

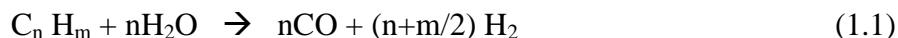
INTRODUCTION

1. Introduction:

Steam reforming is conversion of a carbonaceous material, primarily into a mixture of carbon monoxide and hydrogen (commonly known as syn-gas), using a suitable catalyst and steam as another reactant in a high temperature reactor known as reformer (Holladay et al; 2009). Mixture of carbon monoxide and hydrogen thus obtained is used as feed-stock for producing various gaseous and liquid and chemicals or for obtaining hydrogen through shift reaction. In the early days coal was the main carbonaceous feed-stock for producing syn-gas. Coal was gradually replaced by methane and naphtha obtained from petroleum processing. Currently methane is the most common feed-stock for obtaining hydrogen on large scale for energetic and non-energetic applications. Steam-methane reforming has the lowest capital cost amongst the hydrogen production technologies and efficiency in the range of 60-80% (Coelho et al; 2010). Several large and medium reformers are operating globally to produce hydrogen and syn-gas. In recent years, development of smaller reformer units to produce H₂ for fuel cells has gained momentum (Holladay et al; 2009). In reformers, a carbonaceous material reacts with air or oxygen and steam at high temperatures and produces raw gases, consisting of H₂ and CO along with CO₂, CH₄ and steam. Additionally, carbonyl sulphide, hydrogen sulphide and other impurities are produced (Langer et al; 2007). These impurities are removed by an elaborate purification process for obtaining a pure mixture of CO + H₂ suitable for hydrogen recovery and producing other products.

1.1 Steam Reforming of Carbonaceous Substances:

The general reaction for steam reforming of a hydrocarbon into a mixture of H₂ and CO (syn-gas) is as follows:



This reaction is endothermic ($\Delta H^0 > 0$), therefore, the reactors are limited by heat transfer requirements rather than the reaction kinetics. Hence, these reactors are designed in a manner which promote the heat exchange and are heavy and large. Normally, the further process is conversion of CO in the water gas shift reaction (see eqn1.12) to CO₂ utilizing the steam. Steam reforming of most hydrocarbons occurs at elevated temperatures ($> 800^{\circ}\text{C}$) and specifically over the appropriate catalysts. Most of the CO is converted to H₂ via the water gas shift reaction (eqn1.12) unless there is a requirement for a mixture of CO/H₂ by the customer, .No significant coking is reported on the active part of the catalysts, even at the high reaction severities (Armor et al; 1999). This exothermic reaction requires no high temperature of the gases as they exit the primary reformer. Therefore, the temperature of the process stream should be reduced by generating steam. Typical catalysts operate with low temperature (~30% as CuO, ~33% as ZnO, and ~33% as alumina for inlet temperatures of ~200⁰C or high temperature (90-95% magnetite iron oxide, stabilized with 5-10% chromia for inlet operation temperatures of 340-360⁰C) (Armor et al; 1999).

1.1.1 Steam Reforming of Natural Gas (Methane):

Catalytic steam reforming (CSR) of hydrocarbons (Figure 1.1) was identified in the early 19th century (Petersen et al; 1998). It has been developed by several companies. In recent years, it is one of the principal processes used for the production of H₂ and syn-gas (Meusinger et al; 1998). Compared to partial oxidation and coal gasification methods playing a vital role in H₂ production, CSR is relatively cheaper and energy efficient (Driel et al; 1998).

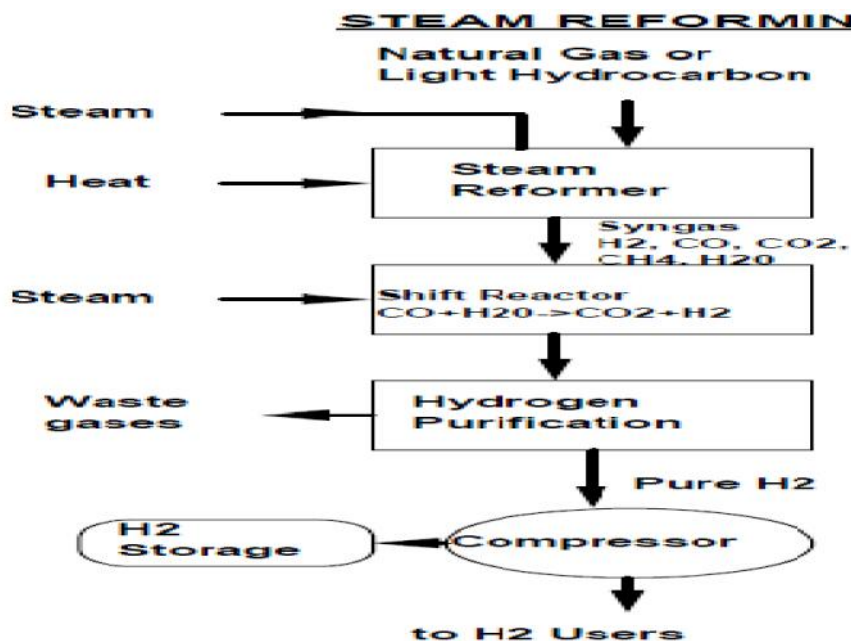
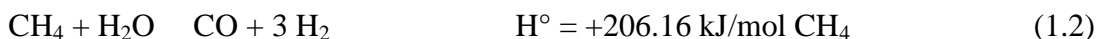


Figure 1.1 Schematic showing the reactions and pathways in steam reforming of a hydrocarbon

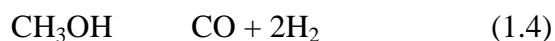
The auto-thermic conversion of CH_4 to H_2 occurs at 850°C in which the process of partial oxidation is combined with catalytic steam reforming. An improved performance was observed for the single-bed configurations in contrast to two-bed systems. It might be attributed to the improved heat-exchange possibilities in the single-bed reactor (Petersen et al; 1998). Hydrocarbon feed (CH_4 or liquid fuel) is reacted with both steam and air to produce a H_2 -rich gas. In the case of CH_4 , both steam reforming and partial oxidation take place, which is given below (Joan et al; 2001).



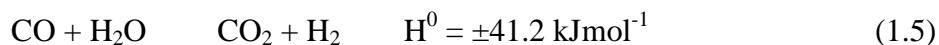
There have been several studies on methane reforming regarding to the effects of nickel and cobalt (Nagai et al; 2006), catalyst incorporated in the carbide layer and $\text{Au/Ni/MgAl}_2\text{O}_4$ (Mayorga et al; 1997), $\text{B/Ni/Al}_2\text{O}_3$ (Xu et al; 2009), $\text{Mo/Ni/Al}_2\text{O}_3$ (Maluf et al; 2009).

1.1.2 Reforming of Methanol:

Alcohol, particularly methanol, is a convenient storage system for hydrogen (Carrette et al; 2001). The alcohol and has little constraints regarding safety than gaseous H₂ and can be easily transported using the existing infrastructure. Transformation of the alcohol into gaseous mixtures enriched with H₂ can be achieved using several reactions such as partial oxidation (PO) (Hohlein et al; 1996), steam reforming (SR) (Hohn et al; 2009) and oxidative steam reforming (OSR) (Wild et al; 2000). Catalytic reforming of the methanol is a well-established technology, which is mainly used for small H₂ production. It is promising technology for the portable electronic devices, for the decentralized refuelling units for H₂-based automobiles or as on-board generation systems for H₂-based internal combustion engines or PEM fuel cells (Wild et al; 2000). Methanol is considered as a suitable source of H₂ due its low cost, safe handling and high storage density. Moreover, renewable and fossil fuels can be used for its production. The steam reforming (SRM) of methanol occurs in two stages by two different pathways. The first one involves the decomposition of methanol into CO and H₂ (eqn. 1.4):



This is followed by the water gas shift reaction (eqn. 1.5):



The second mechanism for methanol steam reforming consists of the reaction of water and methanol to give CO₂ and hydrogen (eqn. 1.6):



This reaction can be followed by a reverse shift reaction to establish the thermodynamic equilibrium (eqn. 1.7):



The main advantage of this process is the generation of low amount of CO. It is important because CO acts as a poison for the fuel cells. The accepted CO level is between 10 and 100 ppm (Nielsen et al; 2001). However, the main disadvantage of SMR is its endo-thermicity, which requires external heating. It makes short start-up and makes difficult to achieve the fast transient behaviour. The schematic for a conventional SRM process is shown in Figure. 1.2.

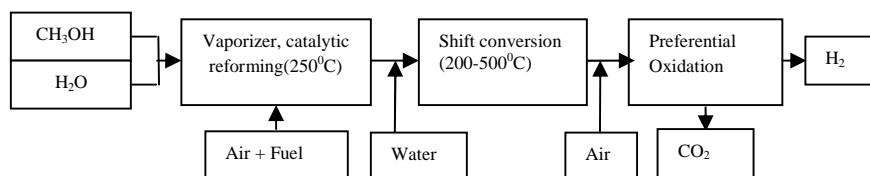


Figure 1.2 Flow-sheet for a conventional SRM process

For the methanol steam reforming process, copper-based catalysts (CuMn_2O_4 and CuCr_2O_4 spinels or CuO/CeO_2 and CuO/ZnO) exhibit a high activity and selectivity. A small amount of Cr_2O_3 in the skeletal copper catalysts considerably enhances the copper surface area, and therefore promoted the activities for SRM (Huang et al; 2004). Supported Cu-Cr on yttria-doped ceria (Y-Ce)/ Al_2O_3 showed a considerable enhancement in the catalyst activity for the SRM at reaction temperatures of 200-250 $^\circ\text{C}$. The concentration of CO in the product was below 0.1% (Liu et al; 2003). This methanol reforming combines the steam reforming reaction with the partial oxidation of methanol in an adiabatic system. A spherical reactor system was observed to be the most attractive configuration for the autothermal process. In this configuration, an inner oxidation catalyst bed is joined with an outer sphere for steam reforming, which promotes internal heat exchange and maximizes the product selectivity (Ma et al; 1996). The hot spot methanol processor uses a combination of POX and SR whereby the relative contributions of the two reactions can be tuned as per the necessity (Edwards et al; 1998).

1.1.3 Reforming of Ethanol:

Reforming of ethanol is a potential way to produce renewable H₂ (Bion et al; 2010). Renewable bio-ethanol can be easily produced using several biomass sources, such as plants, waste from agro-industries (molasses, corn, bole, etc.) or forest residue (Ioannides et al; 2000). Moreover, a bioethanol-to-H₂ system has the major advantage of being CO₂ neutral (Casanovas et al; 2010). The equations 1.8, 1.9 and 1.10 respectively illustrate the steam reforming, partial oxidation and auto-thermal reforming of ethanol.

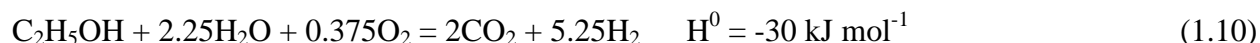
Steam reforming process is endothermic which requires energy input to initiate reactions (Fatsikostas et al; 2001):



Alternatively, hydrogen can be obtained by partial oxidation of ethanol at a temperature of about 500⁰C according to the following reaction (Salge et al; 2005):



However, H₂selectivity of partial oxidation of ethanol is generally low. In order to enhance the H₂ production, auto thermal reforming can be used. Auto thermal reforming, which is alternatively called as oxidative steam reforming, combines the ethanol oxidation and steam reforming. The total reaction for auto thermal reforming of ethanol can be written as (Chen et al; 2009; Hamamre et al; 2010).

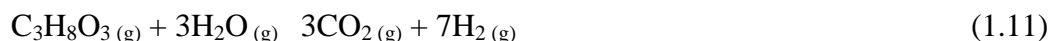


This reaction indicates that the auto thermal reforming attains a thermally sustained operation in addition to maximizing H₂production. Dolgykh et al. (2005) observed the catalytic activity of copper chromite in ethanol steam reforming at low temperatures using mixture of C₂H₅OH (12 wt.%) and water. They observed that appreciable hydrogen production starts at the temperatures

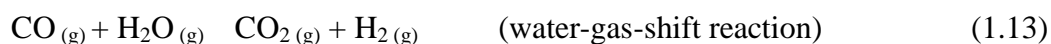
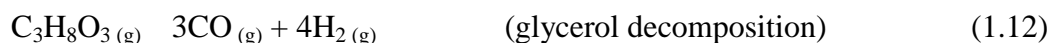
above 300⁰C without catalyst and reaches to a H₂yield 0.3g₂(kg cat.)⁻¹(h)⁻¹ at 400⁰C Use of catalysts allows 9-25 g H₂ (kg cat.)⁻¹ (h)⁻¹at 250-300⁰C.

1.1.4 Reforming of Glycerol:

Glycerol (1, 2, 3-propanetriol), a carbohydrate (C_xH_yO_z), is produced as by product during biodiesel synthesis from vegetable oil and bio-ethanol (Othmer et al; 2004). Though, it is primarily used in various industries such as pharmaceuticals, cosmetics, and food and beverages industries (Bondioli et al; 2003); however, there is also a glycerol glut in the global market. Therefore, its disposal by the emerging biodiesel industry is posing a new challenge for making it more competitive than conventional fossil diesel (Johnson et al; 2007). For this reason, efforts have been directed towards adding value to glycerol. For example, It is being used as a precursor for important chemical feedstock (Brandner et al; 2009) and as potential source of renewable energy (Luo et al; 2008). Specifically, the steam reforming of glycerol to syngas appears a viable option as syn-gas is a major commodity for various petrochemical processing operations. Glycerol steam reforming reaction can be given by (eq. 1.11).



This is essentially a combination of eqn. 1.12 and 1.13.



Luo et al. (2008) performed the pioneering studies on the aqueous phase reforming (APR) of glycerol to H₂, CO, and CO₂. It was typically carried out at high pressure and mild reaction temperatures between 503 and 553K (Shabaker et al; 2004) using Pt, Ru, Re, Pd, and Rh as catalysts (Luo et al; 2008). However, eq. 1.11 and 1.12 suggest that gas phase steam reforming is thermodynamically favorable at low pressure with moderate temperatures (773-873K). Here, the conventional hydrocarbon steam reforming catalysts such as Ni and Co may be used (Lehnert et

al; 2008). Table 1.1 summarizes the catalysts and operating conditions used during reforming of hydrocarbons and alcohols and glycerol.

Table: 1.1 Reforming of fossil fuels & alcohols

S.N.	Type of fuels	Catalyst	Operating condition	Remarks	Ref.
1	Coal		The mixing of pulverized coal with an oxidant, heated to about 1800 ⁰ C	The percentage of carbon dioxide emissions to atmosphere can be reduced is about 90% by implementing the concept of carbon capture and storage in pulverized coal plant	(Fayaz et al; 2012)
			Energy density of primary resource P (MW/km ²)- 750, H ₂ production rate (ton/d)- 150	59% for coal Gasification, 110 kg CO ₂ /GJ in the case of coal, Conversion efficiency to hydrogen- 0.59	(Ewan et al; 2005)
2	Methane, Naphtha	Nickel	T- 700-1100 °C High pressure	Conversion efficiency 65-75%	(Veziroglu et al; 2008)
		Noble metals such as Ni, Co, Ru, Rh, Pd, Pt	T- 600-1100 °C High pressure	Catalytic activity of metal catalysts supported on Al ₂ O ₃ -MgO was reported to follow the order: Ru > Rh > Ir > Ni > Pt	(Nielsen et al; 1993)
		Au/Ni/MgAl ₂ O ₄	T-800-1000 ⁰ C P-14-28bar	CH ₄ to H ₂ Conversion 80-85%	(Mayorga et al; 1997)

3		Au-Ni/Al ₂ O ₃	Molar ratio (M/Ni)- 0.038 Ni-8%	CH ₄ to H ₂ Conversion 70-85%	(Lazar et al; 2011; Lazar et al; 2009 Dan et al; 2012)	
		B/Ni/Al ₂ O ₃	Molar ratio (M/Ni)- 0.18,0.36, Ni- 15%	CH ₄ to H ₂ Conversion 60-80%, 55 kg CO ₂ /GJ in the case of natural gas	(Xu et al; 2009)	
		Mo/Ni/Al ₂ O ₃	Molar ratio (M/Ni)- 0.0005-.002, Ni- 60%	CH ₄ to H ₂ Conversion 70-85%	(Maluf et al; 2009)	
	Oxygenat ed compoun ds	Methanol	Au/N i/Al LDHs	Molar ratio (M/Ni)- 0.011 Ni-79.5%	CH ₄ to H ₂ Conversion 60-75%	(Qi et al; 2005)
			Cu- Ni/Al ₂ O ₃	Molar ratio (M/Ni)- 0.40–2.16 Ni-7%	CH ₄ to H ₂ Conversion 50-70%	(Rogatis et al; 2008)
		Ethanol	Copp er Chro mites	T-300°C High pressure	Hydrogen Productivity 9- 25g ₂ (kg cat.) ⁻¹ (h) ⁻¹ at 250-300 ⁰ C.	(Dolgykh et al; 2005)
			1 mass % Ru/C eO ₂	T-300-500°C High pressure	H ₂ selectivity- 57% Ethanol conversion->90 %	(Erdohelyi et al; 2006)
	Ni/Al ₂ O ₃	6:1 molar ratio of H ₂ O:ethanol and a total liquid flow rate of 2 mL/h. T- 500 to 950 K cataly st prom oted	The reaction data on Ni/Al ₂ O ₃ catalyst suggested that at low temperatures (650 K) the decomposition of ethanol occurs via the	(Liberatori et al; 2007)		

			with Ag and La		intermediate acetaldehyde leading to formation of equimolar mixtures of CH ₄ and CO	
		Glycol	Ni/Ce O ₂	T- 600 ⁰ C, Initial water to-glycerol molar ratio- 12	H ₂ Selectivity-74.7 (%),Glycerol Conversion -100 (%)	(Adhikari et al; 2008)
			Ni/Ti O ₂	T- 600 ⁰ C, Initial water to-glycerol molar ratio- 12	H ₂ Selectivity-28.3 (%),Glycerol Conversion - 60(%)	(Adhikari et al; 2008)
			Ni/M gO	T- 650 ⁰ C, Initial water to-glycerol molar ratio- 6	H ₂ Selectivity-65.6 (%),Glycerol Conversion - 100(%)	(Adhikari et al; 2008)
			Ni/Al ₂ O ₃ /Z rO ₂	T- 600 ⁰ C, Initial water to-glycerol molar ratio- 7	H ₂ Selectivity-71 (%),Glycerol Conversion -100 (%)	(Iriundo et al; 2008)
			Pt/Al ₂ O ₃	T- 250 ⁰ C, Initial water-to-glycerol molar ratio- 46	H ₂ Selectivity-85 (%),Glycerol Conversion -45(%)	(Lehnert et al; 2008)
			Ru/Al ₂ O ₃	T- 900 ⁰ C, Initial water-to-glycerol molar ratio- 6	H ₂ Selectivity-58 (%),Glycerol Conversion -42(%)	(Adhikari et al; 2007)

1.2. Water Gas Shift Reaction:

The water-gas-shift (WGS) (reaction, eq. (1.14) and figure 1.3), is an old industrial process, where water as steam is mixed with reformer gas (CO+H₂) to get more H₂ with an oxidation of CO to CO₂. This catalytic reaction was discovered by Felice Fontana in the year 1780. The WGS reaction is reversible and exothermic ($H_o = -41.2$ kJ/mol) (Farrauto et al; 2003). This reaction is thermodynamically unfavorable at elevated temperatures due to its moderate exothermicity, and

is therefore, carried out in the presence of catalyst at moderate temperatures. Significant researches have been carried out to improve the activity, stability and selectivity of catalyst (Bretado et al; 2003). A schematic representation of the process and chemical reaction is given in Figure. 1.3. WGS occurs in two stages, high temperature shift (HTS) and low temperature shift (LTS):

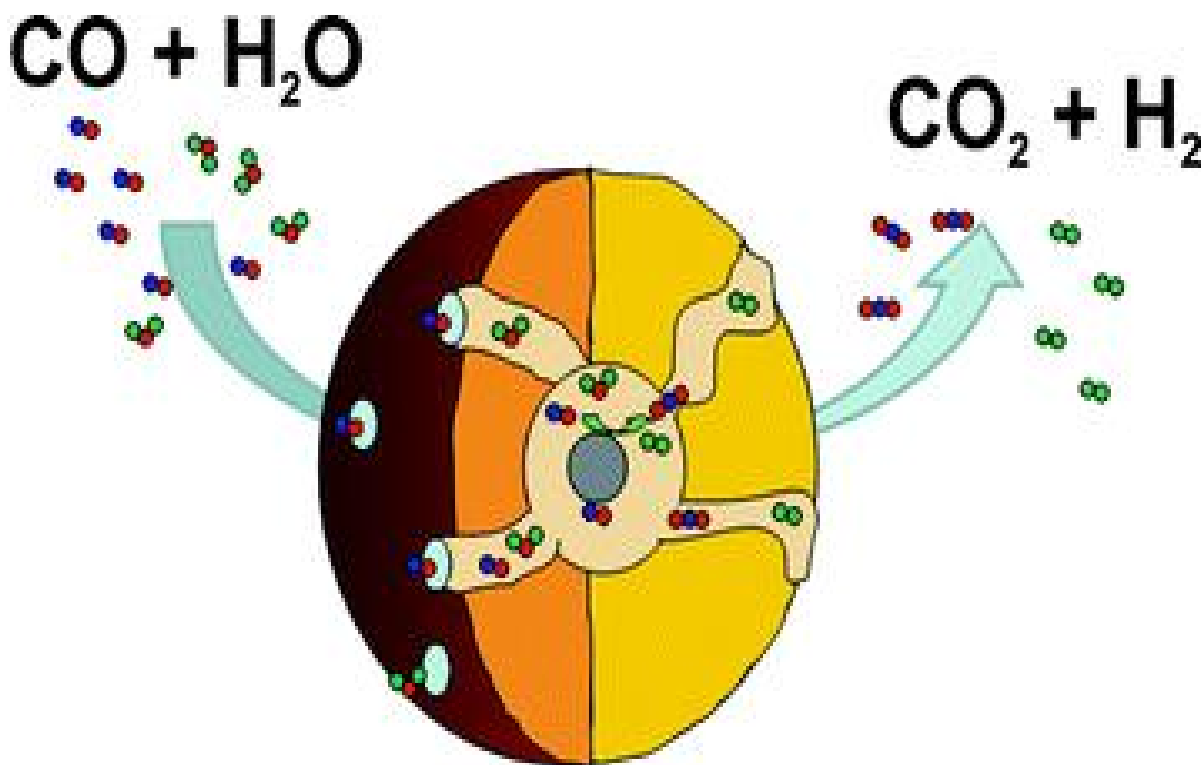
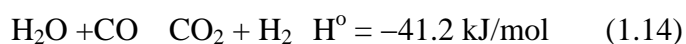


Figure 1.3 Water Gas Shift Reactions

For carrying out water gas shift reactions (WGSRs) Fe-Cr or Cu-Zn-based catalysts are employed (Chen et al; 2010; Chen et al; 2008). High temperature catalyst (oxides of Fe and Cr) at 400-500°C reduces CO concentration to around 2-5%. Low temperature catalyst comprising Cu, Zn oxide and alumina is normally used at 200-400°C to reduce the CO concentration to 1%.

Interests in the use of nanomaterials as a catalyst has increased and have been used for water gas shift reaction also (Tang et al; 2012). In recent past efforts have been made by several researchers to come out with more active catalysts for improving the conversion and several catalysts have been report with encouraging results. For example the WGS activity of Au/CeO₂/Al₂O₃ catalyst was found to be significantly enhanced by the addition of Fe, Cu and Zn to the ceria support and the improved catalytic activity was attributed to the enhanced redox properties and structural promotion (Gibbons et al; 2014). Recently, palladium/copper/ceria electrospun fibers (Pd/Cu= 2/10 wt. %) were investigated and these studies showed that the transition metal incorporated in the ceria lattice facilitated the reduction of energy barriers for oxygen vacancy formation in the lattice and thereby promoted H₂O splitting on the ceria surface (Gibbons et al; 2014). More extensive review of the relevant literature is given in the next section (chapter 2).

In recent years, developing new applications for the powder, nanoparticles and nanofibers have gained momentum. Electrospun nanofibers provide an attractive class of solid supports for the catalysts due to their large surface areas and high porosities. Surface area is the dominant factor which decides the degree of catalysis and its efficiency. The mats of electrospun nanofibers such as CeO₂, Pt/ CeO₂, TiO₂, SnO₂, and ZrO₂, serve as robust substrates for the loading of noble-metal nanostructures for various catalytic applications (Souza et al; 2007; Yang et al; 2007). In the present work, we have made an attempt to synthesize electrospun nanofibers of copper loaded ceria for its possible use as catalyst for the water gas shift reaction.