

Technologies for Clean and Renewable Energy Production
Prof. Prasenjit Mondal
Department of Chemical Engineering
Indian Institute of Technology – Roorkee

Lecture - 24
Hydrogen Production from Natural Gas

Hi friends, now we will discuss on the topic hydrogen production from natural gas. In the last classes, we have discussed on the utilization of natural gas and we have seen that it can be used through the conventional route for electricity production or it can be used to produce syngas and further liquid fuels and it can also be produced to hydrogen. As you know that the hydrogen is considered as a green fuel and the future fuel also.

(Refer Slide Time: 01:03)

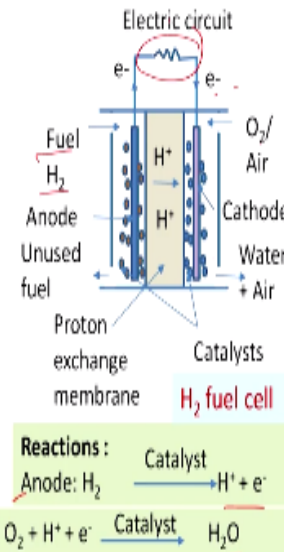
Contents
➤ Hydrogen as a green fuel
➤ Hydrogen production routes
➤ Natural gas as a feedstock for hydrogen
➤ Routes for hydrogen production from natural gas
• Reforming
• Decomposition of methane

So in this class, we will discuss on this content the hydrogen as a green fuel, then hydrogen production routes, then natural gas as a feedstock for hydrogen, and the routes for hydrogen production from natural gas that are reforming and decomposition of methane.

(Refer Slide Time: 01:34)

Hydrogen as a green fuel

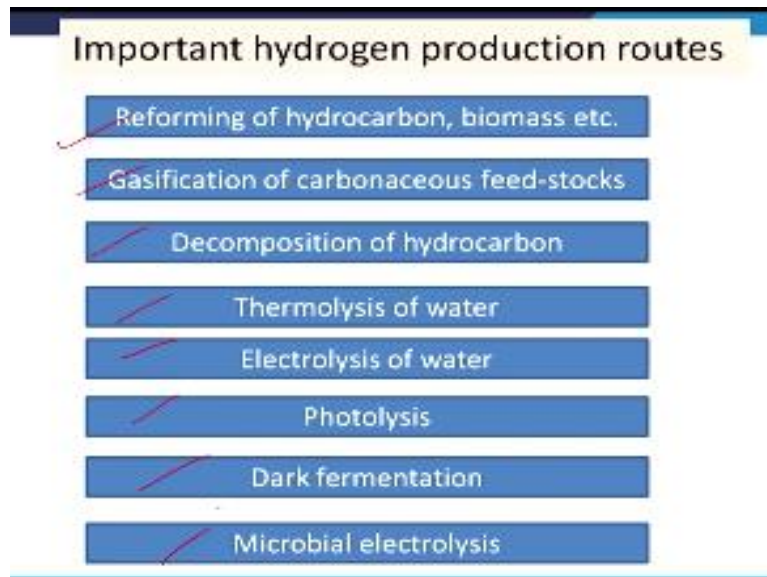
- Hydrogen has high energy density (HHV: 142 MJ/kg)
- It does not produce CO_2 during combustion
- Electricity can be produced in fuel cell using hydrogen



So as you know that the hydrogen is having very high energy density and heating value is 142 megajoule/kg and we also know that hydrogen can be combusted and there will be no carbon dioxide emission. One important feature of hydrogen is that it can be used in fuel cell and electricity can be generated. So here, this figure shows us the electricity generation in the hydrogen fuel cell. So when hydrogen is used as a fuel in this fuel cell where in the anode this hydrogen is coming and then in this here it is converted to H^+ and e^- .

Then H^+ is transported from anodic to cathodic chamber through this membrane, hydrogen transfer membrane, and it is coming to this cathode where oxygen is supplied. So oxygen reacts with H^+ and e^- , e^- or electron which is generated here in the anode, it is transported through the external circuit and comes here, and then this electron and then H^+ which is transported to this membrane and this oxygen reacts and converts to H_2O . As a result what we get, get electricity here. So electricity is the very cleaner mode of energy, that is why hydrogen is considered as the green energy.

(Refer Slide Time: 03:10)



So this hydrogen can be produced from different resources and we will briefly discuss that. So this can be produced from reforming of hydrocarbons or biomass, gasification of carbonaceous feedstock, decomposition of hydrocarbons like say methane, then thermolysis of water, electrolysis of water, photolysis, then dark fermentation and microbial electrolysis. So these are the different methods, which have been reported for the production of hydrogen and we will see the comparison of these processes.

So reforming process as you know it may be of different types, just we have discussed in the previous class; it may be auto thermal, it may be steam reforming, it may be dry reforming or tri deforming, anything it may be.

(Refer Slide Time: 03:54)

Comparison of important hydrogen production technologies			
Technology	Feedstock	Efficiency	Maturity
Steam reforming	Hydrocarbons	70-85%	Commercial
Partial oxidation	Hydrocarbons	60-75%	Commercial
Autothermal reforming	Hydrocarbons	60-75%	Near term
Plasma reforming	Hydrocarbons	9-85%	Long term
Biomass gasification	Biomass	35-50%	Commercial
Methane catalytic decomposition	Hydrocarbons	60-7%	Long term
Coal gasification	coal	60-70%	commercial

(Source: Dincer, 2015; Kalogirou et al., 2013)

We will be comparing those things say steam reforming, partial oxidation, autothermal

reforming, plasma reforming, biomass gasification, methane catalytic decomposition, and coal gasification. If we see here, these are the different feedstocks, some are hydrocarbons, biomass, and coal. The efficiency for hydrogen production is also different and maturity level is also different.

(Refer Slide Time: 04:21)

Comparison of important hydrogen production technologies			
Technology	Feedstock	Efficiency	Maturity
Biomass reforming	Biomass	35-50%	Mid term
Plasma cracking	Hydrocarbons	70-80%	Long term
Liquid phase reforming	Carbohydrates	35-55%	Mid term
Thermolysis	Water+heat	50%	Long term
Electrolysis	Water+Electricity	50-70%	Commercial
Photolysis	Water+Sunlight	0.5%	Long term
(Source: Dincer, 2015; Kalamaras et al, 2013)			

Some other examples are say biomass reforming, plasma cracking, liquid phase reforming, thermolysis, electrolysis, and photolysis. So if we compare, we can see that either hydrocarbons or biomass or coal are the carbonaceous materials that have been used for the reforming process and efficiency is also different. Most important is that their maturity level if you see some are very few are in commercial scale, all are in maturity, either long term maturity or medium term or under development.

So these are the different technologies which are available for hydrogen production. The commercial processes are reforming, then biomass gasification, then coal gasification, and here we are having electrolysis. So basically if we see the methods, then we will be having some important data that is the steam reforming, partial reforming that captures maximum share for the hydrogen production, followed by gasification of coal and biomass, and then electrolysis.

Others are very less, contribution of other processes is very less in commercial scale, they are under development. Now we will discuss on reforming because it will be using hydrocarbons and basically in our case it is natural gas. So natural gas or methane will be converting to hydrogen through the reforming processes.

(Refer Slide Time: 06:01)

Various types of Reforming processes		
Dry reforming	Steam reforming	Partial oxidation
$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	$\text{CH}_4 + 1/2\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$
$\Delta H^\circ_{298} = 247 \text{ kJ/mol}$	$\Delta H^\circ_{298} = 206 \text{ kJ/mol}$	$\Delta H^\circ_{298} = -36 \text{ kJ/mol}$
[900 – 1123] K et [1–20] bar	[970– 1100] K et [21–35] bar	[1473–1673] K et [50–70] bar
H_2/CO ratio = [0.4–1.5]	H_2/CO ratio = [3–5]	H_2/CO ratio = [2–2.5]
Autothermal reforming	Tri-reforming	
$\left[\begin{array}{l} \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \\ \text{CH}_4 + 1/2\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \end{array} \right]$	$\text{CH}_4 + 1/2\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$ [$\Delta H^\circ = -35.6 \text{ kJ/mol}$] $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$ [$\Delta H^\circ = 247.3 \text{ kJ/mol}$] $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$ [$\Delta H^\circ = 206.3 \text{ kJ/mol}$] $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ [$\Delta H^\circ = -880 \text{ kJ/mol}$] [1123 – 1273] K et [20–100] bar H_2/CO ratio = 2	
	[1273] K et [20 bar] H_2/CO ratio = 1.2–1.5	

Different reforming processes are dry forming, steam reforming, partial oxidation, autothermal forming and tri reforming. As we have discussed in a previous class and as evident here also, we see each H_2/CO ratio is maximum in case of steam deforming. As we are interested to get the hydrogen through this route, so obviously the steam deforming can be more suitable route for the hydrogen production. So, we will be discussing some more on steam reforming and already we have discussed other reforming in previous class.

(Refer Slide Time: 06:43)

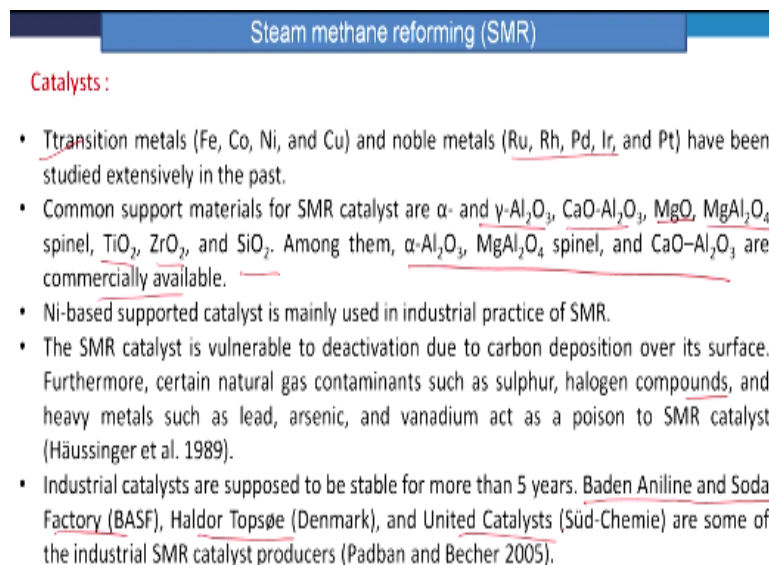
Steam methane reforming (SMR)
<ul style="list-style-type: none"> Catalytic reaction of natural gas with high temperature steam to produce hydrogen rich gas is termed as steam methane reforming. Conventionally, SMR is accomplished in a vertically stacked multi-tubular reactor. The process heat for the endothermic reaction is provided by the burning of a part of natural gas feed (25%) outside of the reactor tubes, in a shell and tube arrangement. Overall reaction of natural gas reforming containing higher hydrocarbons can be written as: $\text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O} \rightleftharpoons n\text{CO} + (2n+1)\text{H}_2 \quad \Delta H^\circ_{298 \text{ K}} > 0$
Process Conditions:
<ul style="list-style-type: none"> SMR requires steam to methane ratio (S/C) in feed as 1:1. However, higher S/C ratio is mostly used in industrial practice to achieve higher methane conversion and to increase the H_2 in product stream The SMR has an energy efficiency of 70–85% CO_2 emission is estimated around to 7 Kg $\text{CO}_2/\text{Kg H}_2$ produced

So in steam reforming, steam is used for the reforming purpose. So, this is our say hydrocarbon and then this is our steam, it will gives us $n\text{CO}$ and H_2 rich gas and this is del H value. So what we are getting here, so if it is C_1 , then n_1 , then it is methane, this is representing methane. Then SMR reactor, it requires steam. What would be the ratio of the

steam and methane that is very important, that is it requires is S/C, steam by methane ratio as 1:1 and if we give more steam and more S/C ratio, we can get more hydrogen.

The SMR has efficiency of around say 70-80% and carbon dioxide emission is 7 kg carbon dioxide per kg of hydrogen produced.

(Refer Slide Time: 07:34)



Steam methane reforming (SMR)

Catalysts :

- Transition metals (Fe, Co, Ni, and Cu) and noble metals (Ru, Rh, Pd, Ir, and Pt) have been studied extensively in the past.
- Common support materials for SMR catalyst are α - and γ - Al_2O_3 , $\text{CaO-Al}_2\text{O}_3$, MgO , MgAl_2O_4 spinel, TiO_2 , ZrO_2 , and SiO_2 . Among them, α - Al_2O_3 , MgAl_2O_4 spinel, and $\text{CaO-Al}_2\text{O}_3$ are commercially available.
- Ni-based supported catalyst is mainly used in industrial practice of SMR.
- The SMR catalyst is vulnerable to deactivation due to carbon deposition over its surface. Furthermore, certain natural gas contaminants such as sulphur, halogen compounds, and heavy metals such as lead, arsenic, and vanadium act as a poison to SMR catalyst (Häussinger et al. 1989).
- Industrial catalysts are supposed to be stable for more than 5 years. Baden Aniline and Soda Factory (BASF), Haldor Topsøe (Denmark), and United Catalysts (Süd-Chemie) are some of the industrial SMR catalyst producers (Padban and Becher 2005).

In this case catalyst as we have discussed in the previous class that nickel based catalyst are used, so mostly used, but other catalyst are transition metals that is iron, cobalt, nickel, copper and the noble metals these are have been reported and these are the active ingredients for the catalyst and some support is required, so basically gamma alumina, CaOAl_2O_3 , MgO , MgAl_2O_4 , TiO_2 , ZrO_2 , SiO_2 have been used. Among them, these are very commercially available.

So these catalysts also coke deposition is a problem for this catalyst and if sulphur and halogen compounds may also deactivate the catalyst. Some industrial catalyst suppliers we see that is Baden Aniline and Soda Factory BASF, Haldor Topsoe and United Catalysts these are the players for the catalyst supply in commercial scale for SMR.

(Refer Slide Time: 08:50)

Mechanism

The basic assumptions made for this kinetic mechanism are as follows:

- H_2O reacts with surface nickel atoms, yielding adsorbed oxygen atoms and gaseous hydrogen. $\text{H}_2\text{O} + \text{s} = \text{H}_2 + \text{O}(\text{s})$ (Eq. 1)
- Methane reacts with surface nickel atoms, yielding adsorbed CH_2 radicals and adsorbed H atoms. $\text{CH}_4 + 3\text{s} = \text{CH}_2(\text{s}) + 2\text{H}(\text{s})$ (Eq.2)
- The adsorbed radicals CH_2 and adsorbed oxygen react to yield adsorbed CHO and adsorbed hydrogen. $\text{CH}_2(\text{s}) + \text{O}(\text{s}) = \text{CHO}(\text{s}) + \text{H}(\text{s})$ (Eq.3)
- Adsorbed CHO dissociates to adsorbed CO and H, or reacts with adsorbed oxygen, yielding adsorbed CO_2 and H in parallel.
 $\text{r}_{\text{cs}} 1 \text{ CHO}(\text{s}) + \text{s} = \text{CO}(\text{s}) + \text{H}(\text{s})$ (Eq.4)
 $\text{r}_{\text{cs}} 2 \text{ CO}(\text{s}) + \text{O}(\text{s}) = \text{CO}_2(\text{s}) + \text{s}$ (Eq.5)
 $\text{r}_{\text{cs}} 3 \text{ CHO}(\text{s}) + \text{O}(\text{s}) = \text{CO}_2(\text{s}) + \text{H}(\text{s})$ (Eq.6)
- Adsorbed CO reacts with adsorbed oxygen to form CO_2 , or desorbs into the gas phase. $\text{CO}(\text{s}) = \text{CO} + \text{s}$ (Eq.7) ; $\text{CO}_2(\text{s}) = \text{CO}_2 + \text{s}$ (Eq.8); $2\text{H}(\text{s}) = \text{H}_2 + 2\text{s}$ (Eq.9)

Now, we will see the mechanism. What is the mechanism for the production of hydrogen through this route? So we have hydrocarbon and we have steam, so steam, and we have some catalyst. So it is gas and solid phase reactions. So we will be having steam, so that steam reacts with surface nickel atoms which is available in the catalyst and then it forms adsorbed oxygen atoms and gaseous hydrogen, this is the first step it is assumed.

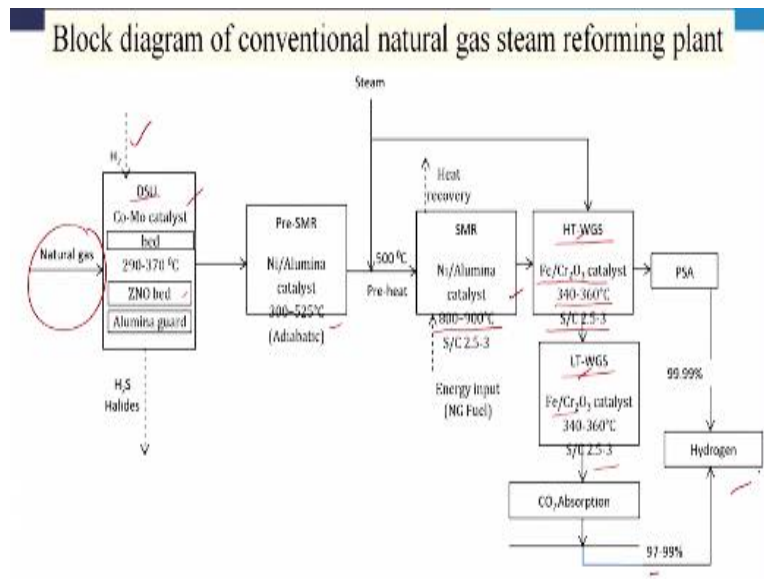
So H_2O it is in the support of the catalyst sides, the nickel sides, it is giving us $\text{H}_2 + \text{O}$ s which is adsorbed. Then again methane we have also, so methane reacts with surface nickel atoms and then it yields CH_2 radicals which is adsorbed and adsorbed H atom, so CH_4 with catalyst side it is giving us CH_2 in adsorbed form and hydrogen also as adsorbed form. So these adsorbed radicals and H and O will further react. So we will see here, the adsorbed radicals and adsorbed oxygen react to yield adsorbed CHO.

So this is the reaction $\text{CH}_2\text{s} + \text{O}$ s it is giving CHO s + H s. Then CHO which is adsorbed that can also be converted to other forms, so as mentioned here that may be possible that CHO is converted to COs + H s adsorbed COs and adsorbed hydrogen and CO is with adsorbed oxygen that can give CO_2 adsorbed + sides and then CHO adsorbed can react with oxygen adsorbed and also it can give a CO_2 adsorbed and hydrogen adsorbed.

So these are the different species which are generated during the process in the catalyst and those with the help of the catalyst and these intermediates the COs can give a CO and the sides and then CO_2 s can give a CO_2 and sides and H s can give us H_2 and sides. That means after desorption of those gas, the sides are made free, so catalyst is now free, our feedstock is

converted to product and that is fuel rich of hydrogen and carbon monoxide, also having carbon dioxide. So this is the mechanism of the SMR reaction

(Refer Slide Time: 11:39)



Now, we will see how the natural gas can be processed through this route. So here we have say natural gas, so that natural gas certainly will have some sulphur and that sulphur will be the poison to the catalyst, so we have to remove it. So for this removing, we are using hydrogen here, so desulphurization unit, DSU, as a first step of the process. Then some catalyst are used that is cobalt molybdenum catalyst, Co-Mo catalyst, and then it is 290-370 degree centigrade and then this is your catalyst where then zinc oxide bed is also used and then alumina guard.

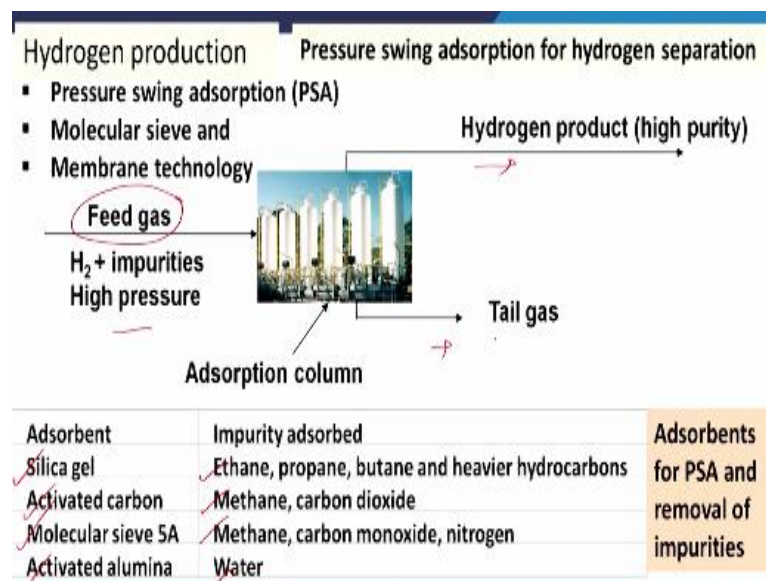
So these are the series of oxides are used in which the DSU reaction is taking place and H2S and halides are separated from the natural gas. The natural gas will be going to now reformer SMR and before going to that, it has gone through the pre-reforming state to raise the temperature from 290 to say it is up to 525 degrees centigrade and then it will be going to SMR reactor where the temperature is higher that is 800-900 degrees centigrade. So here after this SMR reaction, so CO and H2 gas will be there.

So there will be some shift reactions to produce more hydrogen. So high temperature shift, water gas shift reaction is taking place here with the help of Fe/Cr2O3 catalyst at 340 degree to 360 degree centigrade, that is the high temperature water shift reaction with a S/C ratio of 2.5-3. Then, we will be getting more hydrogen rich gas and that will go for pressure swing

adsorption for the separation of hydrogen and then some of it is going to low temperature water gas shift reaction and here Fe/Cr₂O₃ catalyst and 2.5-3 that is S/C ratio.

Then it is going for carbon dioxide absorption. Then after SMR, it is going to shift reaction, it may be at a high temperature water gas or it may be at low temperature water gas reaction, then after that it is going for carbon dioxide separation and then we are getting 97 to 99% purity of hydrogen or here we also get PSA through the pressure swing adsorption we can get the 99.99% purity of hydrogen.

(Refer Slide Time: 14:31)



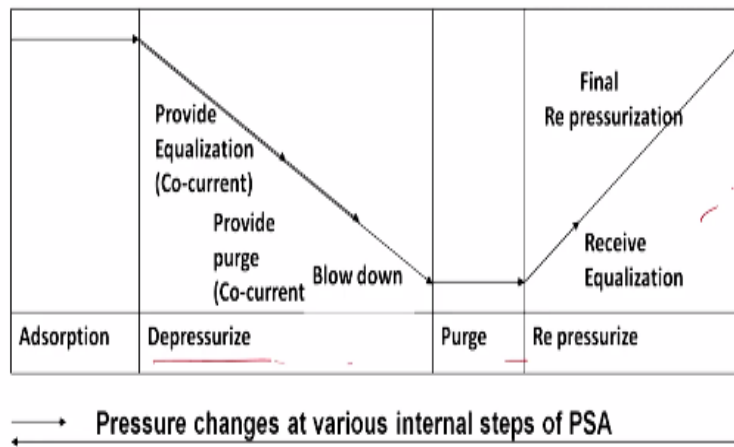
So then we will see how the PSA works, so pressure swing adsorption. Pressure swing adsorption works to separate the impurities present in the hydrogen. Different types of adsorbents are used for the separation of different types of impurities in the gas stream like say silica gel, activated carbon, molecular sieve, and activated alumina have been reported. These components are suitable to remove different type of impurities like silica gel for ethane, propane, butane, etc; activated carbon for methane, carbon dioxide; molecular sieve for methane, carbon dioxide, nitrogen and activated alumina for water.

So these are the different adsorbents, which are used for the separations of other gas components. So here, we use the feed gas hydrogen plus impurities at high pressure. Then it is going through different adsorbent beds and we are getting hydrogen rich gas here and this is our tail gas, hydrogen lean gas, so there is less hydrogen in this gas stream.

(Refer Slide Time: 15:38)

Hydrogen production

Pressure swing adsorption for hydrogen separation

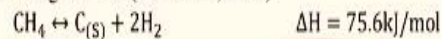


So this PSA works in a cycle. So if we have some adsorption part, so gas adsorption takes place in this case. Then depressurization takes, so high pressure pressurize, gas adsorptions, then we are depressurizing it and then purging it and again re-pressurizing it. So it has some cycle and different operations have certain span in the whole cycle. So, this is the way the hydrogen is produced from the natural gas through steam reforming.

(Refer Slide Time: 16:16)

Methane decomposition

- Decarburation via dry natural gas (methane) cracking is a promising alternative and carbon free technology (Abbas et al., 2010).
- Methane can be thermally decomposed into its elemental species, hydrogen and carbon, according to following reaction (Catón et al, 2001).



- Methane decomposition (MD) reaction enables direct production of hydrogen suitable for fuel cells or any other purpose, free of carbon oxides.
- Methane decomposition requires only half of the energy (37.8 kJ/mol H₂) that is required in SMR (63.3 kJ/mol H₂) (Dunker et al, 2006).
- In spite of that, owing to high strength of C-H bond, this reaction generally takes place at high temperatures around 1200 °C, in order to break it (Abbas, H.F. et al., 2010).
- CO₂ emission from burning of process fuel (methane) is around 0.05 mol CO₂/mol H₂, which is much lower than that of 0.43 mol CO₂/mol H₂ in SMR

Now we will discuss on the methane decomposition. How the methane can be converted to hydrogen through decomposition. So this can be done. The decarburation dry natural gas cracking is a promising alternative and carbon free technology and this can be converted to solid carbon plus hydrogen as per these reactions. So ΔH is 75.6 kilojoule/mol. These reactions requires high temperature, you know it is around say 1200 degrees centigrade

temperature is required because the carbon and hydrogen bond is just double bond and so break it, so it requires high temperature.

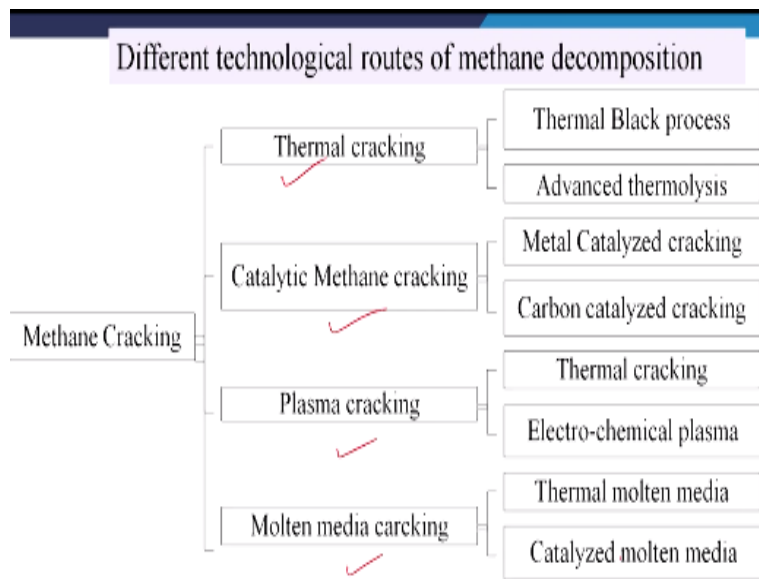
In this case, carbon dioxide emission from burning of process fuel that is your methane is around 0.05 mol CO₂ per mol of hydrogen, which is very less with respect to that used for SMR that is equal to 0.43 mol carbon dioxide per mol of hydrogen.

(Refer Slide Time: 17:15)

- Direct methane decomposition is not economically viable at moderate temperatures due to low yield of hydrogen. However, reaction temperature can be reduced by the addition of supported active metal catalysts to decompose hydrocarbons to produce hydrogen at more moderate temperatures.
- SiO₂ and Al₂O₃ supported catalyst with active metal phase, Co, Ni and Fe can be used for decomposition of methane (NG). Nickel is particularly active for natural gas cracking (Avdeeva et al, 1999).
- Methane catalytic decomposition is reported to suffer by black carbon deposition on the active sites of catalyst and it can inhibit the continuous operation, as required by the industrial process.
- Different reactor configurations for continuous methane cracking have been proposed, such as a set of parallel fixed-bed reactors alternating between different conditions or a fluidized bed/regenerator combination.
- Fluidized bed reactor system offers more flexibility and ease in continuous operation (Lee et al, 2004)

So these things methane to carbon formations and hydrogen production, it is a thermal process, but it is difficult to perform without the presence of catalyst. So use of catalyst reduces the temperature from 1200 to say 500 degrees centigrade and different types of catalyst can be used. For this, the reactor configurations may also be varied, fixed bed to fluidized bed, people have used fixed-bed reactors and alternating between different conditions or a fluidized bed or regenerator combination they have used. Out of these 2 reactors, the fluidized bed offers the flexibility and ease of continuous operation.

(Refer Slide Time: 18:12)



Now if we think about the methane decomposition, then we can get different methods. One is your thermal cracking, another is your catalytic methane cracking or you can get plasma cracking or you can get molten media cracking. So this thermal cracking, thermal black process and advanced thermolysis. This is catalytic methane, metal catalyzed and carbon catalyzed cracking. You have plasma cracking, thermal cracking and electrochemical plasma.

You have molten media cracking, thermal molten media and catalyzed molten media. So these are different types of methods people have used for the production of hydrogen by the decomposition of methane.

(Refer Slide Time: 18:59)

Thermal cracking of methane

- When natural gas is heated alone in a reactor in inert atmosphere, it decomposes into its elemental species, hydrogen and carbon,

$$\text{CH}_4 \leftrightarrow \text{C}_{(s)} + 2\text{H}_2 \quad \Delta H_{298}^\circ = 75.6 \text{ kJ/mol}$$
- Owing to high strength of C-H bond, this reaction generally takes place at a high temperature of $\sim 1200^\circ\text{C}$ and it is not considered economically viable (Abbas and Daud 2010).
- The first industrial implementation of thermal cracking of methane was initiated by the European Commission as SOLHYCARB project in 2009 to produce H_2 and carbon black. The solar powered reactor with capacity of 10 kW was tested for a temperature range of $1467\text{--}1997^\circ\text{C}$ and a pressure of 1 bar and the 55% energy efficiency was achieved (Rodat et al. 2011).
- The major problem in continuous operation of thermal cracking of natural gas is the plugging of reactor due to the carbon deposition and high operating temperature

Now, we will see the thermal cracking. As you mentioned that it is a thermal process, we have to apply heat and around 1200 degrees centigrade, the methane will be converted to

carbon and hydrogen, but as you mentioned that it is endothermic process and also it is not that efficient, the high temperature requirement is there and this temperature can be reduced by application of catalyst, and then it will be termed as catalytic method not a thermal one.

Thermal cracking of methane, the first industrial implementation of this thermal cracking of methane was initiated by the European Commission as this SOLHYCARB project in 2009 to produce hydrogen and carbon black, and in this project, the solar power reactor with capacity of 10 kilowatt was tested for a temperature range of say 1467-1997 degrees centigrade and the pressure of 1 bar and the 55% energy efficiency was achieved. So the major problem in continuous operation of thermal cracking of natural gas is the plugging of reactor due to the carbon deposition.

(Refer Slide Time: 20:03)

Catalytic methane decomposition			
	Temperature range (°C)	Type of deposited carbon	Catalyst
<ul style="list-style-type: none"> • Introduction of supported metal catalyst in to the thermal cracking of methane enables us to operate the cracking reactor around 500°C. Thus, making the hydrogen production more economically attractive. • Various supported or powdered transition metals such as Co, Fe, Mo, Ni, Cu, Ru, Rh, Pt, Re, Ir, Pd, and W have been studied for metal catalysed methane decomposition. Ni or Ni/alumina was found to be the most catalytically active species (Ashik et al. 2015). • However, catalyst deactivation by carbon deposition over catalyst surface and/or in to the pores of catalyst is still the major concern to be answered. • This technology is in development stage. 	500-700	Carbon filaments	Ni-based catalysts
	700-950	Carbon filaments	Fe-based catalysts
	900-1025	Turbo-static carbon/Carbon filaments	Carbon-based catalysts
	675-1100	Graphite carbon/Turbo-static carbon	Co, Ni, Pd, Pt, Cr, Ru, Mo, W catalysts
	1100-1300	Amorphous carbon	Non-catalytic decomposition
Types of deposited carbon and the corresponding temperature range related to catalytic methane decomposition reaction			

So then the catalytic methane decomposition developed, and in this case, the temperature requirement can be reduced from 1200 degrees centigrade to 500 degrees centigrade and different types of catalyst have been tested as shown here using nickel based, iron based, carbon-based catalyst and then these are some other catalyst and this is your say non-catalytic decomposition. So when we are not using any catalyst, our requirement is 1100-1300 degrees centigrade.

Whereas we are using the catalyst, the temperature requirement is decreasing and ultimately we are able to get the 500-700 degrees centigrade by using nickel-based catalyst. So that is the advantage of the use of the catalyst, and when we use these different catalysts, the type of carbon which is deposited on the catalyst bed is also different, we see here. So for this nickel-

based catalyst, we can get carbon filaments, for Fe-based catalyst we can get carbon filaments; for carbon-based turbo static carbon and carbon filaments, and here graphite carbon and turbo static carbon we can get.

So, different types of carbon can be formed by this way. Obviously, the transition metals have been used for the production of catalyst and nickel-based catalyst is having more capacity to get the cracking at lower temperature.

(Refer Slide Time: 21:35)

Plasma cracking of methane

- Methane cracking under high energy plasma has become an attractive method to produce hydrogen in a single stage, non-catalytic operation.
- Plasma is a ionized gas which can be generated by the several means such as high voltage electric discharge, flames, shocks etc.
- Based on the method applied to generate plasma and the temperature difference between electrons and heavy particles, plasma technology is classified in to two categories; thermal and non-thermal (electro-chemical plasma).
- The thermal plasma process uses an electrical power of ~1 kW and the reactor attains a temperature of approximately 5,000–10,000°C. Thus, this process is a highly energy-consuming process.
- Non-thermal plasma can catalyse the decomposition reaction at rather low temperature (350°C–750°C) through the generation of active species of fast electrons.

Then plasma cracking of methane, so as you know that plasma is an ionized gas and it can be produced at high temperature and this can be used for the cracking of the methane also. So based on the method applied to generate plasma and the temperature difference between the electrons and heavy particles, the plasma technology is classified into 2 types, one is your high temperature thermal and non-thermal, one is thermal by using high temperature and another is your non-thermal, the electrochemical plasma.

So 2 types of plasma we can produce. So out of these 2 if you use a thermal plasma, the temperature will be very high and uses an electrical power of around 1 kilowatt and the reactor attains temperature around 5000-10,000 degrees centigrade, so use of this technology is not possible for this case. So, the non-thermal electrochemical plasma can be produced and used for the conversion of this methane to hydrogen, and in this case, the temperature is around 350-750 degrees centigrade.

(Refer Slide Time: 22:54)

Plasma cracking of methane

The benefits of using plasma arc in methane cracking are fourfold:

- high thermal efficiency (>80%),
- high purity of hydrogen (98 vol.%),
- simultaneous production of valuable by-product carbon, and
- very low CO₂ emissions.

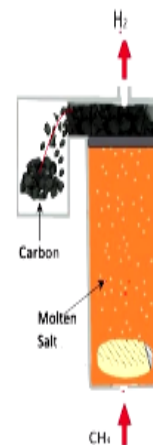
□ However, the consumption of relatively high electrical energy in plasma processes can make their applicability restricted to large-scale processes.

This plasma cracking of the methane has some advantage also. It has high thermal efficiency, it has high purity of hydrogen, simultaneous production of valuable byproduct carbon, and very low carbon dioxide emissions. So these are the advantage of this, but the consumption of relatively high electric energy in plasma process can make this apparently uneconomical and make their applicability restricted to large-scale application.

(Refer Slide Time: 23:21)

Molten salt media cracking of methane

- The cracking of methane takes place in a bubble column reactor containing molten salt (NaCl, NaF) or molten metal (Iron, tin)
- Advantageous in removing the carbon particles from the reaction zone due to the differences in densities of carbon black and molten media.
- This technology offers the opportunity to operate the hydrogen production reactor in continuous mode; deactivating of catalyst or plugging of reactor tubes due to carbon deposition can be avoided.
- The compatibility between hydrogen, carbon, and molten media, and the stability of molten media at various temperature ranges of the process might be the main source of difficulties for this process.
- Presently, this technology is under development.



Then, molten salt media cracking of the methane. So people tried to get the high temperature of a molten salt media to crack the methane, and when the carbon is produced by the cracking of methane, that carbon is also lighter than the density of the molten salt, so it can be go up and can be easily separated. So here, we see methane is coming from the bottom. So this is our molten salt, this is where the reaction takes place, gas and liquid phase reaction, then carbon is formed and hydrogen is formed.

So hydrogen as a gas it is going out and carbon as a solid it is floated as the density of carbon is lesser than the density of the salt media. So carbon will go up and it will be separated from the top. So this is a mechanism through which carbon is separated from the salt media. This technology offers the opportunity to operate the hydrogen production reactor in continuous mode and deactivating of catalyst is eliminated there, there is no chance of the deactivating of catalyst.

The compatibility between hydrogen, carbon, and molten media and the stability of molten media at various temperature ranges will be the major challenge for this process and presently this technology is under development. So we have discussed different types of processes which can be used for the production of hydrogen from the methane or the natural gas, and once we can get hydrogen that can be considered as a green fuel, so up to this in this class. Thank you very much for your patience.