_3	11.34	0.79	12.09[a] 21.11[b] 17.66[c]	0.626[a] 0.581[b] 0.433[c]	[72]
1.31 wt%-Pd(7)-Rh(1)/($CeZrO_2$-Al_2O_3)	-	-	9.0[a] 19.0[d]	0.14[a] 0.12[d]	[54]
10 wt% NiO / 6 wt% La_2O_3-Al_2O_3			10.16	0.6416	[55]
7 wt% NiO – 3 wt% CoO_2/ 6 wt% La_2O_3-Al_2O_3			10.15	0.6399	
8 wt% NiO/Al_2O_3		0.65	14.5	-	[60]
8 wt% NiO /10 wt% CeO_2-Al_2O_3			14.9		
$Ni_{0.1}Ce_{0.95}O_2$			14.9	0.48	[58]
$Ni_{0.26}Ce_{0.87}O_2$			15.7	0.41	

a- Fresh catalyst
b- Used catalyst after stability test at 800 °C
c- Used catalyst after stability test at 700 °C
d- Used catalyst

Table 13: Catalyst performance summary evaluated in SRB and ATRB.

Process	Catalyst	X_{CH4}	X_{CO2}	Yield		Experimental Conditions			
				Y_{H2}	Y_{CO}	S/C	Temp (°C)	CH_4/CO_2	O_2/C
SR	10 wt% Ni onCeZrLa	43	12	47.2	2.1	3	550	1	-
ATR	25% Ni onMgAlCe	52	48	72.7	12	1	873	1.5	-
SR	5 wt% NiO/CeO_2	64.6	36.2	35.8	10.5	1.3	800	2	-
SR	15% Ni on Al_2O_3	82	8.5	-	-	2	1073	1.2	-
SR	0.09 wt%[Pd(7)-Rh(1)]/($CeZrO_2Al_2O_3$]	90	6.5	71.2	0.8	1.5	1073	1.5	-
OSR[g]	Ni/CeO_2	90	65	82	82	0.3	1023	1.5	0.1
SR	4wt%RhO_2/3wt% La_2O_3-Al_2O_3	93	10.5	2.62[a]	0.98[a]	1.3[a]	685[a]	1[a]	-
		97.5	-49.0	3.53[a]	0.39[a]	3.8[a]	650[a]	1[a]	-
SR	1.3 wt %Pd-Rh/$CeZrO_2$-Al_2O_3	93.9	5.0	-	-	1.2[b]	800[b]	1.5[b]	
SR	$Ni_{0.4}Ce_{0.8}O_2$	~96	40	~72.4%[c]	~5%	2	700	3	6.2
ATR	1.5 wt% NiO/CeO_2	97.5	90.5	96.3	1.3[d]	0.3[d]	800[d]	1.5[d]	0.1
SR	7.5wt% Ni/CeO_2	99	4	55	29	1	900	1.5	-
ATR	5 wt% Ni on Mg0.4Al_2O_3	99	15	-	-	3	1073	1.5	0.5
ATR	13 wt% NiO/Ce-Zr-Al_2O_3	99.0	34.4	67.1[e]	1.5[f]	1[f]	800[f]	1.5[f]	0.25[f]
ATR	1wt%RhO_2-13wt% NiO/Ce-Al_2O_3	99.1	39.1	75.3[e]	1.7[f]	1[f]	800[f]	1.5[f]	0.25[f]

a- Experiment was performed using WHSV of 9810 h^{-1}. The yield was calculated on the basis of mol H_2 produced/mol of CH_4. The long term experiments were performed for 40 h.

b- The experiment was performed using WHSV of 20,000 h^{-1} for 200 h.

c- These values are expressed as dry mole fraction of the outlet gas.

d- Experiment was performed at WHSV of 30,000 h^{-1} for 150 h.

e- The H_2 yield is calculated by dividing out volumetric flowrates of H_2 by inlet volumetric flowrates of CH_4 and H_2O.

f- Experiment was performed using WHSV of 161 h^{-1} with Ni and Rh loading of 13 and 1 wt%.

g- Oxidative Steam reforming.

Table 14: Catalyst performance summary investigated in DRB and ODRB

Process	Catalyst	X_{CH4}	X_{CO2}	Yield		Experimental Conditions				Ref
				Y_{H2}	Y_{CO}	S/C	Temp (°C)	$CH4/CO_2$	O_2/C	
DRB	75Ni-25Co/Al_2O_3[a]	25	-	-	0.6	-	600	1	-	[59]
DRB	HT (Mg/Al=2+Ni=2%)	35	45	-	0.6[b]	-	700[c]	1[c]	-	[70]
DRB	15 wt%Ni-5 wt %CoO_2/MgO–Al_2O_3	57.1[d] 80[e]	-	90%[d] 90%[e]	-	-	900	1.25	-	[115]
DRB	13 wt%NiO/Ce-Zr-Al_2O_3	60.1	94.4	63.5	1[b]	-	800[d]	1.5[d]	-	[114]
DRB	1 wt%RhO_2-13 wt% NiO/Ce-Al_2O_3	64.5	85.6	57.5	0.9[b]	-	800[d]	1.5[d]		
DRB	Refomax	67	86	33%[b]	39%[b]	-	750[e]	1.5[e]	-	[143]
ODRB	20 wt%NiO/Al_2O_3	70	85	-	-	-		1.5	0.1	[116]
DRB	8 wt%NiO/20 wt% CeO_2-Al_2O_3	70.5	97	76.5	60	-	860[f]	1.5[f]	-	[60]
DRB	20 wt% NiO/MgO	80	85	-	1.15[b]		750[g]	1.5[g]	0.1[g]	[144]
DRB	26 wt% (nanocast) Ni on La_2O_3	80	82	-	-	-	700	1	-	[145]
DRB	$Ni_{0.4}Ce_{0.8}O_2$	~83	~78	-	-	0.6[h]	700[h]	3[h]	-	[58]
DRB	7 NiO-3 wt%CoO_2/ 6 wt% La_2O_3-Al_2O_3	>90	>90	~95	>95	-	800	1	-	[55]
DRB	7 NiO-3 wt%CoO_2/ 6 wt% La_2O_3-Al_2O_3	93.7	94	95%[i]	98%[i]	-	800[j]	1[j]	-	[56]
DRB	NiAl-HT	93.7	94.4	92.6	85	-	700	1	-	[146]
DRB	7 NiO-3 wt%CoO_2/ 6 wt% La_2O_3-Al_2O_3	95	97	-	-	-	850[k]	1	-	[57]
		95	99	98%[i]	99%[i]	-	850[l]	1[l]	-	[75]
DRB	9 wt% NiO/$Ce_{0.82}Sm_{0.18}O_{1.91}$	~98	~97	0.8	-	-	800	1	-	[136]
DRB	$Ce_{0.70}La_{0.20}Ni_{0.10}O_{2-\delta}$	98	80	-	1.8[b]	-	800[m]	1.04[m]	0.1[m]	[74]

a- The catalyst prepared had a total metal loading of 15 wt%.

b- The yield of CO was measured on the basis of H_2/CO ratio.

c- The catalyst performance was evaluated for 50 h.

d- The catalyst performance was evaluated with 100 ppm S in the feed for 9 h.The selectivity of H_2 was obtained by dividing molar flow rate of H_2 divided by molar flow rate of 2 CH_4 reacted.

e- The selectivity of H_2 was obtained by dividing molar flow rate of H_2 divided by molar flow rate of 2 CH_4 reacted. The catalyst performance was evaluated in absence of S.

f- The performance of the catalyst was evaluated at WHSV of 1200 h^{-1} for 300 min over 8 wt% Ni supported catalyst.

g- The activity of the catalyst was examined over 6h with activity reducing with decreasing MgO content from 100 to 20 wt%.

h- Performance evaluated for 24 h.

i- The H_2 selectivity was calculated by dividingH_2 molar flow rate by molar flow rate of CH_4 reacted. CO selectivity was obtained by dividing CO molar flow rate by molar flow rate of CH_4 and CO_2 reacted.

j- The performance of the catalyst was evaluated using GHSV of 6000 $cm^3\ g_{cat}^{-1}\ h^{-1}$ for 300 h.

k- The catalyst was reduced in H_2 for 2h followed by treatment in CO_2 for 2h at 850 ^oC, over 7 wt% Ni, 3 wt% Co and 6 wt% La_2O_3 promoted Al_2O_3 catalyst, using GHSV of 6000 $cm^3\ g_{cat}^{-1}\ h^{-1}$.The performance of the treated catalyst was evaluated for 30 h.

l- The catalyst was reduced in H_2 for 2 h followed by pre-treated for 1 h in CO_2 at 850^oC using GHSV of 6000 $cm^3\ g_{cat}^{-1}\ h^{-1}$. The performance of the treated catalyst was evaluated for 27 h.

m- The performance of the catalyst was evaluated using 31,000 h^{-1} for 150 h.

Table 15: Comparison of various reforming technologies for H_2 production form bio-gas adopted from [9, 147,148].

Methods	Advantages	Disadvantages
SR	Produces high-purity H_2 fellow carbon formation. Widely used for H_2 production. Cannot use CO_2 in bio-gas. Highest H_2 yield.	Needs to remove H_2S and add oxidizing agents. High operating temperature and energy demand. Catalyst can be moderately expensive. Highest CO_2 emissions. Highest NO_x emissions. Large size reformer
ATR	Produces high-purity hydrogen fuel. High energy efficiency. Can use both CH_4 and CO_2 in biogas. Compact size. Absence of NO_x formation due to use of pure O_2	Complex process control; needs multiple catalyst. Relatively unstable. Lower H_2 yield compared to SR Limited commercial experience. Requires air or oxygen. In case of use of O_2 expensive air separation units are required.
ACR	H_2 yield is comparable to SR. Can use both CH_4 and CO_2 in biogas. Compact size. Lower energy requirement compared to SR. N_2-free H_2 rich gas is obtained. No air separation is required which otherwise is required for PO and ATR reformers.	Process under development stage. Very limited commercial experience only few pilot plants are available. Absence of NOx emissions
DR	Can use both CH_4 and CO_2 in biogas. High conversion efficiency.	Carbon formation. Moderate selectivity. Side reaction consumes hydrogen. High operating temperature and energy demand. Catalyst can be expensive. Lower H_2 yield compared to SR. Limited commercial experience. Large size reformers
PO	High energy efficiency. Relatively low operating temperature. Can be combined with other reforming methods. Feedstock desulfurization not required. With use of O_2 absence of NO_x formation.	May completely oxidize methane to CO_2 and H_2O. Limited industrial application. Lower H_2 yield compared to SR. Soot formation/handling adds process complexity. Low H_2/CO ratio. Very high operating temperate. Highly exothermic reaction leading to catalyst deactivation by formation of hot spots. Danger of explosion. Requires air or oxygen. Lower H_2 yield compared to SR. In case of use of O_2 expensive air