



Advanced Hydrogen Production through Methane Cracking: A Review

Sujoy Kumar Samanta^{*}, Priyanshu Verma

Department of Chemical and Biochemical Engineering, IIT Patna, India

^{*}**Correspondence:** Department of Chemical and Biochemical Engineering, IIT Patna, India, E-mail: sksamanta@iitp.ac.in

Article History

Received: 19 April 2015

Accepted: 21 June 2015

Published: 1 July 2015

Citation

Sujoy Kumar Samanta, Priyanshu Verma. Advanced Hydrogen Production through Methane Cracking: A Review. *Science & Technology*, 2015, 1(3), 109-123

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ABSTRACT

Hydrogen is widely produced and used for our day-to-day needs. It has also the potential to be used as fuel for industry or can be used as an energy carrier for stationary power. Hydrogen can be produced by different processes like from fossil fuels (Steam methane reforming, coal gasification, cracking of natural gas); renewable resources (electrolysis, wind, etc.); nuclear energy (thermochemical water splitting). In this paper, few processes have been discussed briefly. Cracking of methane has been given special emphasis in this review for production of hydrogen. There are mainly two types of cracking, non-catalytic and catalytic. Catalytic cracking of methane is governed mainly by finding a suitable catalyst; its generation, deactivation, activation and filament formation for the adsorption of carbon particles (deposited on metal surface); study of metallic support which helps in finding active sites of the catalyst for the reaction to proceed easily. Non-catalytic cracking of methane is mainly based on thermal cracking. Moreover, several thermal cracking processes with their reactor configurations have been discussed.

Keywords: Energy crisis, Hydrogen production, Methane cracking, Catalyst, Electrolysis etc.

Abbreviation: TCD- thermo catalytic decomposition, NMHC- non methane hydrocarbon, SEM- scanning electron microscope, NG- natural gas, TEM- transmission electron microscope, SMR - steam methane reforming, Nm³ - normal m³, COD- chemical oxygen demand, PEM- polymer electrolyte membrane, CB- carbon black, SOEC- solid oxide electrolysis cell, CNF- carbon nanofibers, AEC - alkaline electrolysis cell, XAFS- X-ray absorption fine structure.

1. INTRODUCTION

Copious and frugal energy is the lifeblood of today's generation. The world's total power consumption lies at about 13 TW (or terawatt, which is equal to 10^{12} W). The estimation includes power in all its forms from electricity to gasoline conversion (Ball and Wietschel, 2009; Hoffert et al. 2012). Figure 1 shows that- oil, coal and natural gas together supplying 85 percent of the world's energy supply in 2008. Currently, we are facing two main problems: 1) High energy demand; 2) Global climate change due to production of enormous volume of CO_2 by using fossil fuel to meet the high energy demand.

So, we have to go for the other sustainable energy and renewable production processes. Among several renewable processes, hydrogen is found out to be more promising and environmentally benign. The amount of energy produced by hydrogen combustion is higher than that evolved by any other fuel on a mass basis with a low heating value, i.e., 2.4, 2.8 and 4 times higher than methane, gasoline and coal, respectively (Marban and Valdes-Soli, 2008). Hydrogen is mainly employed in the fertilizer and paint industries. It is additionally utilized in the food and chemical industries. Food industries use the hydrogen to make hydrogenated vegetable oils such as margarine and butter. In this process, vegetable oils are combined with hydrogen, by using nickel as a catalyst, solid fat substances are formed. In the petrochemical industry, hydrogen is used for crude oil refinements. Significant use of hydrogen will contribute to the reduction of energy-linked environmental impacts including global warming due to anthropogenic carbon emissions, mobile source emissions such as CO , NO_x , SO_x , particulates and NMHC (Elam et al. 2003).

There has been a continuous effort by several researchers to find the existence of a viable "green" or carbon-neutral path from current fossil based to the future hydrogen economy without disturbing a flimsy environmental balance. Hydrogen can be produced as a storable, clean fuel from the world's sustainable non-fossil primary energy sources—solar energy, wind energy, hydropower, biomass, geothermal, nuclear and tidal (Elam et al. 2003).

In this review, we are dealing with different processes of hydrogen production; advantages and disadvantages, mainly methane cracking, and also discuss about catalyst development, carbon filament formation, and catalyst deactivation and regeneration associated with methane catalytic cracking.

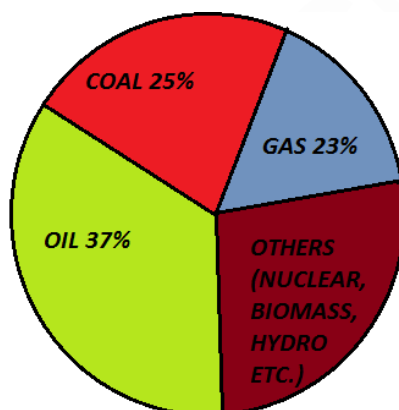


Figure 1

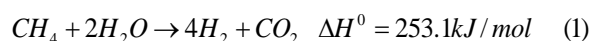
World's energy supply in 2008 (www.planetforlife.com)

2. SEVERAL HYDROGEN PRODUCTION PROCESSES

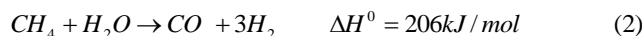
Presently hydrogen finds application in chemical compound rather than a fuel in commercial operations. So, suitable methods for large scale production of hydrogen need to be developed. Hydrogen is the simplest element as the most plentiful in the universe, but it never occurs itself in nature. It is found combined with other element such as oxygen and carbon. Therefore, several hydrogen production processes mainly deal with water or hydrocarbon based reaction which will produce free hydrogen. This water or hydrocarbon can be decomposed or reformed through several processes like application of heat to break down the molecules (thermo-chemical), electric charging (electrolysis) or bio-hydrogen production to get large hydrogen production (Abbas and Daud, 2010). These processes can be classified as follows:

2.1. Steam reforming

This process mainly deals with fossil fuels. Natural gas (NG) is the main reactant in this process, which will react with steam (H_2O) and through a dehydrogenation process free hydrogen is produced along with the harmful gases like CO or CO_2 depending upon the reaction temperature. As NG consists mainly of methane (CH_4) it can otherwise be called as Steam Methane Reforming (SMR). The overall SMR process could be expressed by the following chemical equation:



Steam Reforming is a multiple stage process. The first stage is highly endothermic reforming of methane ($\Delta H^0=206$ kJ/mol) and is a high temperature process (800-900°C) which mainly produce high amount of CO with desirable H₂ and second stage is a water gas shift reaction that also consist of two steps: the first step is conducted at 400-500°C to reduce the CO concentration, produced in first step to 2-5% and the second stage is conducted at 177-257°C for further reduction of CO concentration to 1%.



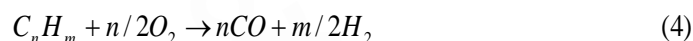
From above two stages of the SMR process, we can clearly see a high production of harmful gases like CO and CO₂. So a third process has to be there for the clean and green production of hydrogen (CO₂ free). So a pressure- swing absorption has been used for the separation of H₂ and CO₂ (Poirier and Sapundzhiev, 1997; Luengnaruemitchai et al. 2003; Otsuka et al. 2004). It also consists of a desulphurization unit and a steam generation unit. So economically it is not very stable, huge amount of money has to be invested. So, two drawbacks have been pointed in this process: one the production of CO₂ and the second is high production and maintenance cost.

In spite of these drawbacks, SMR is still the most important and widely used in the industrial production of hydrogen, amounting to about 80% of the hydrogen produced in U.S. which is almost 40% of the world's total hydrogen production. The remaining 20% is the byproduct of chemical processes such as chlor-alkali production. The global warming potential of hydrogen production via SMR process is 13.7 kg CO₂ per kg of net hydrogen produced. CO₂ emission from the SMR process is 0.44 Nm³CO₂/Nm³H₂ (Scholz, 1993). It has been seen that CO₂ accounts for 77.6% of total global warming gases which can be taken as a combination of CH₄, NO₂, CO₂, and many other greenhouse gas emission which is equivalent for a 100 year lifetime (Spath and Mann, 2001).

2.2. Partial oxidation

It is one of the best renewable ways of hydrogen production. From its nomenclature we can conclude that it is an oxidation reaction, a reaction between fuel (natural gas or heavy hydrocarbon fuel) and air (oxygen). Partial reaction means a sub-stoichiometric fuel-air reaction which means the fuel will be provided with an amount of oxygen less than required. The final product of partial oxidation is CO and H₂ but in case of SMR process the final product is CO₂ and H₂. So it produces more harmful gas than SMR, but on the other hand energy released is quite higher in partial oxidation process (Corbo and Migliardini, 2007). Two types of processes are there: a) partial oxidation b) thermal oxidation.

SMR and Partial Oxidation both are catalytic processes and commonly face the problem of catalytic deactivation phenomenon due to coke formation which will block the active sites of the reactant (Jens, 1974).



Since partial oxidation is an exothermic reaction, some of the heat of combustion is released. The release of energy is converted into heat, which brings the temperature of gas approximately more than 800°C. The temperature of the gas needs to be lowered before entering into the combustion engine. Otherwise the density of the gas is too low to have a good volumetric efficiency, resulting in bump in a gas engine (Jamal, 1994).

2.3. Plasma reforming

It is the method of production of carbon black and hydrogen gas from hydrocarbons such as methane, natural gas and biogas. This process was developed by Norwegian engineering firm Kvaerner in the 1980s. The endothermic reaction separates hydrocarbon into carbon and hydrogen in a plasma burner at around 1600°C.

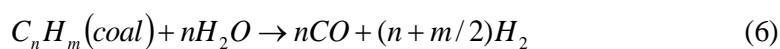


In this process, in comparison to other reformation methods such as steam reforming and partial oxidation, the natural gas is efficiently and completely transformed into pure carbon and hydrogen. Of the available energy of the feed, approximately 48% is contained in the hydrogen, 40% is contained in activated carbon and 10% in superheated steam. It has several classifications; mainly, it can be divided into two parts: 1) Thermal (Kvaerner CB&H); 2) Non thermal (Glidarc).

Plasma reforming of methane has become economically interesting for the several energy applications due to the high hydrogen yield and plasma catalysis consumes sufficiently low energy. The plasma conditions such as high temperature, high degree of dissociation and degree of ionization can be used to accelerate thermodynamic favorable chemical reactions without any catalyst study (Jamal, 1994; Bromberg et al. 1999; Benilov and Naidis, 2006).

2.4. Coal gasification

The huge amount of clean hydrogen can be obtained from coal by gasification by production of syngas (liquid synthetic fuel). Coal gasification works by first reacting coal with oxygen and steam under high pressures and temperatures to form synthesis gas, a mixture consisting primarily of carbon monoxide and hydrogen. The primary reaction of this process is

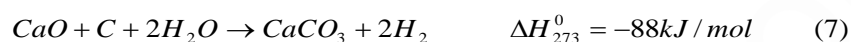


So, from this reaction the main two products are carbon monoxide and hydrogen. The main problem with this process is that it requires an extra process to the primary one (to eliminate CO).

The synthesis gas is cleaned of impurities and the carbon monoxide in the gas mixture is reacted with steam via the water-gas shift reaction to produce additional hydrogen and carbon dioxide. Main reaction has taken place at about a temperature of 1000°C or may be higher than that of it, but the water-gas shift reaction occurred at low temperature of 400°C (Lina et al. 2002).

So, in this process, total three steps involved in it: 1) coal gasification; 2) water gas shift reaction; 3) CO₂ separation. There are several processes for CO₂ separation, but we need to go for the most economical way of separation. Hydrogen is removed by a separation system and the highly concentrated CO₂ stream can subsequently be captured and sequestered. The hydrogen can be used in a combustion turbine or solid oxide fuel cell to produce power, or utilized as a fuel or chemical feedstock. Much research is being conducted day by day to improve the hydrogen produced from coal.

CaO can be used as a sorbent for separation of CO₂. The reaction is exothermic in nature and generally carried out at a temperature 827°C. A HyPr-RING method can be used for this process which has four reactions. The overall reaction of this process is



Use of membrane reactor in the hydrogen production from coal is widely used nowadays because of: a) high hydrogen production efficiency; b) low cost; c) clean product; d) CO₂ sequestration ready; e) power co-generation.

Lina et al. (2002), in their experiment, used 5 g CaO, 0.5 g coal, and a mixture of 0.5 g coal with 2.3 g CaO as material for CaO, coal, and coal/CaO mixture experiments, respectively. The bed temperature was measured with a K-type thermocouple. Once the material was properly placed in the reactor, the pressure in the reactor was increased by nitrogen gas, and the temperature was raised by the electric furnace. The heating rate was about 7 K/min. When the pressure and temperature became stable at set values, high pressure and temperature steam was injected into the reactor to start the reactions. The concentrations of H₂, CH₄, CO, CO₂ in the product gas were continuously measured by using a Micro-GC.

The production of hydrogen from coal offers efficiency and environmental benefits when integrated with advanced technologies in coal gasification, power production and carbon sequestration.

2.5 From water

2.5.1. Electrolysis

The majority of hydrogen (~95%) is produced from fossil fuels by steam reforming or partial oxidation of methane and coal gasification. However, only a small quantity being produced by other routes such as biomass gasification or electrolysis of water (Ogden, 1999). Electrolysis of water generally breaks it into hydrogen and oxygen by passing electricity through it.

There are three main types of cell:

a) Solid oxide electrolysis cells (SOEC'S)

Hydrogen generation through high temperature steam electrolysis (HTSE) using solid oxide electrolysis cells (SOEC) has recently received increasing international interest in the large-scale and highly efficient nuclear hydrogen production field. The outlet process of HTSE can be around 750-900°C with a pressure of 1-5 (*10⁶) Pa. It is expected that combining high temperature reactor and electrolyze the overall thermal efficiency would be around 48-59% (Hauch et al. 2008).

b) Polymer electrolyte membrane cells (PEM)

PEM electrolysis cells typically operate at below 100°C and are becoming increasingly available, commercially (Ogden, 1999). Electrolysis technique based on PEM is an all solid based system with no corrosive electrolyte or electrolytic recycling. It can produce very high quality H₂ (>99.999%) with water and electricity as only input (Clarke et al. 2009).

c) Alkaline electrolysis cells (AEC'S)

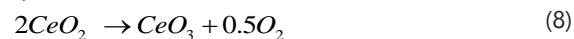
Alkaline water electrolysis has a very long history in the chemical industry. Its application for energy conversion in hydrogen energy system is attracting attention, and advance electrolyser has been developed. The direction of development is towards the high efficiency by applying high temperature and pressure operations. Although, only few successful results have been reported so far (Ogden, 1999).

2.5.2. Thermochemical cycle

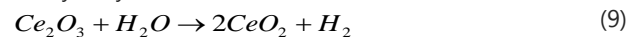
Here heat energy (thermo) with chemical cycles is used to split water into hydrogen and oxygen components. The term cycle is used because aside of water, hydrogen and oxygen, the chemical species used in these processes are continuously recycled. Some processes have been discussed below:

Thermo-chemical hydrogen production via 2-step using cerium oxides; a new thermochemical cycle for H₂ production based on CeO₂/Ce₂O₃ oxides has been successfully demonstrated. It consists of two chemical steps:

a) Reduction



b) Hydrolysis



The hydrogen generation step (water-splitting with Ce (III) oxide) is studied in a fixed bed reactor and the reaction is completed with a fast kinetic in the studied temperature range 400–600°C. The feasibility of the new thermochemical two-stage cycle has been experimentally demonstrated at lab scale that produces hydrogen without fossils and greenhouse gas emission (Abanades and Flamant, 2006).

Thermo-chemical hydrogen production via 2-step using Zn/ZnO redox reaction: The first, endothermic step is the thermal dissociation of ZnO(s) into Zn(g) and O₂ at 2027°C using concentrated solar energy as the source of process heat. The second, non-solar, exothermic step is the hydrolysis of Zn(l) at 427°C to form H₂ and ZnO(s); the latter separates naturally and is recycled to the first step. Hydrogen and oxygen are derived in different steps, thereby eliminating the need for high-temperature gas separation. Maximum efficiency of 29% can be achieved. The critical components for this process are the solar reactor operating at 2300 K, the Zn(g)/O₂ quenching device and the Zn(l)/steam hydrolyser (Steinfeld, 2002).

2.5.3. Thermolysis

An engineering evaluation of various process plant designs for hydrogen production by direct thermal decomposition of water using solar energy is being carried out; mainly, with the aim of improving the process efficiency and possibly reducing the production cost. The most effective hydrogen production in terms of production cost and also in term of thermodynamic feasibility is hydrogen production by direct thermal decomposition of water and gas separation at reaction conditions hybridized with high temperature electrolysis (Baykara, 2004).

2.6. Biological process

Hydrogen can be produced biologically through many processes. It may be fermentative or bio-decomposition or bio photolysis type of reaction. In every case huge amount of biomass is required. Biomass is defined as an organic matter that can be available very easily. It is also a renewable type of hydrogen production resource. It includes wood and wood wastes and residues, crops, trees, plants, grasses, agricultural and forestry wastes, sludge, animal wastes and residues, organic waste materials and municipal solid waste and many other things which can be used through fermentation or photo-water-splitting. Solar energy can also be used directly or can also be used to produce biomass through photosynthesis and the efficiency may be around 0.4%.

The main processes of hydrogen production can be categorized as: 1) Biochemical methods; 2) Thermochemical methods.

Again biochemical methods have five parts: 1) photosynthetic organism; 2) dark fermentation; 3) fermentation; 4) esterification; 5) anaerobic digestion.

Among these processes: in photosynthetic organisms and dark fermentation, hydrogen produced directly; but in other processes, it is produced via intermediate like in fermentation via ethanol, in esterification via bio-diesel, and in anaerobic digestion via biogas.

Thermochemical method also has 3 sub processes like: 1) pyrolysis; 2) hydrothermal liquefaction; 3) combustion and turbine. All these processes produce hydrogen via intermediates (Muradov and Veziroglu, 2008).

The main processes can be divided into three categories:

2.6.1. Bio photolysis of water using algae

This is the same process as photosynthesis, but here it is used for hydrogen production. Photosynthesis involves absorption of light by two distinct photosynthetic systems: 1) water splitting and O₂ evolving system (PSII); and 2) photosystem (PSI), which generates the reductant, used for CO₂ reduction. In these two processes, two photons are used for each electron that is removed from the water and used in CO₂ reduction; and this way hydrogen can be formed. As we all know that in green plants, only CO₂ reduction takes place; as the enzymes that catalyze hydrogen formation are absent there (Das and Veziroglu, 2001).

2.6.2. Fermentative hydrogen production

Hydrogen production through fermentative ways, using organic compounds or biomass, is a very much promising method. In this process, we are interested in the production of bio hydrogen from organic sources through the multi-enzyme system. This process needs no light energy. So, it produces hydrogen in both day and night. For example, photo-fermentation with *Rhodobacter sphaeroides* (SH₂C) can be employed to convert small molecular fatty acids into hydrogen (Tao et al. 2007). Fermentative hydrogen production can be done using direct bio photolysis by green algae; indirect bio photolysis by cyanobacteria; photo-fermentation by anaerobic photosynthetic bacteria; and dark fermentation by anaerobic fermentative bacteria. For example, Hydrogen production using *H. salinarium*, an anaerobic photosynthetic bacterium coupled to a hydrogenase donor like *E. coli* (Prasad et al. 2011).

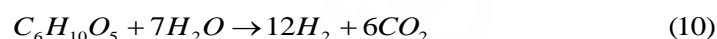
Fermentative hydrogen production can be done by using direct bio photolysis through the green algae (indirect bio-photolysis by cyanobacteria and photo-fermentation by anaerobic bacteria). Macro-alga (*Laminaria japonica*) is used for fermentative hydrogen production by anaerobic mixed bacteria (Liu and Wang, 2014). These processes have many advantages like higher production of hydrogen in the day and night with a good production rate of microorganism and the supply of the reactant is very frequent (Das and Veziroglu, 2001).

2.6.3. Hydrogen production through bio-catalyzed electrolysis

Nowadays, bio catalyzed electrolysis is one of the important bio hydrogen production process. It has huge potential to convert the biomass containing waste water into valuable hydrogen gas. In this process, mainly electrochemical active microorganisms are used which are able to produce electrons or rather say electricity during the oxidation of organic matter or through any enzymatic complex process which is very much economical and acceptable.

Electrochemically active microorganisms are used in an electrochemical cell, which convert dissolved organic material to bicarbonate, protons and electrons. This conversion takes place either by direct contact with an electrode surface or by redox mediators. These microorganisms release the produced electrons to an electrode surface in order to generate a current. By coupling this biological anode to a proton reducing cathode by means of a power supply, a direct conversion of dissolved organic material to hydrogen is accomplished. Oxidation of dissolved organic materials and proton reduction is separated into two chambers in that electrochemical cell (Rozendal et al. 2006).

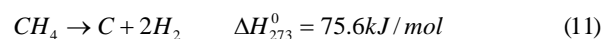
There are many other processes of bio hydrogen production like enzymatic hydrogen production and bio hydrogen production through xylose. In 2007, a non-natural enzymatic pathway was designed which can be capable of producing 12 moles of hydrogen per mole of glucose units of polysaccharides and water (Zhang et al. 2007). The overall reaction of the process is



Where, this water splitting is done by the energy of the carbohydrate which is the main hydrogen carrier. Fermentative hydrogen production from xylose using anaerobic mixed micro-flora is one of the economic and efficient bio hydrogen production processes (Chen et al. 2001; Noike et al. 2004).

Except these processes, photo catalytic water splitting and photo biologically water splitting are very efficient and economical process of hydrogen production. There is the huge effect of pH in bio-hydrogen production; actually, the process takes place through the waste product produced from any industrial plant. This waste product is mainly consists of carbohydrates and react with different enzymes and through several complex processes hydrogen is produced that we have discussed earlier. Clostridia are saccharolytic depending organics; so, they can easily ferment these kinds of things. One of the widely studied saccharolytic clostridia is *Clostridium butyricum* which produces butyric acid as the major fermentation product along with CO₂, acetate and H₂ (Minton and Clarke, 1989). Other fermentation pathways found in sacchrolytic clostridia are by *Clostridium arcticum* (Jones and Woods, 1989), *Clostridium barkeri* (Stadtman et al. 1972) and *Clostridium coccoides* (Kaneuchi et al. 1976). The main products in these processes are propionate, lactate and succinate, accordingly. In many cases, it has been shown that the hydrogen evolution activity may be suppressed in the presence of hydrogen at a huge quantity and this happens especially in the case of hydrogenase. So, it can be said that a decrease in hydrogen formation rate or rather say decrease in the quantity of hydrogen will certainly favor the hydrogen formation and also helps bacteria to metabolize acetyl-CoA for the production of energy in the form of ATP (Elena and Ivan, 1983). It has been also observed that when the pH drops to 4.5 or below, a reaction shift takes place from a hydrogen/acid production phase to a solvent production phase when the population of clostridia is in the stationary growth phase (Byung and Zeikus, 1985). It has been proved that a decrease in the partial pressure of hydrogen results in an increase in the acetate/butyrate ratio, so the hydrogen production rate will be certainly increased (Van Andel et al. 1985).

At very high temperature (around 1200°C) thermal decomposition (TD) of methane takes place to produce elemental carbon and hydrogen.



The main advantage of this process is that there is no formation of oxidants (e.g. H₂O and/or O₂); which reduces the gas conditioning step (e.g., water-gas shift) and gas separation (e.g. CO₂ removal) stages required for conventional technologies (e.g. gas streaming, partial oxidation). But few researchers have stated that the amount of CO₂ emissions from the process could potentially

be as low as 0.05 mole CO₂/mole H₂, compared to 0.43 mole CO₂/mole H₂ for SMR (Muradov et al. 2006). CO₂ emissions seem to be potentially eliminated, if a part of a hydrogen product (theoretically, 16%) is combusted to produce process heat.

Table 1

List of hydrogen production technology: Their advantages and disadvantages

Production technology	Energy efficiency	Advantages	Disadvantages
Bio-hydrogen production process	Dark-fermentation 9.6% Photo-fermentation 25.6% Bio catalyzed electrolysis 25.7%.	1) It can be found very easily at a huge amount. 2) It can be obtained by investing very less money than that of the other process, so it is very much of economical process. 3) Consider as carbon-neutral resource because whatever CO ₂ is produced in this process can also be used in the next process, so it is kind of a cyclic process. But it still depends on the several sub processes of bio hydrogen production.	1) In case of a fermentative hydrogen production further treatment of the product is required as it contain CO ₂ in it. 2) Hydrogen should be removed very quickly otherwise degradation of produced hydrogen taken place with reaction with the enzyme
Partial oxidation of methane	70-80%	1) It requires very less maintenance. 2) Very environment friendly as it produces less NO _x .	1)The oxidation step is an exothermic reaction, reducing the energy content of the fuel
Plasma reforming	65-73%	1) Good reactivity / performance in terms of transient times. 2) Conversion rate increases. 3) No catalyst is required.	1) Lower energy gain than conventional reforming process. 2) Power supply is quite bulky and expensive.
Coal gasification	63%	1) There is an opportunity to remove impurities such as sulfur and mercury and soot <i>before</i> burning the fuel, using readily available chemical engineering processes.	1) Mainly it produces CO ₂ , whose effective storage is still under research. 2) There isn't enough coal in world to maintain all the demands.
Electrolysis	50-80%	1) Production of high purity hydrogen (>99.999%) 2) Scalability and the emission-free production of hydrogen.]	1) High energy requirement
Thermochemical cycle	23-29%	1) The cycle based on the CeO ₃ /Ce ₂ O ₃ redox pair shows significant advantages compared to the other two-step cycles investigated and demonstrated (ZnO/Zn, Fe ₃ O ₄ /FeO and oxygen-deficient ferrites).	1) This process requires very high temperature so it is difficult to prevent O ₂ and H ₂ recombination. 2) There is a storage/ transportation problem of hydrogen.
SMR	83%	1) As it is an endothermic process it increases the burning value of fuel resulting in more efficient fuel.	1) Formation of soot in the reactor at high temperatures 2) Water sequestration

		2) Steam reforming produces less exhaust emissions than burning the feedstock fuel.	from the exhaust is a laborious process.
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3. CRACKING OF METHANE/NATURAL GAS vs. SMR

The present scenario states that SMR contribute around 48% of world hydrogen production. But this process has few limitations too. Figure 2 gives us a clear idea about the net hydrogen yield for cracking and SMR process (with and without CO₂ sequestration). It can be easily observed that although the theoretical hydrogen yield for SMR is twice of that for cracking (TCD) (H₂/CH₄= 4 and 2 mole/mole, respectively), high reaction endothermicity requirement and CO₂ sequestration steps; both consume a significant amount of energy in methane equivalent, would considerably reduce the net yield of hydrogen produced by the SMR process (CO₂ free) (Muradov, 2002). The overall net efficiencies of SMR and cracking (thermo-catalytic) are nearly same (difference of 2%) after 15% energy loss due to CO₂ sequestration in the SMR process (Steinberg, 1999). So, cracking (catalytic) process should be considered good as it produces a valuable byproduct carbon but on the other hand around 40% energy is lost due to high endothermicity and CO₂ sequestration stage. Also in SMR process around 13.7 kg CO₂ equivalents per kg of net hydrogen is produced (Spath and Mann, 2001). CO₂ contributes around 77.6% of global warming. Almost half of the overall CO₂ emissions from the SMR process is released in diluted form, i.e., stack gases with CO₂ concentrations of about 5 vol. %, which are very difficult and costly to treat (Golomb and Angelopoulos, 2001).

The carbon produced as byproduct can be sold which would reduce the hydrogen production cost. The techno-economic assessment showed that the cost of hydrogen produced by methane cracking (TCD) of natural gas (\$58/1000 m³H₂, with carbon credit) was somewhat lower than that for the SMR process (\$67/1000 m³H₂) (Steinberg and Cheng, 1998). Till now, we have discussed about the efficiency, economy and the complex processes related to SMR process and methane cracking. In further sections we will be going to discuss about the cracking of methane in order to produce hydrogen gas.

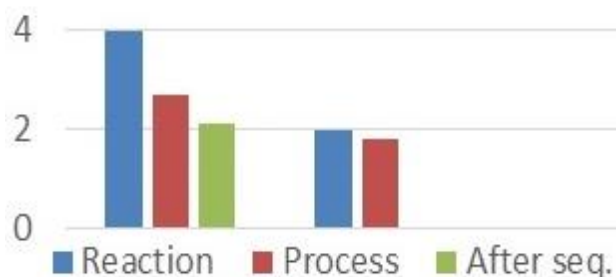


Figure 2

Comparative assessment of net hydrogen yields from SMR and TCD process: Y axis-H₂/CH₄(m³/m³), X axis-process (SMR, TCD) (Muradov, 2002).

4. METHANE CATALYTIC CRACKING

As we are discussing the catalytic cracking, we must have a vast idea regarding the preparation, activation and deactivation, active sites and filamentous growth propagation of the cracking process. As we have discussed that a high temperature is required for the cracking, but if we use metal as a catalyst, the temperature may become moderate and easy to operate the reaction. With the metal catalyst, a metallic support is very helpful for a more moderate temperature and the decomposition of the hydrocarbon will be higher that produces the highest amount of hydrogen gas. Nickel is the most acceptable metal catalyst for the methane catalytic cracking (Avdeeva et al. 1999). But if we consider other metal like cobalt or iron, these are more efficient catalyst in terms of active sites, but the main problems with these metals are: 1) High cost, so the economic stability will not be there; and 2) The toxicity, which is a big drawback. Using these metals, a suitable reactive condition cannot be achieved due to high temperature requirements (Ermakova et al. 2000). Discussing about the catalyst we have to concentrate mainly on two parts of the catalyst which are: 1) Active sites of the catalyst; and 2) Metallic support.

4.1. Active sites of the catalyst

Catalyst is the most important part of the reaction. The main problem with this catalytic cracking is the regeneration of the catalyst. The activity of a catalyst depends on the active sites present in the catalyst; and with the continued propagation of the reaction, these active sites are blocked with the carbon particle and hence the efficiency of the catalyst would decrease gradually. It is very essential to active the catalysts by removing the blocked phases of the catalyst and regenerate them through several processes. Among other hydrocarbons, methane has the highest stability in catalytic cracking (Ermakova and Ermakov, 2002). Therefore, it is much easier to go for the catalytic cracking of methane.

In this catalytic process, the main mechanism of the reaction propagation is the formation of the filament and this small carbon particle which block the active sites of the catalyst; so, we need to activate the catalyst first. This filament formation part we will discuss later. At first we would discuss about the active sites, its preparation and different ratio of several metals (keeping one main metal catalyst constant). Actually, the metal electronic state and the dispersion are the main parameters for working it as a catalyst. The main product of this cracking is carbon particle and hydrogen. The main problem with this carbon particle is to sequester it that produce CO which is far harder to separate. By using a suitable catalyst like using methane on Ni or SiO_2 , CO free hydrogen production can be achieved. It has been experimentally improved the stability to an electronic promotion effect. The improved performance with copper addition is very much high and the dispersion of the nickel accounts high yield of hydrogen production with the formation of nickel aluminate. Actually, in this process, the active metal sites of the nickel will come out more that offers the more efficient production of hydrogen (Figueiredo et al. 2010). Addition of magnesia to a methane cracking, catalyst increases the initial cracking rate. In this case, the initial rate of the reaction increase with the formation of smaller nickel crystals and stronger adsorption sites (Gac et al. 2009). If copper nitrate (3%) is used in nickel, then the production of hydrogen will be more, so in this case the copper is used as an inhibitor (Echegoyen et al. 2007). The reaction propagation is not a linear function of the catalyst loading; If we use Ni catalyst with nickel loading, then up to 30% of loading the reaction rate will increase very sharply and then beyond 30% it will decrease gradually (Venugopal et al. 2007).

The reaction was reported with the iron catalyst also but the proper conversion taken place at a high temperature around 800°C (Muradov, 1993) and copper supported on alumina catalyst was also used, but the problem with this process is that the concentration of the methane in solution is very low (Ammendola et al. 2009). Situation of the pores or the active sites distribution and the surface chemistry plays an important role in the reaction propagation and the catalyst deactivation like if we conduct the cracking with carbon black and activated carbon as catalyst, then in both cases the reaction rate will be high but in case of activated carbon the deactivation takes place very quickly due to the formation of the carbon particle or carbon filament at the gas-metal or the metal-metal surface depending upon the temperature of the reaction (as they blocked the active sites of the catalyst) (Suelves et al. 2007).

So, to reduce this problem, a pretreatment of the catalyst is required. With this pretreatment the metal catalyst will comes to its active phase in which it can be again used in the reactions. A pretreatment process is mainly consists of two steps: 1) calcinations; and 2) reduction, and these processes will help to reproduce the active sites of the metal catalyst. This reaction is mainly depends on the high temperature requirement as it requires temperature around 600°C (Echegoyen et al. 2007).

4.2. Metallic support

In addition to the catalyst, it also needs a support to maintain the reaction temperature and the spontaneous reaction propagation; it also helps in the generation of the filament and rather the activation and deactivation of the main metal catalyst. A lower methane conversion was observed after using magnesia as a support with Ni, but if the reaction takes place with silica, then the conversion will be a little higher (Ermakova et al. 2000). Actually, the main function of metallic support is to change the electronic state of the main metallic catalyst to generate the active sites of the catalyst and keep them in touch with the gas for better conversion. So, it is required to maintain the physical contact between the metal catalyst and the metallic support. Another important work of this metallic support is to help in the adsorption of the carbon particle by the metal catalyst at the time of the reaction propagation which will help to keep the catalyst active for a long duration. Otherwise, if the adsorption of carbon particle will not be there and the active sites of the catalyst will be blocked by the precipitation of the carbon particles.

To observed different effect of different metal support on Ni, X-ray diffraction can be used that will help to choose the proper metallic support depending upon their action condition. The support metal can be classified among SiO_2 , TiO_2 , Al_2O_3 , MgO , etc. In this case, previously discussed process of catalytic pretreatment is also applied, like at first catalysts were calcined in air at 600°C for almost 5 hours, and after that reduction procedure takes place with hydrogen at 550°C for 1 h. For equivalent surface area, it has been observed that lower the interaction between the nickel and the support, higher the methane conversion. It has been proved that titanium and silica support resulted in the highest methane conversions (Takenaka et al. 2001).

It has been experimentally proved that the structure of the metallic support and textural properties like porosity also affect the methane conversion rate. It has been also observed that the working and activity of the catalyst mainly depends on the pore structure of the catalyst for a large scale production. If nickel promoted with silica, it will give more amount of pores so that the highest methane conversion and longest lifetime can be achieved very easily (Ermakova et al. 2000).

4.3. Catalyst deactivation

Deactivation of any catalyst is very much common and probably the main problem for any catalytic process. As we are discussing about another main catalytic hydrogen production process, so we have to discuss about the deactivation phenomenon for the methane catalytic cracking. Sometimes, it has been observed that the adsorption of the carbon particles also deactivates the catalyst. Several studies proved that the some activities like fouling, cocking (small carbon particle deposition) mechanical degradation are the main reasons behind deactivation. That's why, decomposition of the methane was less when we use activated carbon due to the formation of the carbon particles (coking) discussed earlier. Activity of the carbon particle can be defined as the mmol of carbon particle produced per gram of methane reacted per minute (Krzyszynski and Kozlowski, 2008).

Methane cracking using a metallic catalyst mixture of $0.5\%\text{Mo}-4.5\%\text{Fe}/\text{Al}_2\text{O}_3$ was reported with reactor temperature of 700°C . It was observed that the hydrogen production rate decreased for a catalyst bed of 1 g was about 6% hour and if we used catalyst bed

of 3 g, then it was less than 1% hour. The main reason behind the loss in activity was the detachment of metallic particles from the metallic support. XAFS and Mossbauer spectroscopic analyses confirmed that the form of the catalyst remained metallic even after separation by the graphitic layers. Deactivation of the catalyst was done by poisoning or changes in surface chemistry (Shah et al. 2001).

Reaction type, catalyst type, reaction conditions and the carbon gasification and formation rates are the main parameters on which the deactivation of the metal catalyst (due to carbon deposition) depends (Bartholomew, 2001).

It may not be true that the deposition of the carbon particles always deactivate the catalyst; using Ni/SiO₂ catalyst, it has been reported that a very little amount of the catalyst remains activated after a prolonged deposition of carbon particles on the surface. It was later proved by using several electron microscopes like SEM (scanning electron microscope) and TEM (transmission electron microscopy) that the deposition was done by the formation of the filament and the tip of the filament consists of a nickel particle (Ishihara et al. 1995).

Carbon atoms in the filamentous form also cause some effects. It was reported that if methane cracking performed with the metal catalyst Ni/SiO₂, deactivation takes place only after the reaction, due to lack of space in the reactor (Aiello et al. 2000). This is because of formation of filaments in high amount that interfere with each other both inside and outside the catalyst pellet (Zhang and Amiridis, 1998) and due to the space problem some of the active sites are not able to come in contact with the gas phase for the reaction activity and the deactivation of the catalyst takes place.

Deactivation of a Co-alumina catalyst to the methane molecules taken place due to the formation of carbon species which after formation dissolved and diffused through the metal particle. It was shown that the catalyst deactivation occurred when the rate of the formation of the carbon at the surface of the CoO sites is much higher than the rate of carbon diffusion through the metal catalyst particle (Nuernberg et al. 2008). It was observed experimentally that the nickel in a deactivated state of Ni catalysts was in a metallic state. But if we do the reaction taking Ni-Cu catalyst it was shown that almost half of the nickel was dispersed in carbon (Shaikhutdinov et al. 1995).

There are several factors affecting the deactivation of the catalyst like the partial pressure of the reactant (methane) and the product (hydrogen). Deactivation rate is inversely proportional to the partial pressure of the hydrogen (Villacampa et al. 2003). Experimentally, it is reported that the deactivation of the metallic catalyst highly depended on the temperature (Ermakova et al. 2000). A fixed-bed reactor and a 65% Ni supported on silica and alumina catalyst can be used to show the effect of the temperature on the deactivation of the metal catalyst. Using 100% methane and at a reaction temperature of 700°C it was found that with a space time of 1.15 s, catalytic activity did not decay after 16 hours of the operation with a carbon yield of 55.6% (6.3 g of carbon per gram of catalyst). Varying the space time with 0.23 s, the catalyst completely deactivated after 90 min with about 6.7% yield. Then the reaction can be repeated with 550°C and with the space time of 1.15s (Suelves et al. 2005). Effect of hydrogen partial pressure is very much in the reduction of the methane cracking rate as formed hydrogen can keep the active sites of the catalyst away from the methane, so the adsorption of the methane will be hampered with the deactivation of the metal catalyst (Toebes et al. 2002).

4.4 Catalyst regeneration

Activation of the catalyst is a very important part of methane decomposition reaction as it should be done for the propagation of the reaction. The catalyst circulation time, the effect on catalyst performance and the energy required for the process, these are the main three categories that we need to look before going for any regeneration process. Regeneration of catalyst for methane decomposition at temperatures of 850°C and 950°C with five regeneration cycles using CO₂ at temperatures of 950°C and 1000°C provides the activity and stability to the catalyst. It has been observed that the ultimate mass gain of the catalyst decreased after each regeneration step at both the temperature; and several mass gains observed when the reaction occurred at different temperatures (Abbas and Daud, 2009).

In the catalyst regeneration process, there are two main processes that use air or steam. In both the process main reaction takes place with the carbon particle, formed during the decomposition reaction. In both the process the main products are CO₂ and CO. Again, removing these harmful gases is also challenged as the cost involved in this process will increase at a high rate. So, we have to find such a process where the production of the harmful gases will be less. Sometimes, a mixture of both CO₂ and CO can be produced after the reaction of the CO₂ with the carbon particle for the production of the CO.

Air has been used in a particular amount (3%O₂) for the generation of the 30% Ni/Al₂O₃ catalyst. It was observed that the catalyst loses its activity after the first regeneration experiment. The loss of activity after regeneration depends upon the temperature generated during oxidation of the deposited carbon (Villacampa et al. 2003). After the first regeneration, loss of the activity depends on the fact that the catalyst was mixed with air (Rahman et al. 2006). A 16.4% of metal catalyst Ni/SiO₂ used for methane cracking and air oxidation to re-generate the catalyst at a temperature of 550°C. In spite of the fully generation of the catalyst with air oxidation, the sample will convert to a fine powder due to the generation of high temperature during the oxidation process (Zhang and Amiridis, 1998). Another different regeneration process is partial regeneration (Koc et al. 2008). The main process regarding the partial regeneration is very simple, which consists of the removal of the carbon particles partly. A metallic catalyst of 15% Ni can be used for the partial generation at the temperature of 500°C using air and it is observed that after gasifying almost around 90% activation of the coke can be achieved (Koc et al. 2008).

Steam gasification also used for the generation process. A 16.4% Ni catalyst at a temperature of 550°C regenerated using steam gasification and it was observed that the nickel remained in the metallic form after regeneration. Small pockets of carbon were observed after the regeneration process. It was observed that the carbon formed in the reaction was mainly filament type with

thinner wall and the properties of these filaments were different after using steam gasification process (Zhang and Amiridis, 1998). Methane cracking using nickel supported on different metal oxides has been already studied. The main process occurs at a temperature of 500°C, using two parallel fixed beds in a cyclic mode and alternating the feed from methane to steam. Carbon deposited on the catalyst was 0.82 g of carbon per gram of catalyst after cracking and it was shown that the around 90% of the carbon particle removed after the steam gasification (Choudhary et al. 2001).

CO₂ can also be used for the regeneration of carbon catalyst, but the main drawback of this process is the involvement of the high temperature for the elimination carbon particle. It has been observed that after the third regeneration most of the mass of the catalyst originates from the carbon produced after the reaction (Pinilla et al. 2007). It has been considered as an attractive process due to its good catalyst regeneration strategy. The best advantage of this process is that- it is able to balance the carbon deposition rate (Ammendola et al. 2008).

4.5 Filamentous carbon production during catalytic methane cracking

During catalytic cracking free carbon particles are produced which is an advantage of this process than the other processes, but at the same time it has some disadvantages too. There are several types of carbon that can be produced such as pyrolytic or filamentous depending upon the condition of the reaction. Actually, this is happening due to the change in crystallinity of the carbon particles. Depending upon the various types of carbon produced, the cost related to this process varies as the cost of the carbon varies with its types. Amorphous carbons are more active in methane catalytic cracking. Since, the concentration of high-energy sites increases with the decrease in carbon-crystallinity (Muradov et al. 2005).

As we are interested in the filamentous carbon production, so we need to concern about the different kind of catalyst. Depending upon the reaction condition and catalyst type, the produced carbon nature will be different. On Ni catalyst, the methane is first absorbed and then with the production of the hydrogen gas, carbon particles deposited on the Ni surface, creating a uniform layer of carbon that depends on the solubility of the carbon particle (solution) on the Ni surface. It adsorbed in the gas phase and carbon diffuses through the nickel particle towards the metallic support until the carbon solution of nickel is super-saturated and particularly at that time, nucleation of filamentous carbon began (Yang and Chen, 1989; Snoeck et al. 1997).

At starting of the nucleation process Ni surface is covered with the carbon particles which are dissolved through the Ni particles. As the surface is covered with carbon, so the main decomposition reaction of the methane will be less as all the active sides are covered with the carbon particles (Baker et al. 1972).

If we perform the methane cracking over a 50% (wt.) Ni/SiO₂ catalyst then the nucleation takes place through the formation of nickel carbide and it is the main initial process of hydrogen production. After that, through this decomposition of the nickel carbide, nucleation of the graphite at the metal support interface takes place and after that the Ni particles from the support will detach (Kock et al. 1985).

Since, it has been discussed that the formation of the filament depends on the several parameters like temperature. It has been seen that particularly at low temperatures, diffusion through the metal particle is slower than the nucleation rates. A non-hollow solid filament production can be seen here at the metal support interface (Gac et al. 2009). The carbon filament formation was also observed at moderate conditions with a low Ni loading and that temperature had a significant effect on morphology of the formation (Boellaard et al. 1985).

Investigation of the microstructure of the carbon filaments concluded that the coke layers resemble fish-bone-like structures; carbon species are excreted from the metal particle perpendicular to the metal or filament interface; and deposition of carbon on the metal catalyst takes place in a conical form (Sacco et al. 1984; Gac et al. 2009). A thermal phenomenon has been noticed after the nucleation part; the nickel present at the tip of the insulating carbon filament and the metallic support, does not work as a heat source (Baker et al. 1972).

At the time of the filament growth, a constant temperature profile on the nickel particle was observed and the reason behind it is the balance between the heat losses and the heat gains from the surrounding environment and it was seen that the number of filaments remains constant when the maximum number of filaments is nucleated (Bai et al. 2007).

An intermediate product during the filamentous carbon production is selvedge, is formed at the gas-metal interface due to the segregation behavior of carbon particles in nickel. It happened due to the carbon concentration gradient between the surface and atomic layers. Then, filamentous carbon is formed as a product due to the chemisorptions on the metal surface. These carbon filaments diffuse towards the opposite face, where the carbon atoms crystallize in the form of a continuous graphite-like structure; and it is maintained by diffusion of the carbon particle through the metal (McCarty et al. 1983).

Using Ni/SiO₂ as a catalyst: a balance between dissociation of the carbon-containing gases and carbon diffusion through the catalyst particle; and a balance between rate of nucleation and formation of graphitic layers and carbon diffusion through the catalyst particle, has been observed. But we have seen that the formation of the filaments is mainly done by carbon diffusion through the catalyst from the gas side to the support side. The carbon particles are deposited at the nickel and support interface due to the segregation behavior of carbon in nickel (creating a selvedge with a high concentration of the carbon particles at the nickel). A gradient in carbon concentration has been noticed at the surface and very small amount in the bulk flow (Shah et al. 2001).

5. THERMAL CRACKING OF METHANE

Thermal cracking of methane is a very important part of cracking of methane/natural gas for the production of hydrogen. Thermal cracking of methane has been applied for the production of carbon-rich hydrogen and carbon black (Wheeler and Wood, 1928). It is a simple process where involvement of high temperature, heat and pressure help to crack methane, and to produce hydrogen and free carbon particles. This process creates free radicals at the sites where molecular bonds are broken, which can be happened in chemical reactions such as polymerization to create new chemical compounds. A wide variety of compounds are extracted or derived through these types of processes, making it a valuable part especially in petroleum refining. Here, our main interest is to crack methane for the production of hydrogen. It should be noted that cracking of NG is not a new process. It can be used as a supplementary fuel production process like thermal black process. The process has been practiced in a semi-continuous mode using a high operating temperature of around 1400°C in two tandem reactors (Muradov, 2001). Along with the major product like hydrogen; the process produces a very important byproduct: clean carbon, which can be used as a commodity or can be sequestered for other uses. We can also refer cracking of methane as the decarbonization of NG (Steinberg, 1999). In case of methane, C–H bonds are very strong, non-catalytic thermal cracking of methane requires temperatures higher than 1200°C, to obtain a reasonable yield. By using a catalyst, the temperature can be significantly reduced. There are many reports on the use of an electrical furnace as a heating source for the cracking process, while there are rather few focusing on the use of concentrated solar energy, plasma or a molten-metal bath as alternative heating sources. Solar is most likely to be the only source of free energy capable of producing a very large amount of hydrogen. Some researcher also designed and studied several high temperature solar chemical reactor for the thermal splitting of methane to produce pure hydrogen gas (Abanades and Flamant, 2006b). This solar route saves the process energy and the CO₂ emission associated with the production of products through classical methods. In other words, in the solar-thermal process, fossil energy usage and emissions are actually avoided or greatly reduced.

Plasma may also be employed as an environmentally friendly heating source. Generally, very high temperature is required for the plasma process and recent development in the plasma process can help to generate such high temperature (Fulcheri and Schwob, 1995). Microwave (MW) plasma (generated using an MW-frequency signal; typically 2.45 GHz), commonly used in MW ovens has the advantages of easy operation due to several factors such as it is an electrode less reactor, offers high plasma density and high electron mean energy (Tsai and Chen, 2009). The major advantage of this process is that it provides the total conversion of the hydrocarbon into CB (Fulcheri et al. 2002). If we discuss about the position of the heat source or the heating pattern in the cracking process, then we have to keep it in mind that the heat source must be located inside the reaction zone using a heat pipe.

The cracking process could be arranged in a continuous process with the electric furnace as a heating source in combination with quartz micro reactor (Fulcheri et al. 2002). In the reported study, a three zone electrical tubular furnace was used and the reactor was made from quartz tube, 0.042 m i.d. and 0.97 m height. It was observed in the process that the fine carbon particles deposited on the reactor walls and aromatic hydrocarbon condensate in the lines downstream of the reactor (Muradov et al. 2005). A 0.45 m long and 0.022 m i.d. quartz type electric furnace was also used. Under electric furnace heating it has been observed that nitrogen distributed the methane molecules within the AC bed. Under MW heating, the nitrogen has an important role it helps to distribute the methane molecules. The formation of CNF takes place when a combination of nitrogen and MW heating was used (Dunker et al. 2006). A reactor with 2.5 m of height and three graphite electrodes at the top was also analyzed with the plasma power supply for the cracking process. The reactors internal temperatures were measured at four locations using an optical pyrometer. The process was performed with electric power varying between 50 and 100 kW (Fidalgo et al. 2008). In the cracking process a nuclear type of reactor can be used as a good heating source with 0.025 m diameter and 0.35 m height. In this reactor a different procedure can be seen as methane was bubbled through a bed of molten metal and solid media. Bubbling methane through porous metal filters was the most efficient part of this process and at the end of the process generated carbon can be separated from the media (Serban et al. 2003). Another electric furnace consists of cylindrical drum, i.e., rotating around its horizontal axis and having a diameter of 0.065 m, length of 0.8 m with a rotation speed of 1–20 rpm, was used for hydrogen production. However, its rotation speed does not have any significant influence on the production of hydrogen (Pinilla et al. 2009).

6. CONCLUSION

Methane cracking is a promising process to produce green hydrogen. In methane catalytic cracking, different catalysts can be used, including Ni, Co, Fe, activated carbon, carbon black. Carbon filaments are produced as a result of the reaction product of carbon diffusing through the metal catalyst particle, and then the diffusing carbon particle is deposited in filament form on the Ni/support interface. Different catalyst deactivation and regeneration processes have been discussed in details. Moreover, several thermal cracking processes such as plasma, electric furnace, nuclear, etc. and their importance have been also reviewed. In catalytic cracking, though the temperature requirement is less than that of the thermal process, for the latter case an extra amount of methane can be used for the production of extra energy. The main problem with this process is the formation of CO₂, which is a major component of greenhouse gases.

FUTURE ISSUES

In addition to the above discussed processes, which are traditionally used for the production of pure hydrogen gas, we need to study and review some solar thermal energy based cracking processes. Use of solar energy or reactor (i.e., consists of solar concentrator) for methane cracking need to be discussed thoroughly and this technology seems to be an interesting strategy and

shows a promising potential. Therefore, most of the researchers are interested in the solar thermal processes. Although, they are studying different catalytic experiments using solar concentrator and thereby the requirement of energy can be solved using solar power without producing harmful greenhouse gases. However, to achieve the higher temperature requirements (between 700-1500°C), through the solar concentrator only, is still a big challenge for researchers.

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