

Hydrogen Production from Biogas: Methods and Economic Analysis

Ravindra Kumar

Delhi Technological University

Anil Kumar (✉ anilkumar76@dtu.ac.in)

Delhi Technological University <https://orcid.org/0000-0002-2846-4347>

Amit Pal

Delhi Technological University

Research Article

Keywords: Hydrogen production, Biogas, Anaerobic, digestion, Reforming method

Posted Date: June 8th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-457836/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

In present days, H_2 is mainly produced via natural gas from thermochemical methods. The importance of renewable H_2 production has increased due to energy issues, global environmental, fossil fuel depletion, and pure hydrogen demand. Biogas is produced from anaerobic digestion or carbon-based waste fermentation methods. It might be a substitute resource to the creation of hydrogen. Methane (CH_4) and carbon dioxide (CO_2) are two significant constituents of biogas, and these are multipurpose feedstock materials for the generation of valuable chemicals and fuels. This paper presents major hydrogen generation techniques from biogas reforming in detail and a short discussion of biogas reforming's economic analysis. The effective operating parameters such as reaction temperature, gas hourly space velocity and O_2/CH_4 ratio are also discussed. Biogas has more potential; however, it needs more research on some issues such as deactivation of the catalyst, purification of biogas and removable of H_2S . Various reforming methods can be nominated for H_2 production depend on biogas composition, the need for hydrogen purity, investment availability and quantity of the desired hydrogen.

1. Introduction

Growing concern about worldwide climate issues and diminution of fossil fuels, the utilization of renewable energy resources has been more focussed (Avraam et al. 2010). A large scale of H_2 production developed via reforming techniques, mainly natural gas (CH_4) and light hydrocarbons (HCs), used in the chemical industry field (Alves et al. 2013). Hydrogen is abundant and is the most available in renewable energy. Furthermore, only water vapor is produced from the combustion of hydrogen. At present, biogas is an important group from renewable energy sources.

Biogas can be an important path of hydrogen production. It is a combination of dissimilar gases developed via the anaerobic breakdown or fermentation of carbon-based waste material in the existence of microbes (Verma and Samanta 2016). The product of biogas, mainly carbon dioxide (CO_2) and methane (CH_4), associated with touches of additional gases like hydrogen (H_2), ammonia (NH_3), hydrogen sulfide (H_2S), vapor water (H_2O), nitrogen (N_2), and oxygen (O_2) (Alves et al. 2013). The unwanted component of biogas is hydrogen sulfide (H_2S). It is corrosive gas and sustains to damage accessories and equipment during the process of producing energy. Another impurity, like CO_2 and humidity, also decreases biogas' calorific value through explosion for thermal plants (Horikawa et al. 2004). Biogas generally carries different gases as a basis of volume percentage by CH_4 (55–65), CO_2 (35–45) and N_2 (1) in sewage digesters while CH_4 (60–70), CO_2 (30–40) and N_2 (1) in biological waste digesters and CH_4 (45–55), CO_2 (30–40) and N_2 (5–15) in landfills (Lau et al. 2011). It is usually generated in biowaste digesters, sewage sludge and landfills that contain agricultural wastes, crop residue, animal wastes and animal dung etc. (Chattanathan et al. 2014). Some important chemical composites involve in biogas as basis of volume percentage listed in Table 1.

Table 1
Chemically structure of biogas (Alves et al. 2013; Verma and Samanta 2016; Nalbant and Colpan 2020)

| Composite | Percentage |
|------------------|--------------------|
| CH ₄ | 55–70 (volume %) |
| CO ₂ | 30–45 (volume %) |
| H ₂ S | 500–4000 (ppm) |
| NH ₃ | 100–800 (ppm) |
| H ₂ | Below 1 (volume %) |
| N ₂ | Below 1 (volume %) |
| H ₂ O | Below 1 (volume %) |
| O ₂ | Below 1 (volume %) |

H₂ is the simplest element, an atom containing only one proton and one electron. It is a colorless and odorless gas. It is also the most plentiful component in the universe. It is combined with additional chemical substances and detected as part of a different element such as alcohol, hydrocarbon, and water. It is also available in inherent biomass, which contains animals and plants (Kalamaras and Efstathiou et al. 2013). The main benefits of hydrogen are net zero emission of greenhouse gases and high energy content compared to other known substances (LHV;120 MJ/kg and HHV;142 MJ/kg) (Ouyang et al. 2013).

In the present scenario, hydrogen is produced from fossil fuels around 96% and 1% from biomass (Sinha and Pandey 2011). Currently, application H₂ as raw material is widely used in a combustion engine, fuel cell, fertilizer industries, chemical industry, pharmaceutical industry, hydrogenation process, Fischer-Tropsch synthesis, production of ammonia and ammonia, among others (Armor 1999).

Overall, biogas reforming is a favorable and attractive method to generate clean hydrogen gas. The main biogas benefits for reforming purpose in H₂ production are decreased greenhouse gas emissions, local availability, reliability and better environment, and economic (Nalbant and Colpan 2020). The key motive of this paper is to express the numerous biogas reforming technique for H₂ production and its economic analysis.

2. Reforming Of Biogas For H₂ Production

There are several approaches for the invention of H₂. It could be divided into two classes as traditional and non-traditional ways. In traditional methods, hydrogen is obtained from hydrocarbon reforming as

natural gas (CH₄) and hydrocarbon pyrolysis. In non-traditional methods or alternative methods that can use renewable sources (Nikolaiis and Poullikkas 2017).

Interestingly, methane is part of the biogas component, and biogas is generated from waste materials as adopted the renewable source. Therefore, biogas reforming seems to renewable energy from conventional techniques for the production of hydrogen (Nikolaiis and Poullikkas 2017).

To produce pure hydrogen, additional steps are included in any reforming process. A conversion reactor is utilized for converting the CO into CO₂ by using shift reaction (Alves et al. 2013). The final process for hydrogen purification is done in a separate unit by pressure swing adsorption (PSA) (Nikolaiis and Poullikkas 2017). H₂ could be obtained through the methane or reforming of biogas in various temperature limits (873–1273K) over reversible reactions and exothermic or endothermic. The reforming reactions are done by low pressure and high temperature. In several kinds of reforming methods, biogas responds along with representatives like oxygen or air and steam to generate syngas with H₂ and other gases (Galvagno et al. 2013).

There are some purification techniques available for removing toxic and undesirable substances present in biogas: physiochemical and biological treatment (Alves et al. 2013). Figure 1 presents the important steps for the production of H₂ from biogas.

Consequently, the biogas reforming reactions are parallel to natural gas (CH₄) reforming. Table 2 illustrates the chemical reactions formed in reforming methods and its enthalpy of reaction at 298K and 1 atm. There are major reforming techniques for H₂ production from biogas or methane as follows.

Table 2 Chemically reaction involved in reforming methods (Alves et al. 2013; Verma and Samanta 2016)

| Reaction Equation | Name of reaction | Type of reaction | Thermal reaction, $\Delta H_{298\text{K}}$ (kJ/mol) |
|-------------------|--------------------|--|---|
| Eq. 1 | SR | $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ | 206.20 |
| Eq. 2 | Gas-shift reaction | $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ | -41.20 |
| Eq. 3 | Combined reaction | $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}_2$ | 165 |
| Eq. 4 | Methane cracking | $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$ | 74.9 |
| Eq. 5 | Boudouard reaction | $2\text{CO} \rightarrow \text{C} + \text{CO}_2$ | -172.40 |
| Eq. 6 | Reduction of CO | $\text{CO} + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O}$ | -131.30 |
| Eq. 7 | POR | $\text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$ | -35.60 |
| Eq. 8 | Complete oxidation | $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ | -801.70 |
| Eq. 9 | ATR | $\text{CH}_4 + 0.5x\text{O}_2 + y\text{CO}_2 + (1 - x - y)\text{H}_2\text{O} \rightarrow (y + 1)\text{CO} + (3 - x - y)\text{H}_2$ | ≈ 0 |
| Eq. 10 | DR | $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ | 247.40 |
| Eq. 11 | DOR | $\text{CH}_4 + \beta\text{CO}_2 + (1 - \beta)/2 \text{O}_2 \rightarrow (1 + \beta)\text{CO} + 2\text{H}_2$ | $(285\beta - 38)$ $0 \leq \beta \leq 1$ |

2.1 Steam Reforming (SR)

This process is done by methane and water (H_2O) vapor with the catalyst that generates syngas (mixture of CO and H_2 , Eq. 1, Table 2). Methane is required a high temperature for reacting. The reaction of this process is extremely endothermic and needs a high temperature of nearly $650\text{--}850^\circ\text{C}$ to attain a high yield of H_2 in between 60 to 70% (Verma and Samanta 2016). The ratio H_2/CO is three that means the higher yield of H_2 nearly 75%. High temperature can also be reduced by using a suitable catalyst (Shanmugam et al. 2018).

This technique consists of a steam reformer, water gas shift reactor, and direct steam reforming reactions inside the reactor. Initially, methane responds with water in the steam reformer, and the syngas and CO and H_2 are formed in the existence of a suitable catalyst. Then, the syngas is fed in the WGS reactor after cooling in a range of $300\text{--}500^\circ\text{C}$. CO reacts through the water to decrease the CO content of syngas and developed the H_2 and CO_2 (Eq. 2). High conversion of CO content and low kinetic reactions were done by high-temperature WGS reactor. While low CO conversion and high kinetic reactions are done by minimum temperature water-gas shift reactors (Minh et al. 2018). Fe, Cu, Fe-Pd and Mo alloys are mostly used catalysts in water gas shift (Verma and Samanta 2016).

In addition, combined reaction (Eq. (3)), also known as direct steam reforming reaction, is the addition of Eqs. 1 and 2. To yield pure hydrogen, need a separate unit for example, membrane or PSA (pressure swing adsorption), remove all gases as CO_2 , CO, and other gases except H_2 . Figure 2 shows the reactant and products for the steam reforming process.

The working conditions of steam reforming lead to corresponding reactions that reason carbon formation occur over the surface of catalytic as methane cracking reaction (Eq. (4)), Boudouard reaction (Eq. (5)), and reduction of CO reactions (Eq. (6)). When carbon development seems like the form of nanotubes, it offers a lower distribution of carbon at the surface of the catalyst. Consequently, the catalyst activity is conserved for a long duration (Gregorie et al. 2020).

The possibility of carbon formations is a serious issue since coke deposits and leading deactivation on catalyst surfaces such as Ni-catalyst surface and solid material of carbon; denoted by C. The basic arrangements can control the deposition of coke as if they promoted carbon gasification in water improving and its properties of adsorption (Nawfal 2015). The most popular catalyst is Ni-based on ceramic supports for this process due to its affordable, easily available, and high-quality catalytic properties. There are several catalysts established as Ni-based to improve system performance in the term of selectivity and reactivity (Nawfal 2015).

The Combine components to develop catalysts with oxides that are basic properties such as potassium, calcium and magnesium have been studied. Different catalysts such as Pd and Pt-based catalyst have mere stability about coke formation (Alves et al. 2013). Ruthenium-based catalyst is also mostly used in the methane steam reforming method due to its more activity, the high selectivity of H_2 and outstanding stability (Nawfal 2015). Another way to decrease the deposition of coke as a result of a reaction (Eq. 6) is to perform under the condition of high partial pressure of water to shift the equilibrium in the right

direction and control the carbon formation (Noh et al. 2019). Some other studies explain significant development in separation unit process through the selective membrane reactors or filters (Mahecha-Botero et al. 2009).

All chemical reactions are done in a single vessel from a membrane reactor. To membrane system, both the reactions such as steam methane reforming reaction and shift reaction (Eqs. 1 and 2) co-occur inside the reactor, which comprises a catalyst bed. Additionally, membrane offers the good ability to shift the reaction towards a chemical equilibrium that improves hydrogen production and performs the temperature nearly below 500°C for reforming reaction in the direction of chemical equilibrium (Lin et al. 2003; Sato et al. 2010).

2.2 Partial Oxidation Reforming (POR)

Partial oxidation reforming technique (Eq. 7, Table 2) is another alternative path to produce H₂ from methane reforming. This technique reduces energy consumption/cost due to the exothermic nature and is contrary to the steam reforming process that endothermic nature (Verma and Samanta 2016).

A methane (CH₄) molecule is incompletely oxidised to produce H₂ and CO (known as syngas). The ratio of H₂/CO is two that means yields of hydrogen around 67%. The process needs a temperature range (700-900°C) (Patinvoh et al. 2017). The molar ratio of O₂/CH₄ is a key parameter to control this process since the ratio of O₂/CH₄ more than 0.50 leads to perfect combustion of CH₄ (Eq. 8, Table 2) (Lin et al. 2003).

Since CO selectivity slightly decreases, CH₄ reacts with O₂ and obtains CO₂ that permits complete combustion and sudden temperature rise. That reason initiated a hot spot in the reactor bed that deposits coke formation over the surface of the catalyst (Patinvoh et al. 2017). Researchers have been studied the activity and stability of numerous catalysts with the purpose of POR of biogas. Temperature range more than 800°C, catalyst as a solid solution of (Ca-Sr-Ti-Ni), (Ni-Mg-Cr-La-O), (NiO-MgO), and mixed metal oxides and they are used as higher resistance of coke development (Verma and Samanta 2016; Nalbant and Colpan 2020; Gregorie et al. 2020).

2.3 Auto-Thermal Reforming (ATR)

This process is the union approach of SMR and POR and endothermic in nature. This process reduces steam reforming challenges due to its endothermic process and difficulty producing low yield of hydrogen of partial oxidation reforming (Gregorie et al. 2020).

The summation of reactions is expressed by Eqs. 3,7 and 8 (Table 2). It also happens in CO₂, as denoted by Eq. 9 (Table 2) (Araki et al. 2009). When the steam and oxygen are provided into the reformer, reforming and oxidation reactions occur parallelly, become self-sustainable the whole process, and require less energy. (Nikolaiis and Poullikkas 2017; Verma and Samanta 2016). This process produces the maximum hydrogen yield of approximate 74% (about ratio of H₂/CO is 2.8) (Nikolaiis and Poullikkas 2017).

'Autothermal' means that no need to supply from an external source for the process. ATR process stabled the heat requirement of the endothermic process through the heat released by the exothermic process and adopted it as an effective system (Nahar et al. 2017). ATR has more advantages, such as fast reactor processing, higher ratio of H_2/O_2 compared with POR, temperature control of processing, and minimize the hot spots that prevent the deactivation of catalysts (Verma and Samanta 2016; Patinvoh et al. 2017).

To obtain the H_2 through the biogas, the various the ratios range for H_2O/CH_4 , O_2/CH_4 , and H_2/CO are taken as 1.0–2.5, 0.25–0.55, and 2.0–3.5, respectively (Verma and Samanta 2016; Patinvoh et al. 2017; Mosayebi et al. 2012; Cai et al. 2006).

The maximum efficiencies of plant to biogas reforming with ATR method are about 75%, range of temperature 500–700°C and the ratio of O/C close to 0.8–0.9 (Rau et al. 2019).

2.4 Dry Reforming (DR)

In this approach, CH_4 reacts with CO_2 and obtains the mixture of CO and H_2 (Syngas) (Verma and Samanta 2016), refer Eq. 10 Table 2. This process requirements temperature more than 640°C and work on the endothermic process so need the heat of external source. Biogas is very useful for this process because it has two basic compounds available as CH_4 and CO_2 (Gregorie et al. 2020). This reaction of this process can be attractive an environmental point of view because they are strong greenhouse gases (CH_4 and CO_2), but this process can consume it. Contrarily, the rise in CO_2 emissions due to the proven external heat (other burned fuels) to endothermic reaction (Nalbant and Colpan 2020). Dry reforming uses the ratio of H_2/CO nearly 1 and attaining the yield of H_2 about 50%. The H_2/CO ratio built this reaction attractive about requirements to further use synthesis gas as Fischer–Tropsch synthesis (Gregorie et al. 2020).

Based on the previous finding, the main reaction (Eq. 10 in Table 2) could modify by competing along with some parallel reactions, which shifts the CO_2 conversion in (CH_4) methane. These important reactions are mainly such as the reaction of reverse gas water shift (Eq. 2 reverse), Boudouard reaction (breakdown of CO_2 , Eq. 5 in Table 2), and decomposition of methane (Eq. 4, Table 2). DR method attains the ratio of CH_4/CO_2 close to 1-1.5 (Verma and Samanta 2016; Serrano-Lotina et al. 2012). The essential issue of DR method is the coke establishment that causes the deactivation of catalyst and blockage of the pipes and reactors (Alves et al. 2013). Pt-, Ru- and Rh-based catalysts improve the H_2 generation rate, but they are more expensive, very limited availability, and not established at an industrial scale. Generally, common catalysts such as Co- and Ni- based catalysts are more used (Cai et al. 2006).

2.5 Dry Oxidation Reforming (DOR)

This method has been established for governing the congestion of carbon formation over catalyst surface. It is a joined approach of DR and POR process. This process decreases the energy demand of reaction because the exothermic for partial oxidation releases high temperature that is beneficial to the

endothermic and dry oxidation reforming process. The ratio of H_2/CO also increases and achieving yield of H_2 approximately 60% (Gregorie et al. 2020).

There are additional advantages for this process where parallel feeding of CH_4 with CO_2 and O_2 such as the improved conversion of methane, decreased total energy of the process, higher catalyst activity, improved H_2 yield at lower temperatures, and enhanced resistance of deactivation (Chen et al. 2010). Eq. 11 represents the DOR process where β is stoichiometric ratio of CO_2 fed with the traditional DR (Table 2). If β value is 1, the reaction would be non-oxidative type DR reaction; now, if β value is 0, the reaction would be partial oxidation hence, as the β value must be in between 0–1 (Alves et al. 2013; Verma and Samanta 2016; Nalbant and Colpan 2020).

In the DOR process, the process of changing parameters like reaction temperature and O_2 concentration feed supports the control of the ratio of H_2/CO and the appearance of reaction such as exothermic or endothermic. At a specific temperature, the nature of exothermic is increased by the increasing concentration of O_2 . As known, the reaction of POR (Eq. 7) is exothermic and reaction of DR (Eq. 10) is endothermic by nature. Therefore, DOR method can be used as a preferable substitute over the convention DR method using various molar ratios of oxygen. Thus, the production of syngas from biogas through this method has improved energy performance and requires less exterior energy (Avraam et al. 2010; Alves et al. 2013).

3. Economic Analysis Of Biogas Reforming

H_2 generation from biogas through steam reforming processes has reported almost the same efficiency as natural gas or methane. An economic investigation by 2013 presented that US\$0.27/kWh is attained with payback 8 years (time periods) and some others factors such as maintenance cost, operation and investment (Braga et al. 2013). Since the lower heating value (LHV) of H_2 (120 MJ/kg), the parallelly outcome conclusion of US\$8.98/kg H_2 (approx. 8 €/ kg H_2) (Braga et al. 2013).

More current results in order to steam reforming connecting membrane reactors confirm that more than 20% increases the system efficiency by considering the membrane reactor. Indeed, the system efficiencies are informed closely to 25–28% along with a fraction of $S/C = 3$ for a traditional ATR method and between 46–52% and the fraction of $S/C = 4$ to traditional SR. At the same time, the membrane reactor expresses efficiencies approx.70% along with the fraction of $S/C = 3$ (Di Marcoberardino et al. 2018).

H_2 production using membrane reactor gets less cost than traditional reforming WGS-PSA methods from economic analysis. In the year 2018, it described that H_2 obtaining 100 kg per day at H_2 cost rate 4 €/kg by using fluidized membrane reactor approach, whereas H_2 cost rates are 4.2 €/kg and 6.4 €/kg respectively described by using the SR and ATR traditional approaches at the same parameters (Di Marcoberardino et al. 2018). The cost of H_2 production from biogas must depend on methane content in biogas—technology scale and carbon price, both factors that are relevant from an economic point of

view. Tradition reforming techniques have been fully established at large scale for reforming natural gas since the globally natural gas generation, which is reached by about 3750 billion m³ in 2017 and is situated at specific locations (leading to centralized H₂ generation) (Enerdata 2018). Decentralized H₂ generation could be minimum the requirement of distribution infrastructure and reforming methods like dry reforming (DR). Membrane reactors are much more feasible or competitive at a low generation scale. Since biogas has a decentralized feature related to natural gas (CH₄) and a small scale global production of approximately 36 billion m³ of methane (CH₄) in the year 2015 (Scarlat et al. 2018), it looks more appropriate to decentralized production of H₂. In addition, decentralized H₂ generation makes impractical Carbon Capture and Storage (CCS), which is the method to decrease carbon emissions from the sources of natural gas. Hence, biogas and decentralized generation seem fascinating renewable sources and carbon-free hydrogen production, either if few additions are expensive about impurities removal for biogas reforming like sulphur and siloxanes. Additionally, the dry reforming technique seems to be interesting for biogas reforming and mainly depends on biogas compounds as a reactant.

4. Role Of Operating Parameters

The advancement conversion of biogas needs to address thermodynamic problems such as the need for temperature and high pressure to raise the cost of energy intake. Biogas conversion to syngas requires high temperature (500–800°C) due to endothermic reaction (Chen et al. 2017).

4.1 Reaction Temperature

Reaction temperature has found more influencing parameters on catalyst activity in biogas conversion to syngas. Ni-based catalysts are broadly utilized for biogas conversion to syngas due to their low prices and more potential of catalytic activity than other metals (Zain and Mohamed 2018). An increase in conversion of methane and carbon dioxide rises in temperature attributable to the reaction of endothermicity (Serrano-Lotina and Daza 2014). According to Xu et al. (2010) methane and carbon dioxide conversions are higher than the estimation of thermodynamic equilibrium. This could be related to further secondary reactions as a breakdown of methane, steam reforming or RWGS. Shen et al. (2011) informed that renovation of CO₂ is always more than methane conversion due to RWGS reaction. However, Chen et al. (2005) detected higher methane (CH₄) transformation than carbon dioxide (CO₂) transformation, representing that methane decomposition an outsized role on the catalytic performance, as Yasyerli et al. (2011) also conveyed the same process.

Over the catalyst, low variance between the renovation of CH₄ and CO₂ at a temperature less than 450°C or higher than 750°C, RWGS was unfavorable due to endothermic reaction. Conversion of CO₂ was appeared low due to the favorable condition of Boudourad equation. At a temperature of more than 750°C, methane decomposition, methane steam reforming could occur; thus, methane conversion may improve, approaching the transformation of CO₂. A rise in ratio of H₂/CO was detected as the temperature is increased. However, there was below unity in all cases what recommended that reaction of RWGS was

always occur but in low range when temperature is raised (Chen et al.2005; Yasyerli et al.2011). A detail of the effective terms in catalytic conversion of methane to syngas using Ni-based catalysts is offered in Table 3.

Table 3
The impact of operating parameters on methane conversion to syngas at 1 atm.

| Catalyst | Temperature(°C) | GHSV(h ⁻¹) | CH ₄ Conversion (%) | CO ₂ Conversion (%) | Ref. |
|--|-----------------|------------------------|--------------------------------|--------------------------------|---------------------------|
| 3 wt% Gd-promoted Ni/Y ₂ O ₃ | 700.0 | 8000 | 84.0 | 85.0 | (Pechimuthu et al. 2007) |
| ZrOx/Ni-MnOx/SiO ₂ | 500.0 | - | 23.0 | 18.0 | (Yao et al. 2017) |
| 15 wt% Ni-ZrO ₂ | 750.0 | 24000 | 95.0 | 98.0 | (Zhang et al. 2015) |
| Yb-promoted Ni (20 wt%)/γ-Al ₂ O ₃ | 700.0 | 52000 | 82.0 | 89.0 | (Amin et al. 2012) |
| 5 wt%Ni - 10 wt%Co/Al ₂ O ₃ | 700.0 | 36000 | 67.0 | 71.0 | (Siang et al. 2018) |
| 15 wt% Ni-MgO-Al ₂ O ₃ | 750.0 | 43000 | 75.0 | 80.0 | (Akbari et al. 2017) |
| Ni-CeO ₂ /ZrO ₂ | 600.0 | - | 55.0 | 70.0 | (Wolfbeisser et al. 2016) |
| Mg-promoted Co-Ni/SBA-15 | 700.0 | 8000 | 80.0 | 75.0 | (Al-Fatesh et al.2017) |
| Ni/CeO ₂ -Al ₂ O ₃ | 800.0 | 90000 | 75.0 | 85.0 | (Fouskas et al. 2014) |
| 10% Ni/γ- Al ₂ O ₃ | 700.0 | 1150 | 90.0 | 86.0 | (Rathod and Bhale 2014) |

4.2 Gas Hourly Space Velocity (GHSV)

It is volumetric feed gas flow rate to the volume of the reactor (Gregorie et al. 2020). It is an important parameter to design and optimize purpose in steam reformers and has more effect on conversion on methane distribution of temperature inside the reactor (Sadooghi et al. 2015).

Hamedi et al. (2014) investigated the GHSV ranges from 16,500 per hour to 34,500 per hour and it related to the rate of gas feed flow on reforming performance and temperature profile. An increase in the GHSV changes the location of the maximum temperature drift of the catalyst. However, the extreme temperature remains the same. The normal catalyst temperature is rather higher when raising the flow rate due to the uniform distribution of temperature. It found a low yield of hydrogen to entirely simulated ratios of

O₂/CH₄ when increasing feed gas space velocity. It must be well known that the residence time reduces from 0.22 second to 0.11 second.

Avraam et al. (2010) reported catalytic behavior at temperature 715°C of 5%Ru/Al₂O₃ catalyst by the effect of space velocity. Gas feed molar composition was CH₄(25%), CO₂ (25%), H₂O (50%) and 1 bar inlet pressure. The results were found methane conversion raises from 46–93% as GHSV reduces from 76,000–10,000 per hour.

4.3 O₂/CH₄ Ratio

Leading the ratio of O₂/CH₄ increases the peak temperature in the reactor. The concentration of O₂ is increased in feeding gas that promotes the rates of oxidation reaction as additional fuel energy is delivered as a form of heat (Hamedi et al. 2014). Lau et al. (2012) stated that there is no activity of reforming observed at lower exhaust gas temperatures. The main point is that the enthalpy of the reactant is inadequate to control the activation energy barrier of reforming reactions. An increase in the reactor's temperature could be seen by providing the oxygen in reactor feed as a result of incomplete oxidation catalytic incineration of the CH₄ nearby entrance of catalyst (when the temperature of the reactor is high than the catalyst temperature light-off) (Lee et al. 2005).

5. Conclusion

Reforming biogas is a promising method to generate green H₂ and minimize the overload on natural gas (CH₄). The main difficulties of biogas reforming methods are raised associated with coke establishment over the catalyst surface done by most researchers and specialists. It also reviewed related to toxic conditions on account of sulfur content which causes catalyst inactivation and diminishes the production of H₂. Ni-based catalysts are mostly used in miscellaneous reforming techniques such as natural gas reforming and biogas reforming. A huge quantity of examining works is also attentive to the effectiveness of catalyst support and some additional promoter elements to reduce the issues of coke formation.

The utilization of catalyst in the reaction of H₂ generation must be advanced to a longer usage life cycle to avoid coke formation over the active catalyst surface. The ideal catalysts are Ni-based in reforming processes because of their lower cost. DR and DOR methods are appeared more attractive techniques for H₂ generation from biogas. However, these methods are not favorable as carbon development on the surface of catalysts and extra oxidant is needed.

ATR process could be attractive because of higher conversion efficiency and H₂ yields; however, this technique is a highly complex control system. At present, mostly H₂ generation form biogas is attained in steam reforming method though conventional reformer. However, it is possible to obtain H₂ from biogas with advanced membrane reactors (only in one step) and at low temperatures (i.e., reforming process and separation happens at the same location).

GHSV is an essential parameter to design and optimization purpose in steam reformers and has more effect on conversion on methane distribution of temperature inside the reactor. Important operating parameters such as temperature mostly utilized the range from 700-800°C for maximum conversion of CH₄ and CO₂ and different catalysts as reviewed by this present paper.

The economic analysis point of view that more current results to steam reforming connecting membrane reactors confirm that more than 20% increases the system efficiency by considering the membrane reactor. The cost of H₂ production from biogas must depend on methane content in biogas. Hydrogen generation cost from biogas (0.07 €/ kWh) is higher than natural gas (0.03 €/kWh).

Various reforming methods can be nominated for H₂ production depend on biogas composition, the need for hydrogen purity, investment availability, and quantity of the desired hydrogen.

6. Declarations

Ethics approval and consent to participate: Not applicable.

Consent for publication: Not applicable.

Availability of data and materials: The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Funding: There is no funding.

Competing interests: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contribution: Conceptualization: Anil Kumar, and Ravindra Kumar; Formal analysis and investigation: Anil Kumar; Writing - original draft: Ravindra Kumar; Writing - review and editing: Anil Kumar; Supervision: Anil Kumar and Amit Pal.

Acknowledgments: Authors are highly grateful to Department of Mechanical Engineering and Centre for Energy and Environment, Delhi Technological University Delhi (India), for providing basic facilities to compile this work.

7. References

1. Akbari, E., Alavi, S. M., & Rezaei, M. (2017). Synthesis gas production over highly active and stable nanostructured NiMgOAl₂O₃ catalysts in dry reforming of methane: Effects of Ni contents. *Fuel*, 194, 171-179. <https://doi.org/10.1016/j.fuel.2017.01.018>
2. Al-Fatesh, A. S., Arafat, Y., Atia, H., Ibrahim, A. A., Ha, Q. L. M., Schneider, M., & Fakeeha, A. H. (2017). CO₂-reforming of methane to produce syngas over Co-Ni/SBA-15 catalyst: Effect of support

- modifiers (Mg, La and Sc) on catalytic stability. *Journal of CO₂ Utilization*, 21, 395-404.
<https://doi.org/10.1016/j.jcou.2017.08.001>
3. Alves, H. J., Junior, C. B., Niklevicz, R. R., Frigo, E. P., Frigo, M. S., & Coimbra-Araújo, C. H. (2013). Overview of hydrogen production technologies from biogas and the applications in fuel cells. *International journal of hydrogen energy*, 38(13), 5215-5225.
<https://doi.org/10.1016/j.ijhydene.2013.02.057>
 4. Amin, M. H., Mantri, K., Newnham, J., Tardio, J., & Bhargava, S. K. (2012). Highly stable ytterbium promoted Ni/γ-Al₂O₃ catalysts for carbon dioxide reforming of methane. *Applied Catalysis B: Environmental*, 119, 217-226. <https://doi.org/10.1016/j.apcatb.2012.02.039>
 5. Araki, S., Hino, N., Mori, T., & Hikazudani, S. (2009). Durability of a Ni based monolithic catalyst in the autothermal reforming of biogas. *International journal of hydrogen energy*, 34(11), 4727-4734.
<https://doi.org/10.1016/j.ijhydene.2009.03.041>
 6. Armor, J. N. (1999). The multiple roles for catalysis in the production of H₂. *Applied Catalysis A: General*, 176(2), 159-176. [https://doi.org/10.1016/S0926-860X\(98\)00244-0](https://doi.org/10.1016/S0926-860X(98)00244-0)
 7. Avraam, D. G., Halkides, T. I., Liguras, D. K., Bereketidou, O. A., & Goula, M. A. (2010). An experimental and theoretical approach for the biogas steam reforming reaction. *International Journal of Hydrogen Energy*, 35(18), 9818-9827. <https://doi.org/10.1016/j.ijhydene.2010.05.106>
 8. Braga, L. B., Silveira, J. L., Da Silva, M. E., Tuna, C. E., Machin, E. B., & Pedroso, D. T. (2013). Hydrogen production by biogas steam reforming: A technical, economic and ecological analysis. *Renewable and Sustainable Energy Reviews*, 28, 166-173. <https://doi.org/10.1016/j.rser.2013.07.060>
 9. Cai, X., Dong, X., & Lin, W. (2006). Autothermal reforming of methane over Ni catalysts supported on CuO-ZrO₂-CeO₂-Al₂O₃. *Journal of Natural Gas Chemistry*, 15(2), 122-126.
[https://doi.org/10.1016/S1003-9953\(06\)60018-2](https://doi.org/10.1016/S1003-9953(06)60018-2)
 10. Chattanathan, S. A., Adhikari, S., McVey, M., & Fasina, O. (2014). Hydrogen production from biogas reforming and the effect of H₂S on CH₄ conversion. *International journal of hydrogen energy*, 39(35), 19905-19911. <https://doi.org/10.1016/j.ijhydene.2014.09.162>
 11. Chen, L., Zhu, Q., Hao, Z., Zhang, T., & Xie, Z. (2010). Development of a Co–Ni bimetallic aerogel catalyst for hydrogen production via methane oxidative CO₂ reforming in a magnetic assisted fluidized bed. *international journal of hydrogen energy*, 35(16), 8494-8502.
<https://doi.org/10.1016/j.ijhydene.2010.06.003>
 12. Chen, X., Honda, K., & Zhang, Z. G. (2005). A comprehensive comparison of CH₄-CO₂ reforming activities of NiO/Al₂O₃ catalysts under fixed-and fluidized-bed operations. *Applied Catalysis A: General*, 288(1-2), 86-97. <https://doi.org/10.1016/j.apcata.2005.04.037>
 13. Chen, X., Jiang, J., Li, K., Tian, S., & Yan, F. (2017). Energy-efficient biogas reforming process to produce syngas: The enhanced methane conversion by O₂. *Applied Energy*, 185, 687-697.
<https://doi.org/10.1016/j.apenergy.2016.10.114>

14. Di Marcoberardino, G., Foresti, S., Binotti, M., & Manzolini, G. (2018). Potentiality of a biogas membrane reformer for decentralized hydrogen production. *Chemical Engineering and Processing- Process Intensification*, 129, 131-141. <https://doi.org/10.1016/j.cep.2018.04.023>
15. Enerdata, *Global Energy Statistical Yearbook* (2018). Accessed 10 June 2019. <https://yearbook.enerdata.net>.
16. Fouskas, A., Kollia, M., Kambolis, A., Papadopoulou, C., & Matralis, H. (2014). Boron-modified Ni/Al₂O₃ catalysts for reduced carbon deposition during dry reforming of methane. *Applied Catalysis A: General*, 474, 125-134. <https://doi.org/10.1016/j.apcata.2013.08.016>
17. Galvagno, A., Chiodo, V., Urbani, F., & Freni, F. (2013). Biogas as hydrogen source for fuel cell applications. *International Journal of Hydrogen Energy*, 38(10), 3913-3920. <https://doi.org/10.1016/j.ijhydene.2013.01.083>
18. Götz, M., Lefebvre, J., Mörs, F., Koch, A. M., Graf, F., Bajohr, S., & Kolb, T. (2016). Renewable Power-to-Gas: A technological and economic review. *Renewable energy*, 85, 1371-1390. <https://doi.org/10.1016/j.renene.2015.07.066>
19. Gregorie, E. F., Lamb, J. J., Lien, K. M., Pollet, B. G., & Burheim, O. S. (2020). Hydrogen and biogas. In *Micro-Optics and Energy* (pp. 131-155). Springer, Cham
20. Hamed, M. R., Tsolakis, A., & Lau, C. S. (2014). Biogas upgrading for on-board hydrogen production: Reforming process CFD modelling. *International journal of hydrogen energy*, 39(24), 12532-12540. <https://doi.org/10.1016/j.ijhydene.2014.06.017>
21. Horikawa, M. S., Rossi, F., Gimenes, M. L., Costa, C. M. M., & Da Silva, M. G. C. (2004). Chemical absorption of H₂S for biogas purification. *Brazilian Journal of Chemical Engineering*, 21(3), 415-422. <https://doi.org/10.1590/S0104-66322004000300006>
22. Kalamaras, C. M., & Efstathiou, A. M. (2013). Hydrogen production technologies: current state and future developments. In *Conference papers in science* (Vol. 2013). Hindawi. <http://dx.doi.org/10.1155/2013/690627>
23. Kumar, R., Kumar, A., & Pal, A. (2020). An overview of conventional and non-conventional hydrogen production methods. *Materials Today: Proceedings*. <https://doi.org/10.1016/j.matpr.2020.08.793>
24. Lau, C. S., Allen, D., Tsolakis, A., Golunski, S. E., & Wyszynski, M. L. (2012). Biogas upgrade to syngas through thermochemical recovery using exhaust gas reforming. *Biomass and bioenergy*, 40, 86-95. <https://doi.org/10.1016/j.biombioe.2012.02.004>
25. Lau, C. S., Tsolakis, A., & Wyszynski, M. L. (2011). Biogas upgrade to syn-gas (H₂-CO) via dry and oxidative reforming. *International Journal of Hydrogen Energy*, 36(1), 397-404. <https://doi.org/10.1016/j.ijhydene.2010.09.086>
26. Lee, S. H., Applegate, D. V., Ahmed, S., Calderone, S. G., & Harvey, T. L. (2005). Hydrogen from natural gas: part I—autothermal reforming in an integrated fuel processor. *International Journal of Hydrogen Energy*, 30(8), 829-842. <https://doi.org/10.1016/j.ijhydene.2004.09.010>
27. Lin, Y. M., Liu, S. L., Chuang, C. H., & Chu, Y. T. (2003). Effect of incipient removal of hydrogen through palladium membrane on the conversion of methane steam reforming: experimental and

- modeling. *Catalysis Today*, 82(1-4), 127-139. [https://doi.org/10.1016/S0920-5861\(03\)00212-8](https://doi.org/10.1016/S0920-5861(03)00212-8)
28. Mahecha-Botero, A., Chen, Z., Grace, J. R., Elnashaie, S. S. E. H., Lim, C. J., Rakib, M., & Shirasaki, Y. (2009). Comparison of fluidized bed flow regimes for steam methane reforming in membrane reactors: A simulation study. *Chemical engineering science*, 64(16), 3598-3613. <https://doi.org/10.1016/j.ces.2009.04.044>
29. Minh, D. P., Siang, T. J., Vo, D. V. N., Phan, T. S., Ridart, C., Nzihou, A., & Grouset, D. (2018). Hydrogen production from biogas reforming: An overview of steam reforming, dry reforming, dual reforming, and tri-reforming of methane. *Hydrogen Supply Chains*, 111-166. <https://doi.org/10.1016/B978-0-12-811197-0.00004-X>
30. Mosayebi, Z., Rezaei, M., Ravandi, A. B., & Hadian, N. (2012). Autothermal reforming of methane over nickel catalysts supported on nanocrystalline $MgAl_2O_4$ with high surface area. *International journal of hydrogen energy*, 37(2), 1236-1242. <https://doi.org/10.1016/j.ijhydene.2011.09.141>
31. Nahar, G., Mote, D., & Dupont, V. (2017). Hydrogen production from reforming of biogas: Review of technological advances and an Indian perspective. *Renewable and Sustainable Energy Reviews*, 76, 1032-1052. <https://doi.org/10.1016/j.rser.2017.02.031>
32. Nalbant, Y., & Colpan, C. O. (2020). An Overview of Hydrogen Production from Biogas. *Accelerating the Transition to a 100% Renewable Energy Era*, 355-373. https://doi.org/10.1007/978-3-030-40738-4_16
33. Nawfal, M. (2015). Valorisation catalytique du biogaz pour une énergie propre et renouvelable (Doctoral dissertation).
34. Nikolaiis, P., & Poullikkas, A. (2017). A comparative overview of hydrogen production processes. *Renewable and sustainable energy reviews*, 67, 597-611. <https://doi.org/10.1016/j.rser.2016.09.044>
35. Noh, Y. S., Lee, K. Y., & Moon, D. J. (2019). Hydrogen production by steam reforming of methane over nickel based structured catalysts supported on calcium aluminate modified SiC. *International Journal of Hydrogen Energy*, 44(38), 21010-21019. <https://doi.org/10.1016/j.ijhydene.2019.04.287>
36. Ouyang, L. Z., Huang, J. M., Wang, H., Wen, Y. J., Zhang, Q. A., Sun, D. L., & Zhu, M. (2013). Excellent hydrolysis performances of Mg_3RE hydrides. *International journal of hydrogen energy*, 38(7), 2973-2978. <https://doi.org/10.1016/j.ijhydene.2012.12.092>
37. Patinvoh, R. J., Osadolor, O. A., Chandolias, K., Horváth, I. S., & Taherzadeh, M. J. (2017). Innovative pre-treatment strategies for biogas production. *Bioresource technology*, 224, 13-24. <https://doi.org/10.1016/j.biortech.2016.11.083>
38. Pechimuthu, N. A., Pant, K. K., & Dhingra, S. C. (2007). Deactivation studies over Ni- K/CeO₂- Al₂O₃ catalyst for dry reforming of methane. *Industrial & engineering chemistry research*, 46(6), 1731-1736. <https://doi.org/10.1021/ie061389n>
39. Rathod, V., & Bhale, P. V. (2014). Experimental investigation on biogas reforming for syngas production over an alumina-based nickel catalyst. *Energy Procedia*, 54, 236-245. <https://doi.org/10.1016/j.egypro.2014.07.267>

40. Rau, F., Herrmann, A., Krause, H., Fino, D., & Trimis, D. (2019). Efficiency of a pilot-plant for the autothermal reforming of biogas. *International Journal of Hydrogen Energy*, 44(35), 19135-19140. <https://doi.org/10.1016/j.ijhydene.2018.04.014>
41. Sadooghi, P., & Rauch, R. (2015). Experimental and modeling study of hydrogen production from catalytic steam reforming of methane mixture with hydrogen sulfide. *International journal of hydrogen energy*, 40(33), 10418-10426. <https://doi.org/10.1016/j.ijhydene.2015.06.143>
42. Sato, T., Suzuki, T., Aketa, M., Ishiyama, Y., Mimura, K., & Itoh, N. (2010). Steam reforming of biogas mixtures with a palladium membrane reactor system. *Chemical engineering science*, 65(1), 451-457. <https://doi.org/10.1016/j.ces.2009.04.013>
43. Scarlat, N., Dallemand, J. F., & Fahl, F. (2018). Biogas: Developments and perspectives in Europe. *Renewable energy*, 129, 457-472. <https://doi.org/10.1016/j.renene.2018.03.006>
44. Serrano-Lotina, A., & Daza, L. (2014). Influence of the operating parameters over dry reforming of methane to syngas. *International Journal of Hydrogen Energy*, 39(8), 4089-4094. <https://doi.org/10.1016/j.ijhydene.2013.05.135>
45. Serrano-Lotina, A., Martin, A. J., Folgado, M. A., & Daza, L. (2012). Dry reforming of methane to syngas over La-promoted hydrotalcite clay-derived catalysts. *International Journal of Hydrogen Energy*, 37(17), 12342-12350. <https://doi.org/10.1016/j.ijhydene.2012.06.041>
46. Shanmugam, K., Tysklind, M., & Upadhyayula, V. K. (2018). Use of liquefied biomethane (LBM) as a vehicle fuel for road freight transportation: a case study evaluating environmental performance of using LBM for operation of tractor trailers. *Procedia CIRP*, 69, 517-522. <https://doi.org/10.1016/j.procir.2017.11.133>
47. Shen, W., Momoi, H., Komatsubara, K., Saito, T., Yoshida, A., & Naito, S. (2011). Marked role of mesopores for the prevention of sintering and carbon deposition in dry reforming of methane over ordered mesoporous Ni–Mg–Al oxides. *Catalysis today*, 171(1), 150-155. <https://doi.org/10.1016/j.cattod.2011.04.003>
48. Siang, T. J., Singh, S., Omoregbe, O., Bach, L. G., Phuc, N. H. H., & Vo, D. V. N. (2018). Hydrogen production from CH₄ dry reforming over bimetallic Ni–Co/Al₂O₃ catalyst. *Journal of the Energy Institute*, 91(5), 683-694. <https://doi.org/10.1016/j.joei.2017.06.001>
49. Sinha, P., & Pandey, A. (2011). An evaluative report and challenges for fermentative biohydrogen production. *International Journal of Hydrogen Energy*, 36(13), 7460-7478. <https://doi.org/10.1016/j.ijhydene.2011.03.077>
50. Verma, P., & Samanta, S. K. (2016). Overview of biogas reforming technologies for hydrogen production: advantages and challenges. In *Proceedings of the first international conference on recent advances in bioenergy research* (pp. 227-243). Springer, New Delhi. https://doi.org/10.1007/978-81-322-2773-1_17
51. Wolfbeisser, A., Sophiphun, O., Bernardi, J., Wittayakun, J., Föttinger, K., & Rupprechter, G. (2016). Methane dry reforming over ceria-zirconia supported Ni catalysts. *Catalysis Today*, 277, 234-245. <https://doi.org/10.1016/j.cattod.2016.04.025>

52. Xu, J., Zhou, W., Li, Z., Wang, J., & Ma, J. (2010). Biogas reforming for hydrogen production over a Ni–Co bimetallic catalyst: effect of operating conditions. *International Journal of Hydrogen Energy*, 35(23), 13013-13020. <https://doi.org/10.1016/j.ijhydene.2010.04.075>
53. Yao, L., Wang, Y., Shi, J., Xu, H., Shen, W., & Hu, C. (2017). The influence of reduction temperature on the performance of ZrOx/Ni-MnOx/SiO₂ catalyst for low-temperature CO₂ reforming of methane. *Catalysis Today*, 281, 259-267. <https://doi.org/10.1016/j.cattod.2016.05.031>
54. Yasyerli, S. E. N. A., Filizgok, S., Arbag, H., Yasyerli, N. A. İ. L., & Dogu, G. (2011). Ru incorporated Ni–MCM-41 mesoporous catalysts for dry reforming of methane: Effects of Mg addition, feed composition and temperature. *International Journal of Hydrogen Energy*, 36(8), 4863-4874. <https://doi.org/10.1016/j.ijhydene.2011.01.120>
55. Zain, M. M., & Mohamed, A. R. (2018). An overview on conversion technologies to produce value added products from CH₄ and CO₂ as major biogas constituents. *Renewable and Sustainable Energy Reviews*, 98, 56-63. <https://doi.org/10.1016/j.apenergy.2016.10.114>
56. Zhang, X., Zhang, Q., Tsubaki, N., Tan, Y., & Han, Y. (2015). Carbon dioxide reforming of methane over Ni nanoparticles incorporated into mesoporous amorphous ZrO₂ matrix. *Fuel*, 147, 243-252. <https://doi.org/10.1016/j.fuel.2015.01.076>

Figures

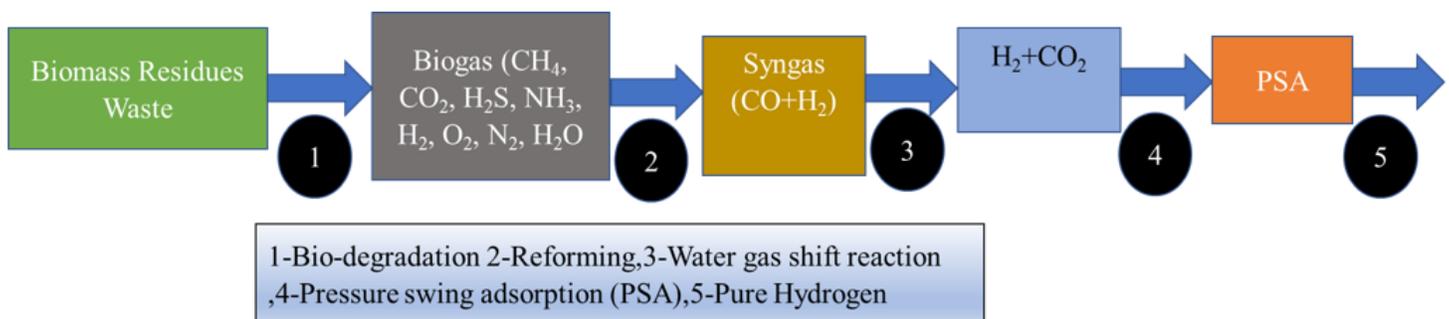


Figure 1

The flow process of hydrogen generation from biogas (Nalbant and Colpan 2020)

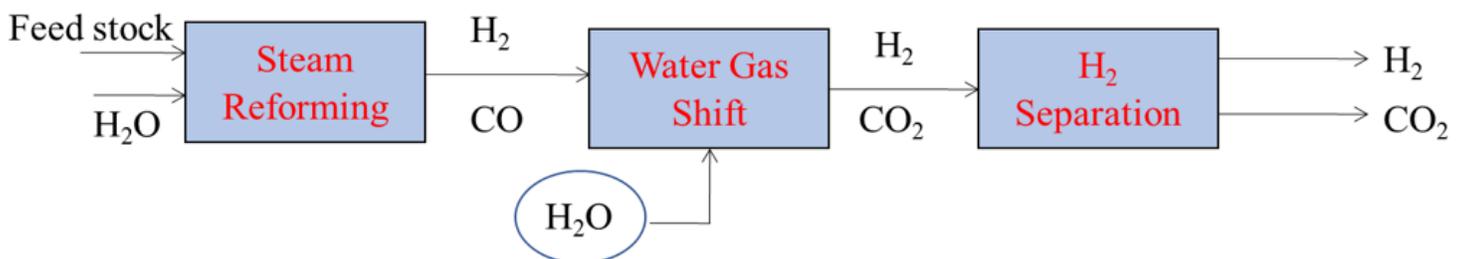


Figure 2

Flow process of steam reforming process for generation of hydrogen (Kumar et al. 2020)