DECLARATION

I hereby declare that the work, which is being presented in this dissertation entitled "**Reforming of Propane: Thermodynamic Analysis**" in partial fulfillment of the requirements for the award of the degree of Integrated Dual Degree (Bachelor of Technology & Master of Technology) in Chemical Engineering with Specialization in "Hydrocarbon Engineering", submitted in the department of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during the period from May 2013 to June 2014 under the supervision of **Dr.(Mrs.) Shashi**, Associate Professor, Department Of Chemical Engineering, Indian Institute of Technology Roorkee, Roorkee, India.

The matter presented in this report has not been submitted by me for the award of any other degree of this or any other institute

Date:

Place: IIT Roorkee   **Sandeep Kumar**

CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

The thermodynamic analysis of propane steam reforming (SRP) with and without H_2 or CO_2 removal, dry reforming (DRP) and oxidative steam reforming (OSRP) has been performed to identify suitable reforming process and favourable operating conditions for producing (i) high Yield of H_2 (close to 10) with low content of CO, CH_4 and carbon, (ii) syngas with H_2/CO ratio in the range 1-3. The results indicates that SRP with H_2 removal is most efficient reforming process to produce high H_2 yield of 9.93 moles with very low content CO, CH_4 and carbon at relatively low temperature of 750K, WPR=12, P=1atm, 99% H_2 removal and complete conversion of propane. Dry reforming is not suitable for high yield of H_2 because it produce maximum 4 mole of H_2 per mole of propane. OSRP can produce H_2 comparable to SRP only at high temperature, high WPR and low OPR. Molar H_2/CO ratio in syngas in the range of 1:3 are found at T≥1000K, WPR≤6 in SRP, at T≥900K, f≥0.4 in SRP with H_2 removal, and at T≥1000K, WPR≤6, OPR≥0.2 in OSRP. OSRP can produce high amount of syngas at this condition. SRP with fractional removal of H_2 can produce the syngas in the desired ratio at the above mentioned condition but at the expense of amount of syngas. Molar H_2/CO ratio in syngas in the range of 1:3 by dry reforming of propane could be produced at many different combination of temperature and CPR.

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NOMENCLATURE

a_{JI} Number of $j-$type atoms in component i

b_j Number of j-type atoms in feed

f_i° Standard state fugacity of component i

$\widehat{f_i}$ Fugacity of component i

ΔG_{fi}° Standard Gibbs function of formation of component i

G Total Gibbs free energy

G_i^o Partial molar Gibbs free energy at standard state

K_y Product of equilibrium constant in terms of composition

n_i Number of moles of the ith component in the system

P Pressure of the system

S Entropy of the system

T temperature of the system

V Volume of the system

Greek Symbols

$\widehat{\phi}_i$ fugacity coefficient of component i

μ_i chemical potential of the component i

Abbreviations

ATR   Autothermal Reforming

CPOx   Catalytic Partial Oxidation

CPR CO_2 to propane feed ratio

DRP   Dry reforming of propane

OPR   Oxygen to propane feed ratio

OSRP   Oxidative reforming of propane

POx   Partial Oxidation

SRP   Steam reforming of propane

WGS   Water gas shift reaction

WPR   Water to propane feed ratio

CHAPTER 1

INTRODUCTION

Energy is very important for our life. It is used in the production of food, transportation, power communication, heating and cooling and for many other purposes. In recent years people are gaining energy easily due to infrastructure development. Hence the energy requirement of the world has been increasing over the past few years at an average annual rate of 2.6% and 1.8% in 2012 [1]. The most widely used sources of energy are the fossil fuels including natural gas, coal, crude oil and crude oil based products. As energy requirements are increasing the fossil fuel consumption is also increasing proportionally.

Higher consumption of fossil fuels carries severe environmental, social and health costs. The is because fossil fuels burn with emission of pollutants like CO_x; SO_x; NO_x; C_xH_x, ash, and other compounds [2]. Also, it's a fairly known fact that our reserves of fossil fuels are depleting soon. Many had predicted the peak oil curve as soon as the start of 21st century (albeit there are no consolidated studies and assertion of the fact). Experts are of the opinion that technology might not keep pace with the growing demand to extract fossil fuels from more obscure and unconventional sources and we could witness the dearth of energy. Prices of fuels are poised to rise even more and further imbalance between the supply and demand equations is going to exacerbate the inequality in demographic term and between the nations as well.

These problems i.e. high rate of fossil fuel consumption, coupled with environmental issue and diminishing reserves of fossil fuels drive us to search for more cleaner and efficient source of energy [3]. Hydrogen is the best alternative as it burns without any emission of pollutant except water [4] and it can also be used in fuel cells [5].

1.1 HYDROGEN AND ITS USES

At normal temperature and pressure conditions hydrogen is a non-toxic gas and have no colour, odour, and taste. It is highly combustible, non-metallic and consists of two molecules with the molecular formula H_2.

Hydrogen occurs in nature with other elements, like with oxygen in water, with carbon as hydrocarbon and in fossil fuels. When it split from other elements, it become a

clean fuel and for this a process require another source of energy. Hence hydrogen is not an energy source rather it is an intermediate medium to store and carry energy. And as other energy carrier it must be produced from primary energy source. As electricity is energy carrier which does not impact on environment, hydrogen is also an energy carrier with the same benefit [6].

Its heat of combustion is 141.8 MJ/kg, while for natural gas it depends on the source and quality but taking the higher heating value for its main constituent methane we can take a value of approximately 55.4 MJ/kg [7]. The value for coal and liquid fuels is even lower. This shows that a plethora of energy is available in hydrogen fuel.

Hydrogen is used in the following:

- Hydrogen is used as a fuel. It is having very high heating value and end product is water. So, it is a clean fuel, having no harmful effect on environment.
- Hydrogen is also used in manufacturing of Chemicals like Ammonia, H_2O_2. Ammonia being the essential component for fertilizer production, production of it accounts for near 45% of the total hydrogen used for various purposes [8].
- Hydrogen is also used in Bergius process by which Coal can be converted into Hydrocarbons.
- Hydrogen is used in hydrogenation processes: like in Hydrocracking to produce diesel and gasoline from higher boiling Hydrocarbon molecules, Hydrotreating to remove sulphur and Nitrogen from petroleum products. Hydrogenation of edible oils to remove double bond, which raise the melting point and improve its resistance to rancid oxidation.
- Hydrogen is also used in welding, oxy-acetate is used in general for this purpose, but when higher Temperature is required then hydrogen is used.
- Hydrogen also finds application in steel industries for annealing. Hydrogen is mixed with argon for welding stainless steel.
- Hydrogen is also used as a coolant in electrical generators.

Apart from above applications hydrogen gas is also used as a fuel in bulk quantities for providing energy to space shuttles. Fuel cell technology is fast developing as a potential source to convert chemical energy stored in hydrogen gas into electricity. Great amount of research work is going on in this field with application to provide power in remote areas, hydrogen powered cars etc. Hydrogen is hailed as a fuel of future.

1.2 VARIOUS ROUTES OF HYDROGEN PRODUCTION

Hydrogen can be produce from fossil fuels, biomass and water. Main feedstock for hydrogen production is fossil fuels (>85%) [9].

Hydrogen can be produced from fossil fuels by following methods:

(a) Steam reforming.

(b) Dry reforming.

(c) Oxidative reforming.

(d) Coal gasification.

Hydrogen can be produced from biomass by following methods:

(e) Pyrolysis or gasification

Hydrogen can be produced from water by following methods:

(f) Electrolysis.

(g) Photo electrolysis

In all these above processes, steam reforming is the most widely used process for hydrogen production. Nearly 90% of hydrogen is produced by steam reforming of natural gas or light oil. Out of the above listed processes, nearly 90% of hydrogen is produced by the reactions of natural gas or light oil fractions with steam at high temperatures (steam reforming) [2].

1.2.1 Steam Reforming

Steam reforming is the oldest and most widely used process for industrial reforming. As the name entails steam is added in this type of reforming process. It is a catalytic reaction between Hydrocarbon (mainly lighter hydrocarbon, natural gas, LPG and light Naphtha) and steam at high Temperature. The major reactions involved in the steam reforming are:

Steam Reforming: $\quad C_3H_8 + 3H_2O \rightleftharpoons 3CO + 7H_2 \qquad \Delta H^o_{298K} = 499 kJ/mol \qquad (1.1)$

Water gas Shift: $\quad CO + H_2O \rightleftharpoons H_2 + CO_2 \qquad \Delta H^o_{298K} = -41\ kJ/mol \qquad (1.2)$

Methanation: $\quad CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad \Delta H^o_{298K} = -206\ kJ/mol \qquad (1.3)$
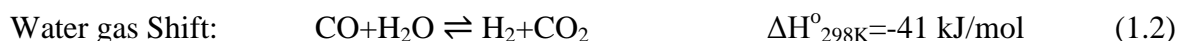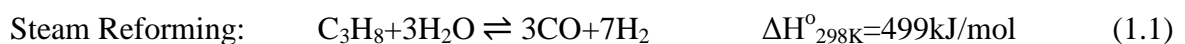
The steam Reforming is usually carried out at around 950K over a Ni/Al_2O_3 catalyst packed into the tubes of a reforming furnace. Since this reaction occurs at high temperature, cracking reactions also take place.

These can be summarized as:

$$C_3H_8 \rightleftharpoons C_2H_4 + CH_4 \qquad \Delta H^o_{298K} = 89 \text{ kJ/mol} \qquad (1.4)$$

$$C_2H_4 \rightleftharpoons 2C + 2H_2 \qquad \Delta H^o_{298K} = -52 \text{ kJ/mol} \qquad (1.5)$$

$$CH_4 \rightleftharpoons 2H_2 + C \qquad \Delta H^o_{298K} = 75 \text{ kJ/mol} \qquad (1.6)$$

Due to this cracking reaction carbon produces and deposit on the catalyst. CO further converted into CO_2 and H_2 through water-gas shift reaction. After this the gas mixture contains CO_2 and hydrogen. CO_2 is removed by different processes, which is discussed later in this report. After CO_2 removal many plants use methanation reaction-the reverse of reforming-to remove the remaining traces of carbon oxides.

The process gas leaving the reformer can be used as a heat source for additional reforming. Reforming catalyst is packed in the tubes of a heat exchanger, and the primary reformer outlet gas flows in the shell. Here the hot gas from the primary reformer mixes with the gas leaving the open-ended catalyst tubes and then flows along the outside of the catalyst tubes.

The temperature in the heat-exchange reformer is lower than that in the primary. The steam/carbon ratio in the heat-exchange reformer can be increased to correct this which affects the reforming equilibrium. This also shifts the reforming heat load to a lower temperature, improving the heat balance.

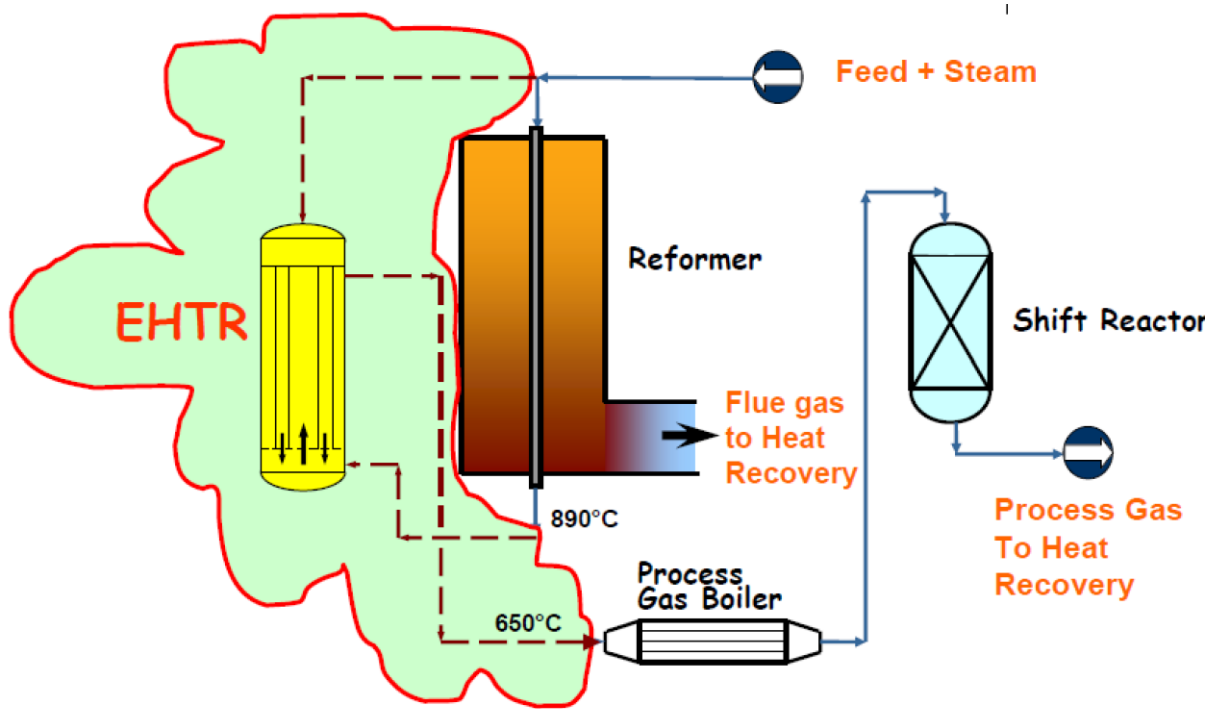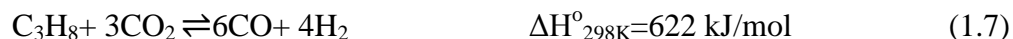The main effect of the heat-exchange reformer is to reduce the fuel demand and steam generation [10].

Fig. 1.1 Heat-exchange reforming[11]

1.2.2 Dry Reforming

The reforming is termed as 'dry' because there is no involvement of any water/steam and steam is replaced by carbon dioxide in the reforming reaction.

$$C_3H_8 + 3CO_2 \rightleftharpoons 6CO + 4H_2 \qquad \Delta H^o_{298K} = 622 \text{ kJ/mol} \qquad (1.7)$$

This reaction is of industrial interest because of the lower H_2/CO ratio in the product gas. The aforesaid reaction has attracted interest as a CO_2 consuming reaction. However literatures have time and again reported that the reforming via the means of carbon dioxide is not feasible in the industry.

The dry reforming of light hydrocarbons (C1 – C4) for the production of syngas has attracted considerable attention because of the advantage of converting two greenhouse gases CO_2 and CH_4 to useful intermediates while simultaneously effecting an emission reduction [14]. Furthermore, both gases are cheaply available as natural gas and biogas from landfill in ratios suitable for the reforming reaction [15, 16]. More importantly, the syngas produced from this dry reforming generally composition has H_2: CO ratio (~1) which is more suitable for downstream conversion in Fischer-Tropsch synthesis, unlike conventional hydrocarbon steam reforming where this product ratio is greater than 3. However ,catalyst coking with attendant deactivation is common to both dry and steam reforming and hence, the development of carbon-tolerant catalysts , the combination oxidation with the reforming reaction, and using a coke gasifying agent are some of the coke control approaches that need to be adopted.

1.2.3 Oxidative Reforming

When oxygen is supplied in conjunction with Hydrocarbon to achieve the reforming reactions, it is termed as the oxidative reforming process. The supplied oxygen can be in the form of pure oxygen or as air. The former requires equipment to produce pure oxygen which is most commonly achieved by liquefaction of air. This method is cost intensive. However, using pure oxygen gives better selectivity and gets rid of the wasted volume of inert gases like nitrogen which make up almost three-fourth of atmosphere. The drawback is additional equipment and capital cost along with cooling costs if liquefaction of air is employed as the method of choice for the production of pure oxygen.

1.2.3.1 Partial Oxidation (POx)

In Partial oxidation (POx), hydrocarbon reacts with oxygen at high temperature to produce hydrogen and other compounds namely CO, CO_2 etc. It is a non-catalytic reaction hence heavier hydrocarbons can also be used as a feedstock, since there is no difficulty of catalyst deactivation with heavy hydrocarbon. Capital cost of partial oxidation is very high hence, in general for light feedstock steam reforming is used and for heavy feedstock Partial oxidation is the only feasible choice.

Partial oxidation of propane over Ni catalysts proceeds via Combustion (1.8), followed by steam (1.1) and dry reforming reactions (1.7).

$$C_3H_8 + 3/2O_2 \rightleftharpoons 3CO + 4H_2 \qquad \Delta H^o_{298K} = -227 kJ/mol \qquad (1.8)$$

1.2.3.2 Catalytic Partial Oxidation (CPOx)

The catalytic partial oxidation uses catalyst for partial oxidation process. Since catalyst is used lower temperature will be required for CPOx than POx. Also, light hydrocarbon should be used as a feedstock for CPOx since it uses a catalyst. Oxygen required is less than the stoichiometric amount to avoid total oxidation of feedstock. When noble metal catalyst like Pt, Pd, Ru, Rh is used hydrocarbon can be converted into syngas within milliseconds. [15] Since in CPOx residence time required is low, conversion rate is high, and selectivity for Hydrocarbon is also high it is a better choice for small scale applications. [16]

Since oxygen is used in the feedstock in POx, so lower steam/carbon ratio is required to prevent coke formation. Since steam requirement is lower hence production of hydrogen will also be lower and more CO will be formed. Hence, POx is desirable where more CO is required like in synthesis gas for chemical production. Since Partial oxidation capital cost is high due to requirement of oxygen production, Hence it is generally used where oxygen is already available. [10].

1.2.3.3 Autothermal Reforming (ATR)

Autothermal reforming combine the partial oxidation and steam reforming i.e exothermic and endothermic reaction. Hence It does not requires external heat and its thermal efficiency is high. Also, its start-up is very rapid which makes it very attractive.

$$C_xH_yO_z + nO_2 + (2x - z - 2n)H_2O \longrightarrow xCO_2 + (2x - z - 2n + \frac{y}{2})H_2 \quad \Delta H^o_{298K} = 0 \ kJ/mol \quad (1.9)$$
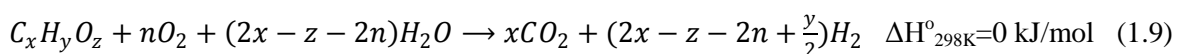
ATR uses group VIII transition metals such as Pt, Rh and Ni as catalysts these catalyst can also be used for steam reforming and catalytic partial oxidation process. ATR can also uses non-noble metal catalysts with perovskite structure ABO3 [17]. Since endothermic steam reforming relies on exothermic Catalytic partial oxidation, hence better heat integration is required for high efficiency.

For low hydrogen production such as in small and medium fuel cell or in other mobile application, Catalytic partial oxidation (POX) and auto-thermal reforming (ATR) are better choice. CPOx is exothermic and ATR is thermo-neutral process which requires adiabatic reactor. While steam reforming is endothermic and requires a complicated and expensive reactor [18].

1.2.4 Coal or Biomass Gasification

Gasification is a thermochemical process which convert solid feedstocks into gaseous products by supplying less O_2 that is needed for complete combustion. Hydrogen production from coal gasification is competitive only when the cost of natural gas remain high. [19].

1.2.5 Electrolysis of Water

When electricity is passed through the water, it breaks up H_2O molecule into H_2 and O_2.

$$2H_2O(l) + \text{Electrical energy} \rightarrow 2H_2(g) + O_2(g) \qquad (1.9)$$
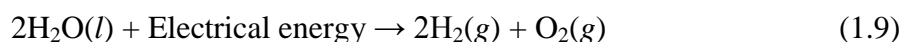
Electrolytic process produces high-purity H_2 and consists of passing direct current (DC) through an aqueous solution of alkali. NaOH or other electrolyte is added to make water conductive. This hydrogen gas is 99.7% pure and is suitable even for hydrogenating edible oils.

1.2.6 Photoelectrolysis of Water

Solar energy can be used to split the molecule; being renewable in nature it is environmentally friendly. As major part of solar spectrum consists of visible light thus it is essential to find a process so that visible light can be used to decompose molecule photo catalytically.

1.3 PURIFICATION OF HYDROGEN STREAMS

There are many processes to purify hydrogen stream. Depending upon the composition of gaseous stream, pressure and flow rate, different method for purification is used.

1.3.1 Wet Scrubbing

After shift reactor, which convert CO into CO_2. Wet scrubbing systems remove acid gases such as H_2S or CO_2 using potassium carbonate or amine systems. In general Wet scrubbing has been replaced by Pressure swing adsorption (PSA) units, since wet scrubbing only remove acid gases. It does not remove light gases such as methane, hence product purity is not very high. It is used only when CO_2 is to be recovered or when hydrogen rich gaseous stream is to be desulfurized to use as a fuel gas.

1.3.2 Pressure Swing Adsorption (PSA)

PSA unit utilizes the adsorption process to purify the hydrogen stream. It uses more than one bed of solid adsorbents which selectively adsorbs the impurity and produces a very pure hydrogen stream as a product and a tail gas stream which contains impurities. After adsorption process bed gets saturated and hence it regenerated by depressuring and purging. Part of the hydrogen typically 10-20% is lost into the tail gas. The cost of the system is relatively insensitive to capacity. This makes PSA more economic at larger capacities, while membrane units tend to be favoured for smaller plants. PSA is generally the first choice for steam reforming plants because of its combination of high purity, moderate cost, and ease of integration into the hydrogen plant.

1.3.2 Membrane Separation

Membrane separation units utilizes the difference in rates of diffusion through membranes. In general hydrogen diffuse faster through membrane and become permeate while impurities diffuse slower and become retentate. The advantage of membrane separation process is that it does not contain moving parts and its reliability is very high. The main disadvantage is that aromatics or other such component attack on the membrane and plug it. Membrane is usually more cost effective for lower capacities. For high capacity more membrane modules has to be added which increases the cost.

1.3.3 Cryogenic Separation

In cryogenic separation process gaseous stream is cooled and condensed into liquid and then separation is done by flashing or distillation process. Cryogenic units tend to be more expensive than other processes, especially in smaller sizes. This is so because of the feed pre-treatment required to remove compounds which would freeze, such as water or CO_2. They are therefore used in very large sizes.

1.4 MEMBRANE REACTOR TO PRODUCE PURE H_2

Reforming reaction conventionally takes place in the reactor tubes inside a furnace. Steam reforming process is endothermic in nature, thus to get substantial amount of conversion it has to be operated at an elevated temperature (900K-1000K). Being endothermic in nature process is thermodynamically constrained. At elevated temperature following problems are faced:

- High coke formation and subsequent blockage of tubes.
- High pressure inside the tubes due to reduced area.
- Formation of hot spots inside the reactor due to high temperature.
- Chance of material failure (rapture) at such high thermal stresses.

It is clearly evident from above that high operating temperature poses challenges in the operation of reforming. If thermodynamic constraint can be overcome, then at lower temperature substantial amount of H_2 can be produced. This concept gives the basic philosophy of separation integrated reactors.

If a separation mechanism can be integrated with the reactor which separates out product as soon as they are formed then equilibrium can be shifted forward. This in turn can increase the rate of formation of the desired product and hence can enhance the yield. Thus equilibrium constraint is overcome and system can be operated at a relatively lower temperature.

1.5 MEMBRANE REACTOR

Membrane reactor is an integrated unit of separation section and a reaction section. To separate the product continuously a selective membrane is integrated with the reactor side. It consists of two concentric tubes. One side is the reactor side in which catalyst is filled and reactant gas enters into it and reacts to produce the product. Other side is the permeate side through which sweep gas flows to sweep away the formed product.
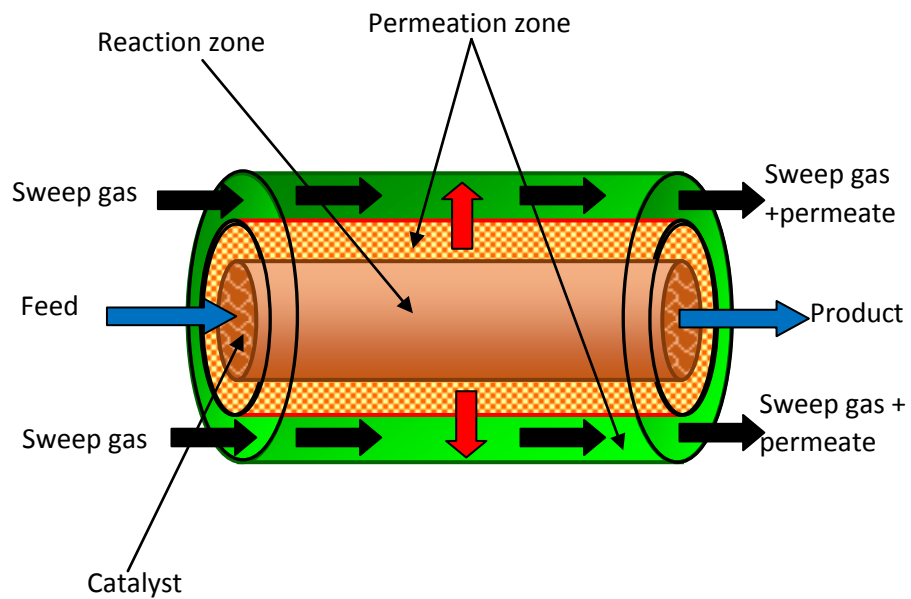
Fig. 1.2 Catalytic membrane reactor

Between the interface of the reaction and permeation side a membrane is integrated through which only a specific component can permeate selectively. In our case a hydrogen perm selective membrane is integrated which selectively allows only hydrogen to pass through it. Based on the reaction and permeate sides selection following two configurations are possible.

As reported in many experimental studies, higher conversion is obtained in membrane reactors as compared to traditional reactors. Literature survey shows that 91-96% conversion is obtained in Membrane Reactors at 450-600°C as compared to 800-950°C for Traditional reactors [20].

1.6 OBJECTIVES

To perform thermodynamic analysis for the production of H_2 and syngas with low amount of undesired product by following reforming processes.

- Steam reforming of propane (SRP)
- Dry reforming of propane (DRP)
- Oxidative reforming of propane (OSRP)
- Steam reforming of propane with fractional removal of H_2
- Steam reforming of propane with fractional removal of CO_2
- Dry reforming of propane with fractional removal of H_2

CHAPTER 2

LITERATURE REVIEW

In the past 1-2 decades there has been a great interest in research in the use of membrane technology for reactors. As hydrogen is considered as the future fuel, assiduous research work is going on in the field of reforming of hydrocarbons in the membrane reactors. Although large amount of exhaustive research work is available, literature pertinent to the topic is presented here in two parts covering experimental studies first and then theoretical modeling and simulation studies.

2.1 PROPANE AS A FEEDSTOCK

Schadel et al. (2009) [21] studied steam reforming of first four hydrocarbon i.e. methane, ethane, propane and butane over a monolithic honeycomb catalyst. The authors analyzed distribution of product as a function of steam-to-carbon ratio (2.2–4) , temperature (250–900°C) and for two honeycomb channel densities (600 and 900 cpsi) and an uncoated monolith by gas chromatography and mass spectroscopy. They found that heavier hydrocarbon i.e. Ethane, propane, and Butane can converted at much lower temperature than methane, even in natural gas mixtures if heavier hydrocarbon percentage is high then conversion can be attend at lower temperature than pure methane.

Corbo et al. (2006) [22] have reported that reforming of methane requires higher temperature than reforming of other fuels. Hence they concluded that methane is not a better choice for fuel cells and mobile application. For mobile application liquid fuel works better as its energy density is high and also handling of liquid fuel is easy. Hence, for fuel cell and mobile application reforming of liquid fuel such as liquefied petroleum gas (LPG), methanol and diesel plays an important role.

LPG as a feedstock for reformers provides several advantages namely it's storage and transportation is easy, It is having less coking tendency and surface recrystallization of Ni catalyst compare to heavier hydrocarbons due to its composition and absence of sulphur atoms, also in fuel cell vehicles it matches some features of IC (internal combustion) engine and emit less pollutants.

Rakib et al. (2010) [23] carried out steam reforming of propane rather than natural gas for production of hydrogen. They used fluidized bed membrane reactor and since

membrane extract pure hydrogen, reaction (1.1) shifted towards the completion. They used hydrogen permselective $Pd_{77}Ag_{23}$ membrane panels to extract pure hydrogen.

Table 2.1

Density of liquid/liquefied hydrocarbons at ambient pressure[23].

Hydrocarbon	Hydrocarbon Conditions	Liquid density (kg/m^3)	Molar density (kmol/m^3)	Hydrogen content (kg H_2/m^3 hydrocarbon)	Hydrogen proportion (kg H_2/kg hydrocarbon)
Methane	Ambient Pressure -165°C	424.9	26.48	106.7	0.25
Methane	11.86 bar -120.5°C	352.9	21.99	88.66	0.25
Propane	8.62 bar 20°C	500.3	11.35	91.53	0.18
n-Butane	2.07 bar 20°C	578.8	9.96	100.4	0.17
n-Heptane	Ambient Pressure 20°C	682.4	6.81	109.8	0.16

They have also reported a Table 2.1 which shows hydrogen content in methane, propane, n-butane and n-propane all in liquid state i.e. methane at similar condition of LNG storage, propane at similar condition of LPG tanks, and n-heptane at ambient condition. The table shows that though hydrogen content is maximum for methane, volumetric hydrogen density is more for heavier hydrocarbon. Based on this Table they have drawn the following inferences.

Though the most frequently used feedstock for hydrogen is methane i.e. natural gas due to its low price, easy availability and less coking tendency, heavier hydrocarbon provides several advantage over methane. Heavier hydrocarbon may be preferred feedstock for hydrogen production where local price is lower and its availability is lower. For example in refineries demand of different hydrocarbon varies and hence in some situation price of heavier hydrocarbon feedstock for hydrogen generation may be lower. Also, In fuel cell application which demands on-board hydrogen production, feedstock should have high volumetric hydrogen density at ambient condition or near ambient condition.

Liquefied Petroleum Gas or LPG is easily available from refineries and can be liquefied at relatively low pressures. Also, LPG is cleaner feedstock than heavier hydrocarbon and it contains high weight percent of hydrogen. LPG in refinery is usually in surplus in summer and less available in winter due to heating requirements.

2.2 EVALUATION OF PROCESS FOR HYDROGEN PRODUCTION

Zeng *et al.* (2010) [24] performed a thermodynamic analysis of propane oxidative steam reforming by Gibbs free energy minimization method. By adding oxygen thermal efficiency increases as enthalpy of the system reduces and requirement of heat supply decreases. They investigated the effects of Temperature (300, 500, 700 and 900°C), steam to propane ratio (1.0-20.0) and oxygen to propane ratio (0.0-2.0) on equilibrium composition under thermo-neutral (TN) and oxidative conditions. They found that at 973K with steam to propane ratio higher than 7.0 and/or oxygen to propane ratio above 1.3 are good condition for hydrogen production and also for suppression for methane and coke formation. At this condition they mentioned that around 9 moles of hydrogen can be produced per mole of propane. It was mentioned that for thermo-neutral condition, equilibrium composition and autothermal temperature depend strongly on oxygen to propane ratio compare to steam to propane ratio.

Wang *et al*. (2010) [25] performed thermodynamic analysis of sorption enhanced steam reforming (SESR) of propane by Gibbs free energy minimization method and compared with steam reforming (SR) of propane. They evaluated equilibrium composition, and also tendency of carbon formation as a function of temperature (700-1100 K), pressure (1-5 atm), and water to propane ratio (WPR, 1-18). They demonstrated that water to propane ratio of 12 and one atmospheric pressure are best suitable for H_2 production from both steam reforming and sorption enhanced steam reforming of propane. As WPR increases, tendency of carbon formation decreases, when WPR was more than 6 then carbon production completely eliminated in both steam reforming and sorption enhanced steam reforming. They found that the best temperature for hydrogen production is 950 K by steam reforming and 825 K (125K lower) by sorption enhanced steam reforming of propane. Also, in steam reforming 9.1 mol can be produced per mole of propane feed, while in sorption enhanced steam reforming around 10 mole can be produced which is the stoichiometric amount. They also mentioned that sorption enhanced steam reforming of propane provide other advantage too i.e. the hydrogen

produced is 99% pure which is much high compared to 74% in steam reforming of propane. Only impurity which was produced is CH_4 in sorption enhanced steam reforming of propane.

Wang _et al._ (2010) [26] performed thermodynamics analysis of steam reforming (SR) and dry reforming (DR) of propane using Gibbs free energy minimization method. They investigated equilibrium composition as a function of temperature (700-1100 K), pressure (1-5 atm), CO_2/C_3H_8 ratio (CPR, 1-12) and H_2O/C_3H_8 ratio (WPR, 1-18). It was demonstrated that from a thermodynamic perspective, for synthesis gas production which is having useful composition for chemical production; dry reforming is better than steam reforming while for hydrogen production steam reforming is better than dry reforming. It was shown that conversion of propane was 100% for the range of variables used in this study. One atmospheric pressure was best suitable for both dry and steam reforming. They showed atmospheric pressure is preferable for both DR and SR. They also mentioned different condition for different ratio of H_2/CO in synthesis gas. For example for H_2/CO ratio=1, 975K and CO_2/C_3H_8 ratio (CPR) =3 was found optimum; for H_2/CO ratio=2, 1100 K and CO_2/C_3H_8 ratio (CPR) =3 was found optimum. For temperature more than 1000K and CO_2/C_3H_8 ratio more than 6, around 10 mol of synthesis gas was produced per mole of propane. They also reported optimum condition for hydrogen generation from steam reforming i.e. temperature 925-975K and water to propane ratios WPRs=12-18. At this condition production of hydrogen was 9.1 mol per mol of propane and also at that condition methane and carbon formation was suppressed.

Rakib _et al._ (2010) [27] reviewed different type of reforming options and find that, dry reforming of propane is un-economical in comparison with steam reforming of propane since dry reforming is slower. Also, Partial oxidation was reported as preferred reforming option only when oxygen is easily available and syngas with high concentration of CO was desired. Based on their study they claimed that steam reforming is the best option in terms of hydrogen production economically.

2.3 CATALYST USED FOR STEAM REFORMING OF PROPANE

Laosiripojana _et al_. (2005) [28] studied autothermal and steam reforming of a mixture of propane and butane i.e. LPG. They used high surface area CeO_2 (CeO_2 (HSA)) which was synthesized by a surfactant assisted approach under solid oxide fuel cell (SOFC) operating conditions. This catalyst was working better than Ni/Al_2O_3 in terms of

activity and selectivity as it showed resistance toward coking. It was explained that advantage of that catalyst was due to redox property of CeO_2.

Harshini *et al.* **(2011) [29]** prepared $Ni/LaAlO_3$ catalyst for steam reforming of propane by different methods like solvo-thermal, impregnation, and deposition precipitation. They also synthesized other catalyst by solvo-thermal method like Ni/CeO_2 and Ni/Al_2O_3. They found that activity and stability of $Ni/LaAlO_3$ was dependent on the method of preparation and it is better than Ni/CeO_2 and Ni/Al_2O_3 catalysts. $Ni/LaAlO_3$ prepared by solvo-thermal method was highly stable, it maintained its activity for around 100 hours. $LaAlO_3$ provides better oxygen transport ability than Ni/CeO_2 and Ni/Al_2O_3. Hence formation of carbon was suppressed even at low steam to carbon feed ratio. Also, oxygen storage capacities (OSC) was highest for $LaAlO_3$ support within temperature 573K-1173K and hence it suppresses coke formation.

Natesakhawat *et al.* **(2005) [30]** used sol–gel Ni/Al_2O_3 catalysts for their study and investigated the effect of some lathanide like La, Ce and Yb on the behaviour of the catalyst for steam reforming of propane. They found that if small amount of lanthanide (2 wt.%) is added in the catalyst then activity and stability of catalyst improves a lot. Also, small amount of lanthanide improves catalyst reducibility, reduces catalyst deactivation and increases nickel surface area. They concluded this based on X-ray photoelectron spectroscopy (XPS) and Temperature-programmed reduction (TPR) characterization. It was shown by H_2 chemisorptions data that 20% Ni–2% Ce/Al_2O_3 catalysts is better than 20% Ni/Al_2O_3 catalysts in terms of nickel surface area

Lim *et al.* **(2009) [31]** prepared catalyst for autothermal reforming of propane by Ce modification in $Ni/LaAlO_3$ catalysts which improves the thermal stability and resistance to carbon deposition. They studied with different amount of Ce loading in the $Ni/LaAlO_3$ catalyst and found that 5% loading is best in terms of reforming performance. Due to high activity the reaction temperature required for reforming gets lower and hence CO concentration also gets lower. They used perovskite-type catalysts which was mentioned as cheaper, more active and thermally stable compared to supported noble metal catalyst for catalytic reforming of hydrocarbon. The general formula for perovskite-type catalyst was mentioned as ABO_3, where A was rare earth cation (La, Gd, Pr, Nd, or Er) and B was transition metal cation (Cr, Mn, Fe, Ni, Al, or Co). Where A-site deals with amount of sorbed oxygen while B-site deals with nature of sorbed oxygen.

2.4 MEMBRANE REACTOR FOR STEAM REFORMING

Shu *et al.* **(1994) [32]** applied electrolessly deposited Pd- and Pd-Ag/porous stainless steel composite membranes in methane steam reforming. It was reported that conversion of methane improved significantly by partial removal of hydrogen through Pd membrane. They found that methane conversion is doubled by using Pd/SS membrane compared to non-membrane reactor for a specific condition using Ni/Al_2O_3 catalyst. Condition was temperature=$5OO^0C$, steam to methane ratio=3 , total pressure=136 kPa. For the effect of partial removal of hydrogen by membrane on methane conversion they developed a computer model.

They also reported that reforming of hydrocarbon is more economic than other processes like gasification, electrolysis of water and partial oxidation; for hydrogen generation used in fuel cells.

They have reviewed some paper which shows that by using membrane separation which separate hydrogen, one can get conversion of methane up to 96%. Also, around 90% conversion of methane could obtained below 850°C by Pd membrane with 50 pm thickness.

Kusakabe *et al.***(2008) [33]** used yttria-stabilized zirconia (YSZ) membrane reactor for hydrogen production in the range of temperature 400-600°C using propane steam reforming (SR). YSZ membrane allows selective diffusion of hydrogen. On the basis of the results obtained from packed bed reactor for low temperature steam reforming of propane they used Rh-supported $Ce_{0.15}Zr_{0.85}O_2$ catalyst for packing in the membrane reactor. Due to partial removal of hydrogen the conversion of propane was higher in case of membrane reactor compared to packed bed reactor. Also, it reduces CO fraction in the product and increase CO_2 fraction. It means water-gas shift reaction plays an important role in distribution of product. But methane fraction does not alter by removal of hydrogen through membrane.

CHAPTER 3

THERMODYNAMIC MODELLING AND SIMULATION

3.1 METHODOLOGY

The thermodynamic analysis of propane steam reforming, dry reforming and Oxidative reforming; by non-stoichiometric method has been presented in this chapter to determine the favourable operating conditions for synthesis gas or H_2 production with minimal CH_4, CO and carbon formation. The influence of temperature, pressure, water to propane feed ratio (WPR), Carbon dioxide to propane feed ratio (CPR), oxygen to propane feed ratio (OPR) on equilibrium compositions of reforming products has been investigated. The performances of all different possibilities are compared to identify the best process scheme for producing synthesis gas H_2 production.

The thermodynamic analysis of the process at a given condition provides what will be the equilibrium compositions of different products (desired and undesired). Hence it ensure that whether an experimental investigation would be worthwhile or not. Therefore, before running the reformer, It would be advantageous to get the operating condition which provides high yield of desired product and suppresses the undesired product. The thermodynamic equilibrium calculations can be performed via two approaches: stoichiometric approach and non stoichiometric approach [34]. In stoichiometric approach, a set of stoichiometric reaction is used to describe the system. In this approach Thermodynamic analysis is based on equilibrium constants for these reactions. Equilibrium constant is written as a function of temperature. Since, equilibrium constant

$$K = K_y P^v \tag{3.1}$$

is the product of equilibrium constant in terms of composition and P^v where v is the sum of the coefficient of the reaction with positive sign for products and negative sign for reactants. Now K_y can be written in terms of extent of reaction. And then equation 3.1 can solved for extent of reaction and hence equilibrium composition can be determined. In non-stoichiometric approach, the biggest advantage that there is no need to write all possible chemical reaction which might occur in the system apart from that there is no need for an accurate estimation of initial equilibrium compositions, easy achievement of

convergence in computation and easy incorporation of adsorption and carrier gas effects. In this approach the first step is to defined a list of chemical compounds using atomic combination of the elements in the feed like (C,H,O) which might coexist in the system at equilibrium. Using direct minimization of Gibbs free energy the equilibrium compositions of these products can be derived. Since in this study non-stoichiometric approach has been used, a brief discussion of this approach is given below.

It is known that for multicomponent system differential form of the Gibbs free energy can be given by [35]:

$$dG = -SdT + VdP + \sum_{i=1}^{N} \mu_i dn_i \tag{3.2}$$

where G is the total Gibbs free energy, T is temperature, S is the entropy, V is the volume, P is the pressure, n_i is the number of moles of the ith component in the system and μ_i is the chemical potential of the component i.

For constant temperature and pressure the first two term of the right hand side will vanish and one will left with:

$$dG = \sum_{i=1}^{N} \mu_i dn_i \tag{3.3}$$

Hence the total Gibbs free energy of the system can be given by:

$$G = \sum_{i=1}^{N} \mu_i n_i \tag{3.4}$$

We know that for a system in equilibrium at a given temperature and pressure the free energy must be minimum, which implies the first derivative of G with respect to n is zero. To get G as a function of n_i and hence to get set of n_i which minimizes the value of G; μ_i can be written in terms of fugacity and standard chemical potential.

Since the fugacity of component i is related to the chemical potential of the component i as [35]:

$$d\mu_i = RT \, d(\ln \overline{f_i}) \tag{3.5}$$

It follows that

$$\Delta \mu_i = RT \ln \frac{\widehat{f_i}}{f_i^o} \tag{3.6}$$

Where $\qquad \Delta \mu_i = \mu_i - \mu_i^o \tag{3.7}$

μ_i^o is nothing but partial molar Gibbs free energy at standard state i.e. G_i^o

Hence
$$\mu_i = G_i^o + RT\ln\frac{\widehat{f_i}}{f_i^o}\qquad(3.8)$$

Since fugacity of component i can be given in terms of fugacity coefficient as

$$\widehat{f_i} = \widehat{\phi}_i y_i P\qquad(3.9)$$

$\widehat{\phi}_i$ is the fugacity coefficient of the component i. and $f_i^o = P^o$ where P^o is standard state pressure which is 1 bar. Since G_i^o for chemical element in its standard state is zero, $\Delta G^o = \Delta G_i^f$ for each component is assumed. Hence total Gibbs free energy can be given by

$$G = \sum_{i=1}^{N} n_i \left(\Delta G_i^f + RT\ln y_i P + RT\ln\widehat{\phi}_i\right)\qquad(3.10)$$

Or

$$G = \sum_{i=1}^{N} n_i \left(\Delta G_i^f + RT\ln\frac{n_i}{n_T}P + RT\ln\widehat{\phi}_i\right)\qquad(3.11)$$

Equation (3.11) should be minimize to get equilibrium composition, subject to the following equality constraint.

The constraint is based on the elemental balances:

$$\sum_{i=1}^{N} a_{ji}\, n_i = b_j\qquad(3.12)$$

Where j represents the type of atom hence a_{ji} is the number of j-type atoms in the component i. b_j represent the number of j-type atom in the feed. So, for C,H,O there will be 3 constraint equation. So, In non-stoichiometric approach equilibrium composition is determined by direct minimization of equation (3.10) subject to the constraint (3.11).

$$\bar{G}_{C(g)}=\bar{G}_{C(s)} = G_{C(s)} \cong \Delta G_{fC(s)}^{\circ} = 0\qquad(3.13)$$

During reforming of propane, carbon on solid, is formed due to various reaction as given in Table 4.2. The vapour-solid phase equilibrium is applied to define the Gibbs free energy of solid carbon Eq. (3.13). In order to avoid numerical instability in solving the problem with solid carbon formation, Eq. (3.11) is modified to Eq. (3.14).

$$G = \sum_{i=1}^{N} n_i \left(\Delta G_i^f + RT\ln\frac{n_i}{n_T}P + RT\ln\widehat{\phi}_i\right) + \left(n_C\Delta G_{fC(s)}^{\circ}\right)\qquad(3.14)$$

3.2 OPERATING CONDITIONS AND SIMULATION

In the present thermodynamic investigation, 2 feed components (propane, steam); 2 feed components (propane, Carbon dioxide) and 3 feed components (propane, steam, oxygen) are considered for SRP, DRP and OSRP respectively. In all type of reforming, 8 gaseous products (H_2, CO, CO_2, H_2O, CH_4, C_2H_4, C_2H_6, C_3H_6) and one solid product (Carbon) are considered. For computations, code has been developed in MATLAB R2013a. The total Gibbs free energy function Eq. (3.14) is minimized using in-built fmincon function available in MATLAB software. The fmincon function used for optimization of single or multivariable nonlinear expressions subject to various linear and nonlinear constraints.

The component composition at equilibrium are estimated at different operating condition of temperature (600-1100K), steam/propane ratio WPR, (1-18) in feed, CO_2/propane ratio, CPR (1-9) in feed, oxygen/propane ratio, OPR (0-2) in feed, pressure (1-5 atm), fractional removal of H_2 (f_1=0-0.99), and fractional removal of CO_2 (f_2=0-0.99). All these calculations are performed on the basis of 1 mol of propane in the feed to reformer.

CHAPTER 4

RESULTS AND DISCUSSION

The equilibrium composition of all selected chemical components at the exit of the system are estimated at all operating conditions mentioned in section 3.2. The molar flow rates of few gaseous components under study are given in Table 4.1. This table clearly shows that propane is completely converted and C_2H_4, C_2H_6, C_3H_6 exist only in trace amounts at equilibrium. These products can be considered as intermediates which are not thermodynamically stable at complete conversion of propane. However, since in practice, reforming reactions are kinetically controlled in presence of suitable catalysts and complete conversion of propane is not achieved, the occurrence of these intermediate products in experimental work can be observed. The components present at equilibrium are H_2, CO, CO_2, CH_4, H_2O and carbon over the whole range of operating conditions mentioned in section 3.2. Thus, the list of products for further thermodynamic equilibrium analysis is restricted to H_2, CO, CO_2, CH_4, H_2O and carbon.

The possible major chemical reactions concerned with the production of predominant thermodynamically feasible products (H_2, CO, CO_2, CH_4) by reforming of propane are listed in Table 4.2. The carbon formation reactions are also included in this list (R13-R17). The temperature limit for which the reaction is feasible to occur, is also mentioned.

The thermodynamic analysis of propane reforming has been performed for five reforming systems. The first reforming system represents the steam reforming of propane (SRP). The second reforming system represents the dry reforming of propane (DRP). In the third reforming system, steam reforming is described with fractional co-feeding of O_2 with steam and propane as oxidative steam reforming of propane (OSRP). In the fourth reforming system, steam reforming is considered with in situ fractional removal of H_2 or CO_2. In the last reforming system, dry reforming is considered with in situ fractional removal of H_2 or CO_2. All these reforming systems are studied to analyze the production of H_2, CO, CH_4, carbon and syngas.

Fig. 4.1 illustrates the effect of pressure on H_2 production at various temperature and pressure conditions for WPR of 6 and 12. Similar trends are obtained at both WPR

values. It is clear that elevating the pressure does not favour H_2 production by suppressing reactions R1 and R2 and by promoting methanation reactions R8 and R9. Since low pressure positively affects the H_2 production, the pressure of 1 atm has been selected for further thermodynamic studies of all reforming systems.

Table 4.1

Number of moles of the species with the exit product steam per mole of propane by steam reforming at T=950 K, P=1 atm, WPR=12.

Species	Number of moles produced
Propane (C_3H_8)	7.55E-14
Ethylene (C_2H_4)	9.25E-09
Ethane (C_2H_6)	2.86E-08
Propene (C_3H_6)	2.02E-13

Table 4.2

Reactions in reforming of propane [25] [34] .

| Reactions		ΔH^o_{298K} (kJ/mol)	Reaction no.	Feasibility of Reactions
Steam reforming of propane (SRP)	$C_3H_8 + 3H_2O \rightleftharpoons 3CO + 7H_2$	497	R1	T>715
Total reforming of propane (TRP)	$C_3H_8 + 6H_2O \rightleftharpoons 3CO_2 + 10H_2$	374	R2	
Dry reforming of propane (DRP)	$C_3H_8 + 3CO_2 \rightleftharpoons 6CO + 4H_2$	620	R3	T>763
Partial reforming of propane (PRP)	$C_3H_8 + 3/2O_2 \rightleftharpoons 3CO + 4H_2$	-229	R4	
Total oxidation of propane (TOP)	$C_3H_8 + 5O_2 \rightleftharpoons 3CO_2 + 4H_2O$	-2046	R5	
Oxidative reforming of propane (OSRP)	$C_3H_8 + 3/2O_2 + H_2O \rightleftharpoons 3CO_2 + 10H_2$		R6	
Water gas shift reaction (WGS)	$CO + H_2O \rightleftharpoons H_2 + CO_2$	-41	R7	T<1080
Methanation	$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	-206	R8	T<894
Methanation	$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$	-165	R9	T<863
Methane dry reforming	$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	247	R10	T>900
Methane steam reforming	$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	205.8	R11	T>894
Propane cracking	$C_3H_8 \rightleftharpoons C_2H_4 + CH_4$	89	R12	T>575
Ethylene cracking	$C_2H_4 \rightleftharpoons 2C + 2H_2$	-52	R13	
Methane cracking	$CH_4 \rightleftharpoons C + 2H_2$	75	R14	T>817
Co reduction	$CO + H_2 \rightleftharpoons C + H_2O$	-131	R15	T<947
Co$_2$ reduction	$CO_2 + 2H_2 \rightleftharpoons C + 2H_2O$	-90	R16	T<905
Boudouard reaction	$2CO \rightleftharpoons C + CO_2$	-172	R17	T<977
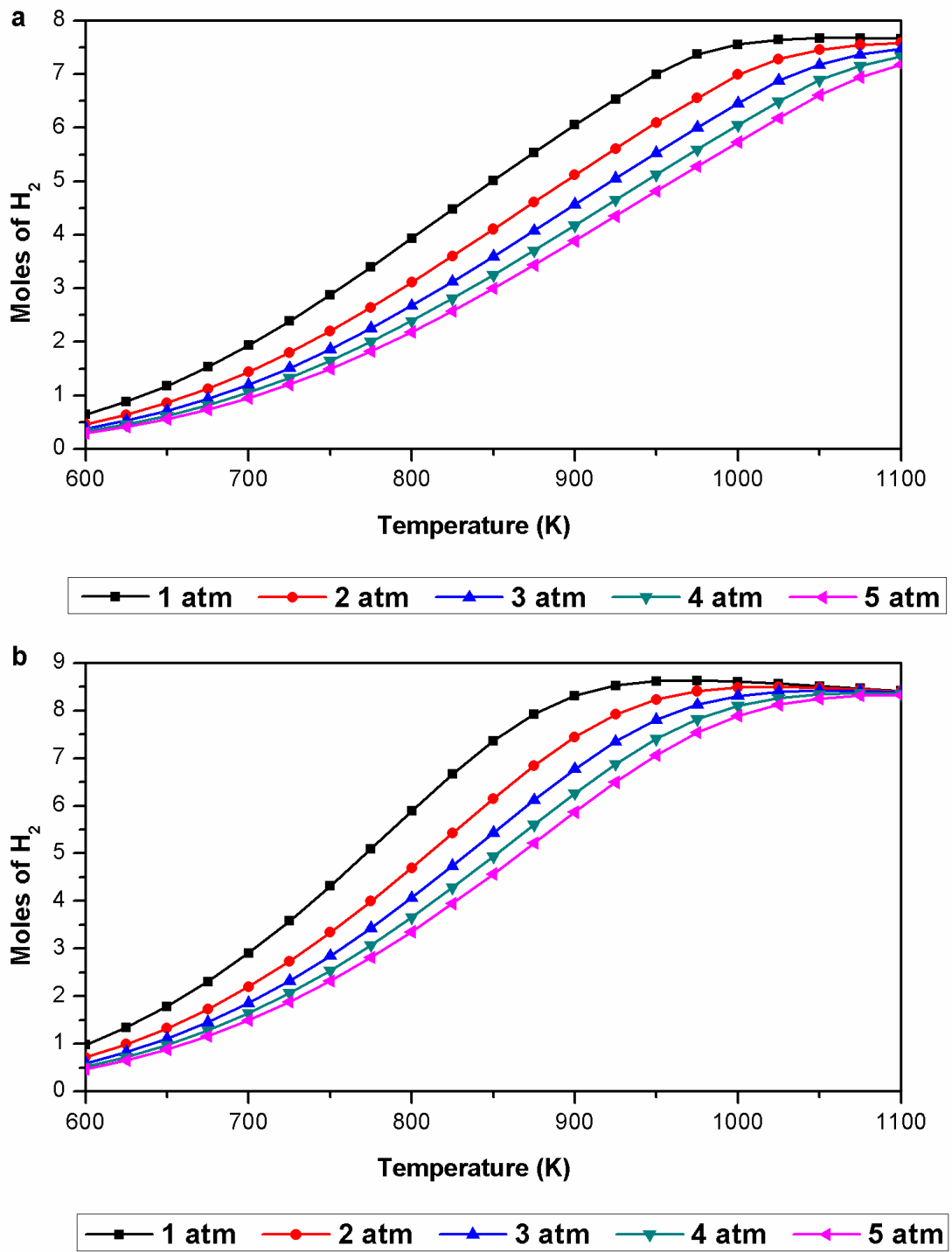
Fig. 4.1 Variation in H₂ production by SRP with temperature and pressure at (a) WPR=6, (b) WPR=12

4.1 STEAM REFORMING OF PROPANE (SRP)

Fig. 4.2 depicts the variation in H_2 and CH_4 production by SRP as a function of WPR and temperature at atmospheric pressure. It can be seen from figure that production of hydrogen increases with increase in WPR at a given temperature. This is attributed to the fact that steam is one of the reactants in SRP and WGS reactions (R1 & R7). Hence high WPR favours the forward reaction. However, a very high WPR is not economically suitable since it requires high energy input to vaporize the water, reactor volume required for high WPR will be high, also additional energy required for downstream separation of hydrogen from water. For a given WPR (WPR below 6), production of hydrogen increases with increasing temperature. For WPR greater than 6, production of hydrogen first increases, goes to peak around (925-975K) and then decreases. At low T (below 800K) very less amount of H_2 produced, possible reason for that is the SRP (R1) reaction is thermodynamically limited. Below 750K; Equilibrium constant for this reaction is in the vicinity of 1 and hence varying the WPR and temperature has considerable influence on the distribution of the products. The maximum amount of hydrogen produced is 9.1 mol at 950K with a WPR of 18. Based on these observation, optimum condition for hydrogen production is therefore a WPR=12 at around 950K and one atmospheric Pressure.

At a given WPR moles of CH_4 decreases with increasing temperature. This is because high temperature favours methane cracking (R14), reverse methanation reactions (R8 & R9). These all reactions reduce CH_4 production. Since methane is the competitive product of hydrogen hence high temperature is favourable for pure hydrogen production, because high temperature inhibits the methane production. Methane production varies in complex nature with WPR at a given temperature. But after 850 K and WPR more than 12, methane production decreases with increase in WPR. Hence optimum condition WPR=12 at around 950K and atmospheric pressure is also suitable to inhibit methane production. Thermodynamically, methane production can be inhibited almost entirely over 950K with WPRs more than 12.

Fig. 4.3 depicts variation in CO and carbon production in SRP as a function of temperature and WPR at atmospheric pressure. For a given WPR number of moles of CO produced increases with increasing temperature. Since water gas shift reaction WGS (R7), methanation reactions (R8 & R9) are exothermic in nature high temperature favours the backward reaction hence CO conversion decreases at high temperature. At a given temperature carbon monoxide production first increases up to WPR=6 (stoichiometric

ratio) and then decreases with increasing WPR. Initially CO production increases via R1 indicating that WPR favours CO production. However, on further increase in WPR, CO is converted to CO_2 and H_2 via WGS reaction (R7). Since CO acts as impurity in the product gas, hence low content of CO facilitates the purification of hydrogen, when hydrogen is the main product. So, it also suggests that high WPR is favourable for hydrogen production.

One very clear observation from this figure, that, for WPR greater than 12, there is no carbon formation regardless of the temperature. Hence high WPR also favourable for carbon formation reduction. For a given WPR, carbon formation first increases and then decreases. So, high temperature is also favourable in terms of carbon formation reduction. Possible explanation of these observations are; at high temperature CH_4 production reduces as explained earlier. Now, as we know from Table 4.2 carbon formation occurs mainly due to methane cracking (R14) at high temperature. Hence, at high temperature carbon formation reduces. At low temperature carbon formation occurs due to hydrogenation of CO and CO_2 (R15 & R16) and Boudouard reaction (R17). At high WPR reverse hydrogenation reactions occur. Hence at high WPR less carbon formation occurs. Boudouard reaction does not occur due to very less CO formation at low temperature.
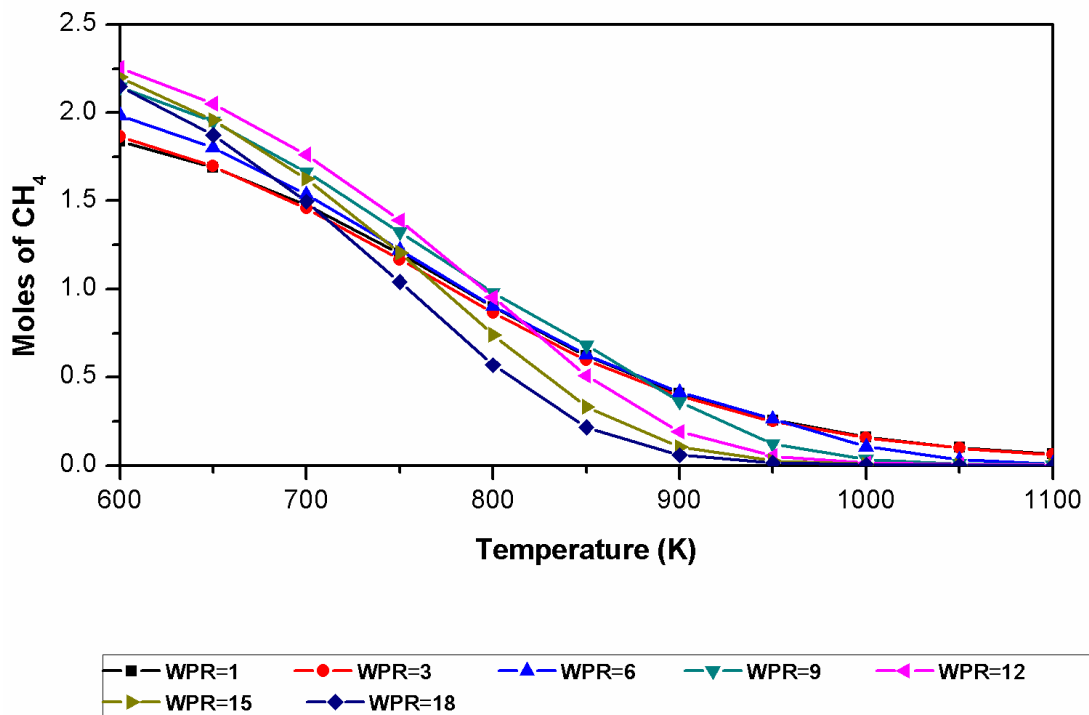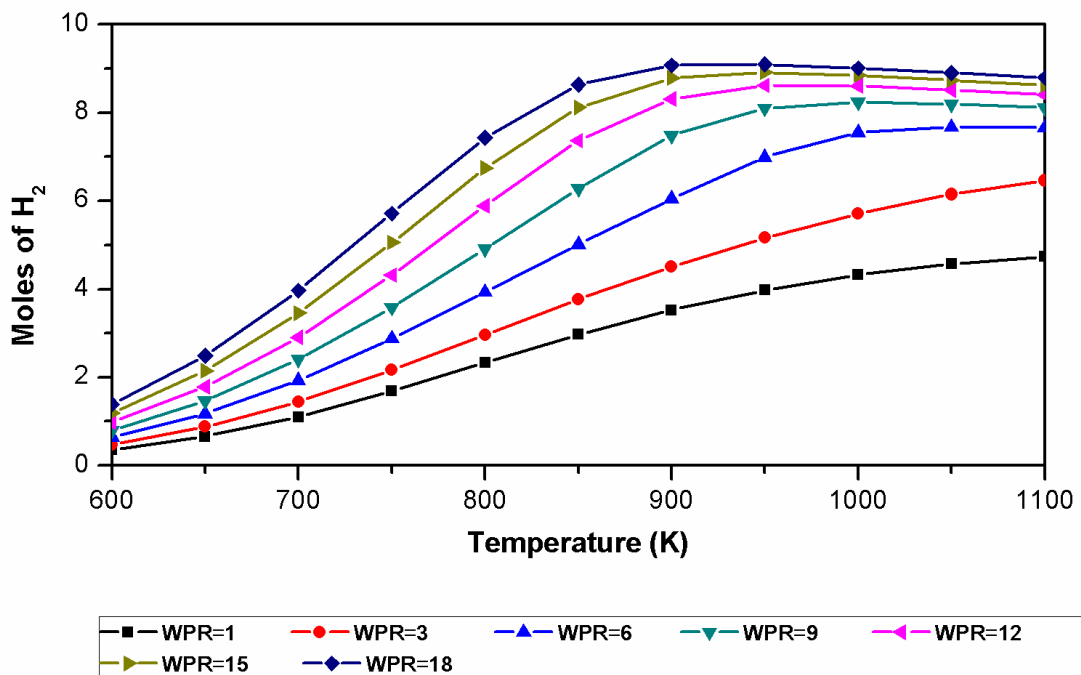
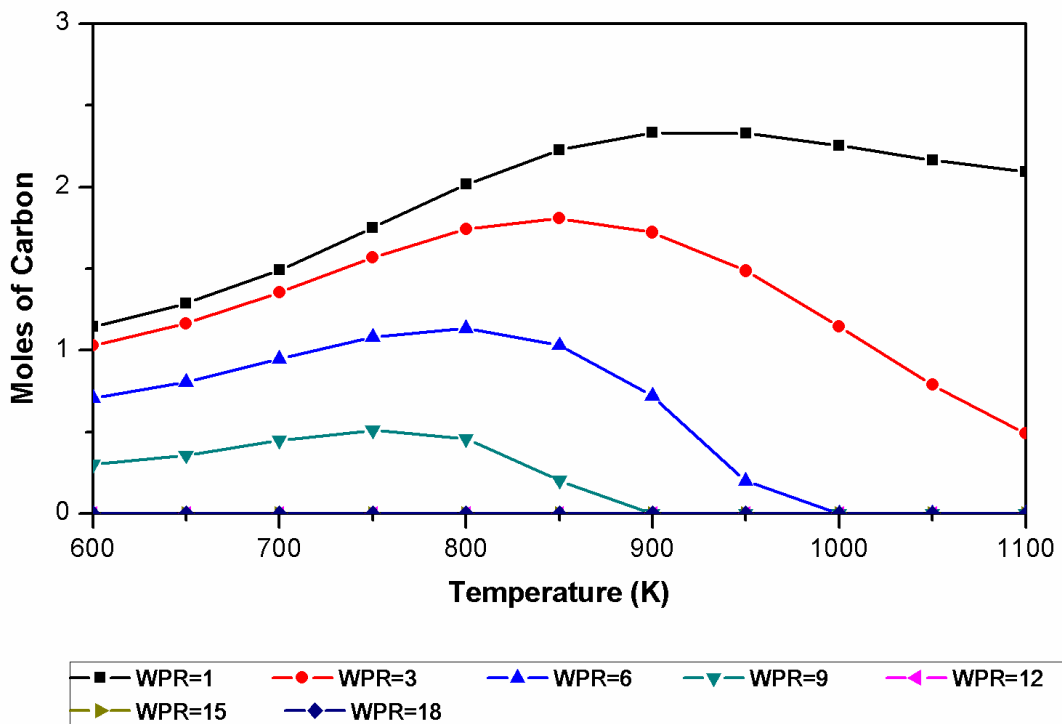**Fig. 4.2 Variation in H₂ and CH₄ production by SRP with temperature and WPR at 1 atm pressure.**
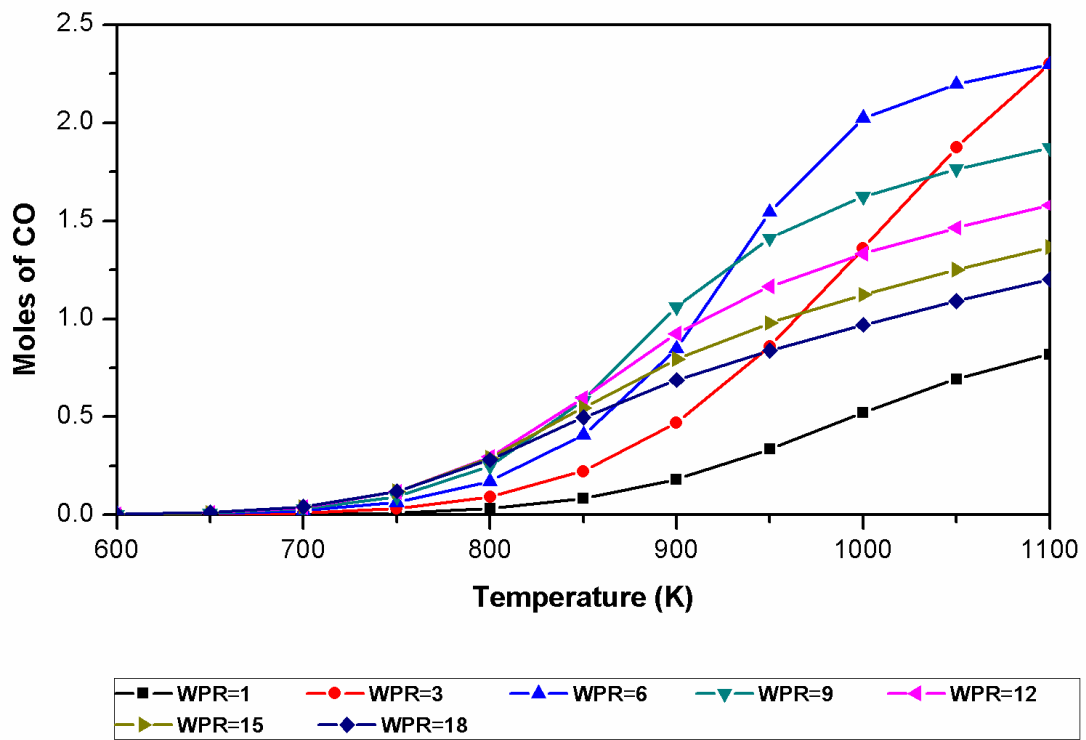
Fig. 4.3 Variation in CO and carbon production by SRP with temperature and WPR at 1 atm pressure.

4.2 DRY REFORMING OF PROPANE (DRP)

Fig. 4.4 depicts the variation in H_2 and CH_4 production in DRP as a function of CO_2 to propane feed ratio (CPR) and temperature at 1 atm pressure. It can be seen from figure that for CPR below 3, hydrogen production increases with increase in temperature. This is because DRP reaction (R3) is endothermic in nature; hence high temperature favours the forward reaction. For CPR greater than 3, hydrogen production first increases, goes to peak around (1000-1050 K) and then decreases, since at very high temperature reverse WGS (R7) occurs. At a given temperature, hydrogen production decreases with increase in CPR due to reverse WGS (R7). For temperature greater than 1000K and CPRs between 1 and 6; more than 3 moles of hydrogen (theoretical amount is 4 mole) can be produced. Comparing to steam reforming of propane hydrogen production is much less in dry reforming of propane. In SRP maximum amount of hydrogen produced is 9.1 mol (Theoretical amount is 10 mol), while in DRP maximum amount of hydrogen produced is 3.7 mol (Theoretical amount is 3 mol). At a given CPR, CH_4 production decreases with increase in temperature and for a given temperature CH_4 production decreases with increase in CPR. Since we know that CH_4 is undesired product as it competes with production of hydrogen. So, high temperature and high CPR which is favourable for synthesis gas production (explained in section 4.6) is also favourable for inhibition of CH_4 production.

Fig. 4.5 depicts variation in CO and carbon production by DRP as a function of CPR and temperature. For a given CPR, CO production increases with increase in temperature. if hydrogen is our main product then CO acts as impurity. But if synthesis gas is the desired product, then high temperature is favourable as more CO, will reduce the H_2/CO ratio. At a given temperature moles of CO produced increase with increase in CPR. Carbon formation is almost stable regardless of the temperature when CPR=1. However, high CPRs favor the inhibition of carbon formation at high temperature. Carbon formation can also be eliminated under conditions where the maximum amount of synthesis gas can be obtained. Hence it can be concluded that high temperature and high CPR is the favorable operating condition for suppressing the impurities i.e. CH_4 and carbon and this condition also reduce the H_2/CO ratio (detail in section 4.6).
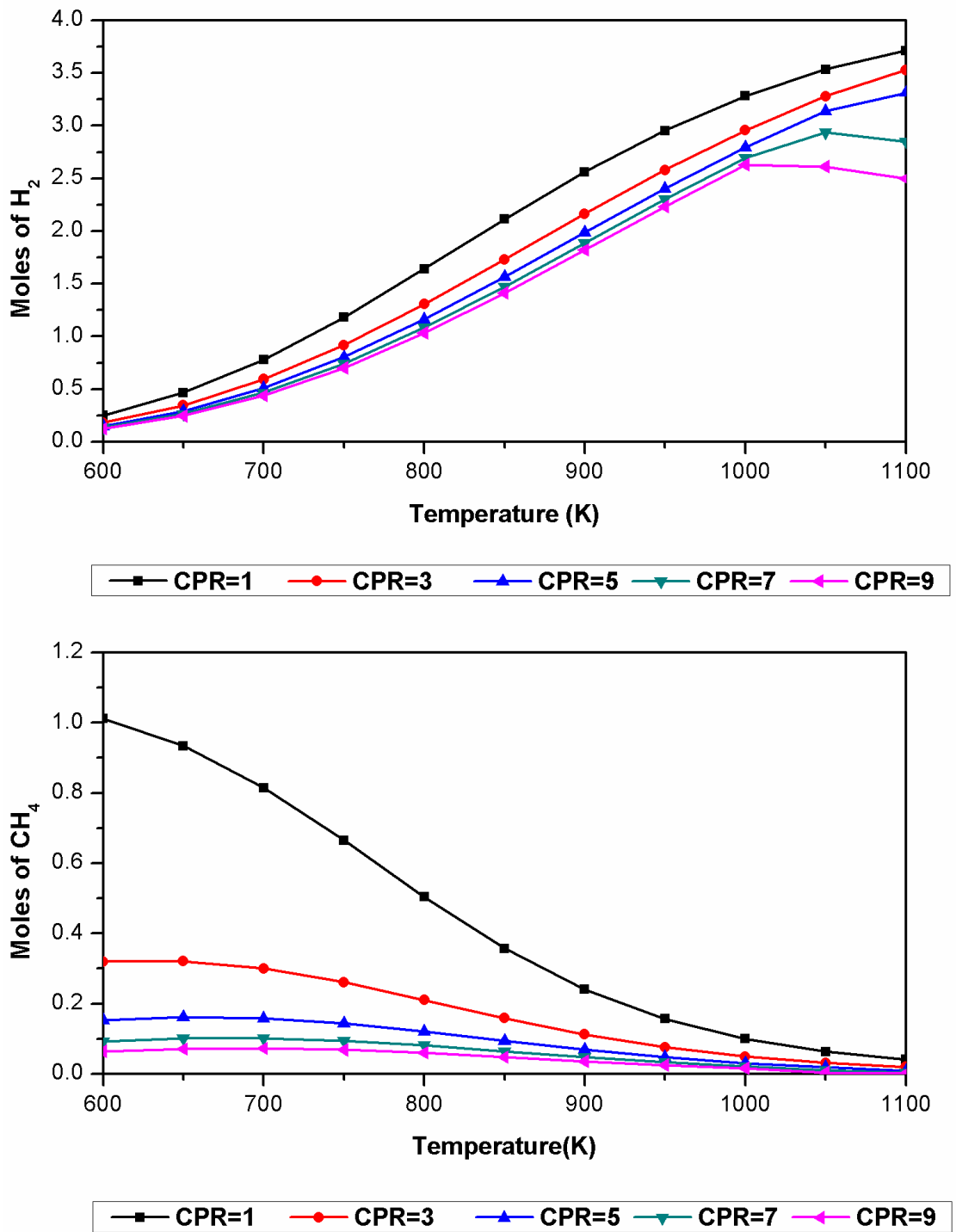
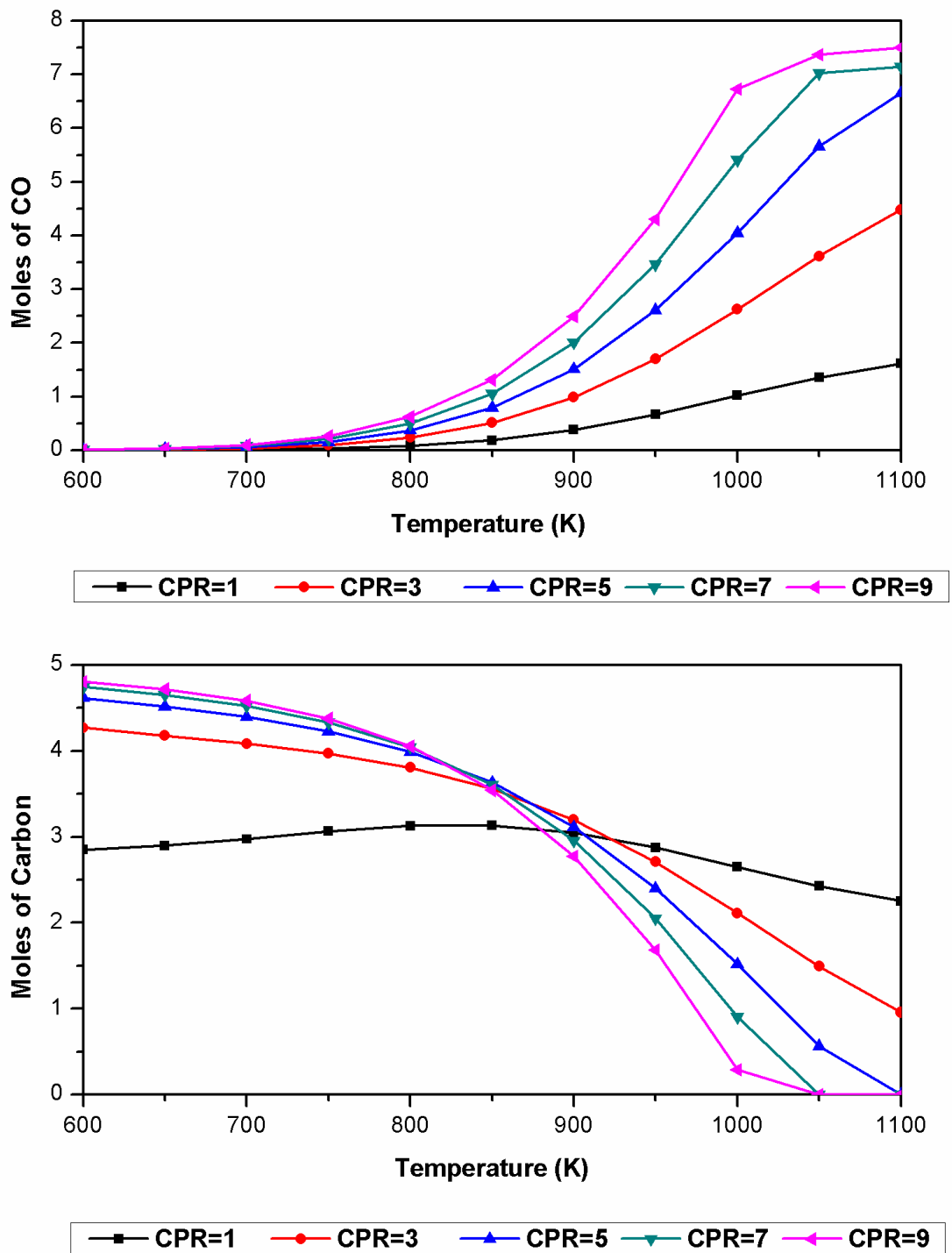**Fig. 4.4 Variation in H₂ and CH₄ production by DRP with temperature and CPR at 1 atm pressure.**

Fig. 4.5 Variation in CO and carbon production by DRP with temperature and CPR at 1 atm pressure.

4.3 OXIDATIVE STEAM REFORMING OF PROPANE (OSRP)

The advantage of co-feeding of O_2 with propane and steam is the reduction in heat energy requirement for the endothermic steam reforming reaction by exothermic oxidation reaction. This reforming is analyzed at 1 atm pressure and temperature of 800-1200K, WPR of 6-18 and oxygen to propane ratio (OPR) of 0-2.0. At all these conditions, the conversion of propane has been found to be 100%. Figs 4.6, 4.7 and 4.8 depict the variation in moles of H_2 and CH_4 as a function of OPR and WPR at 800K, 1000K and 1200K respectively. It is clear from these figure that high temperature significantly enhances the hydrogen production. But high OPR reduces the H_2 and CH_4 production at fixed values of T and WPR. At high OPR the reduction in CH_4 is advantageous as CH_4 adversely affects the formation of H_2. High value of OPR oxidizes the produced H_2 to H_2O resulting in the reduction in H_2. Thus high temperature, high WPR and low OPR favours H_2 production. Figs 4.9, 4.10, and 4.11 illustrates the variation in moles of CO and carbon as a function of WPR and OPR at 800K, 1000K and 1200K respectively. These figures show that higher temperature promotes the production of CO but higher WPR does not favour. These trends are due to endothermic nature of steam reforming of propane and exothermic nature of water gas shift reaction. At one value of temperature and WPR, the production of CO decreases (WPR>9) with increase in OPR values. Higher value of OPR oxidizes the produced CO and converts CO into CO_2. In view of these trends, this may be concluded that in order to reduce CO in the reforming gaseous products, low temperature, higher OPR and higher WPR are most suitable operating conditions.

The production of carbon decreases with increase in WPR, OPR and temperature. At 1000K and 1200K, carbon production becomes negligibly small (not visible in the figs 4.10 and 4.11) at all values of OPR and WPR. These trends are observed due to exothermic CO reduction, CO_2 reduction and Boudouard reactions. Higher values of WPR shift the equilibrium of CO reduction and CO_2 reduction reactions towards left resulting in reduction in carbon formation. At higher temperature, WPR & OPR, CH_4 production drops down which in turn reduces the formation of carbon by methane cracking reaction. These observation implies that higher temperature, WPR & OPR values may reduce the undesired carbon formation to a great extent.
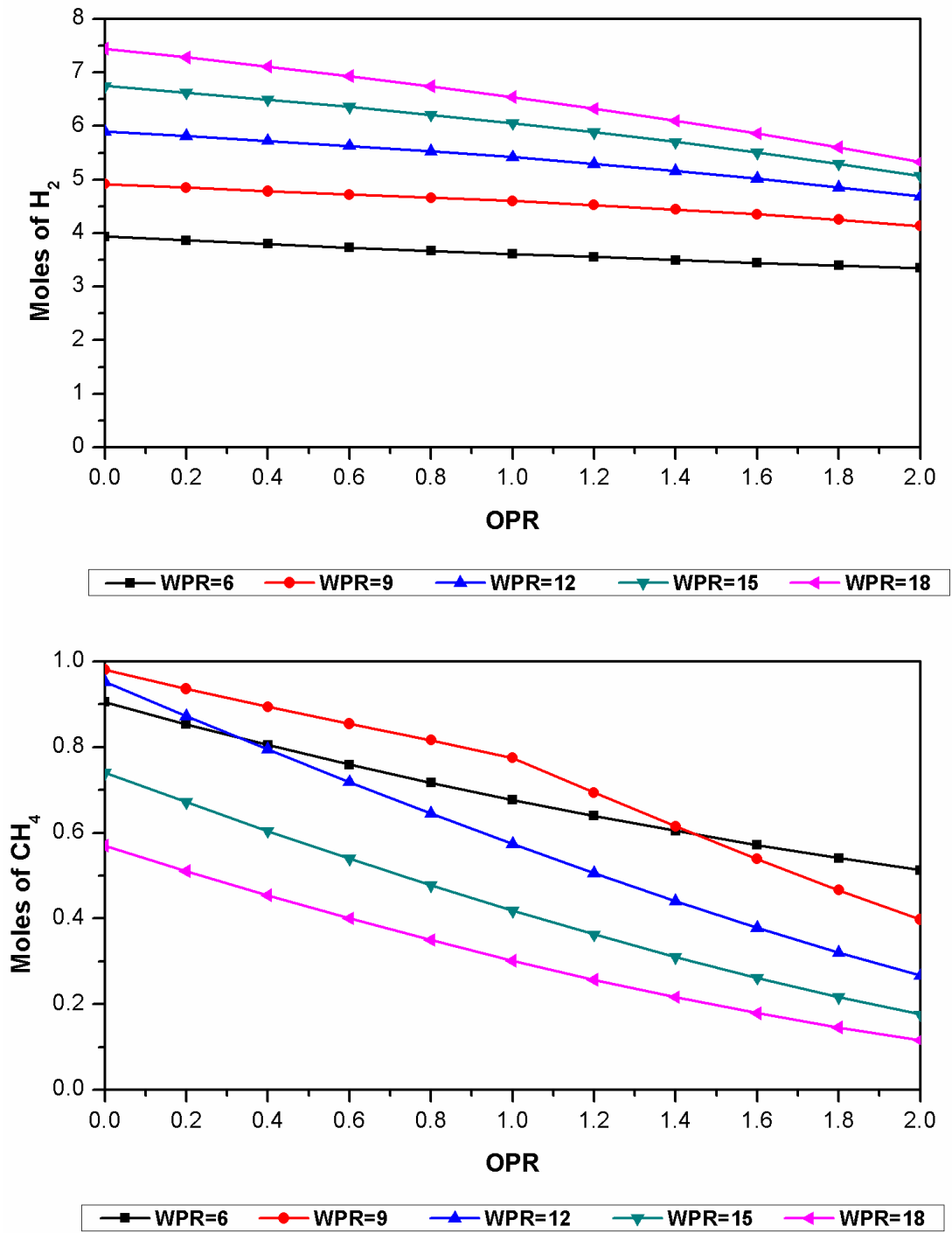
Fig. 4.6 Variation in H_2 and CH_4 production by OSRP with OPR and WPR at 800K and 1 atm pressure.
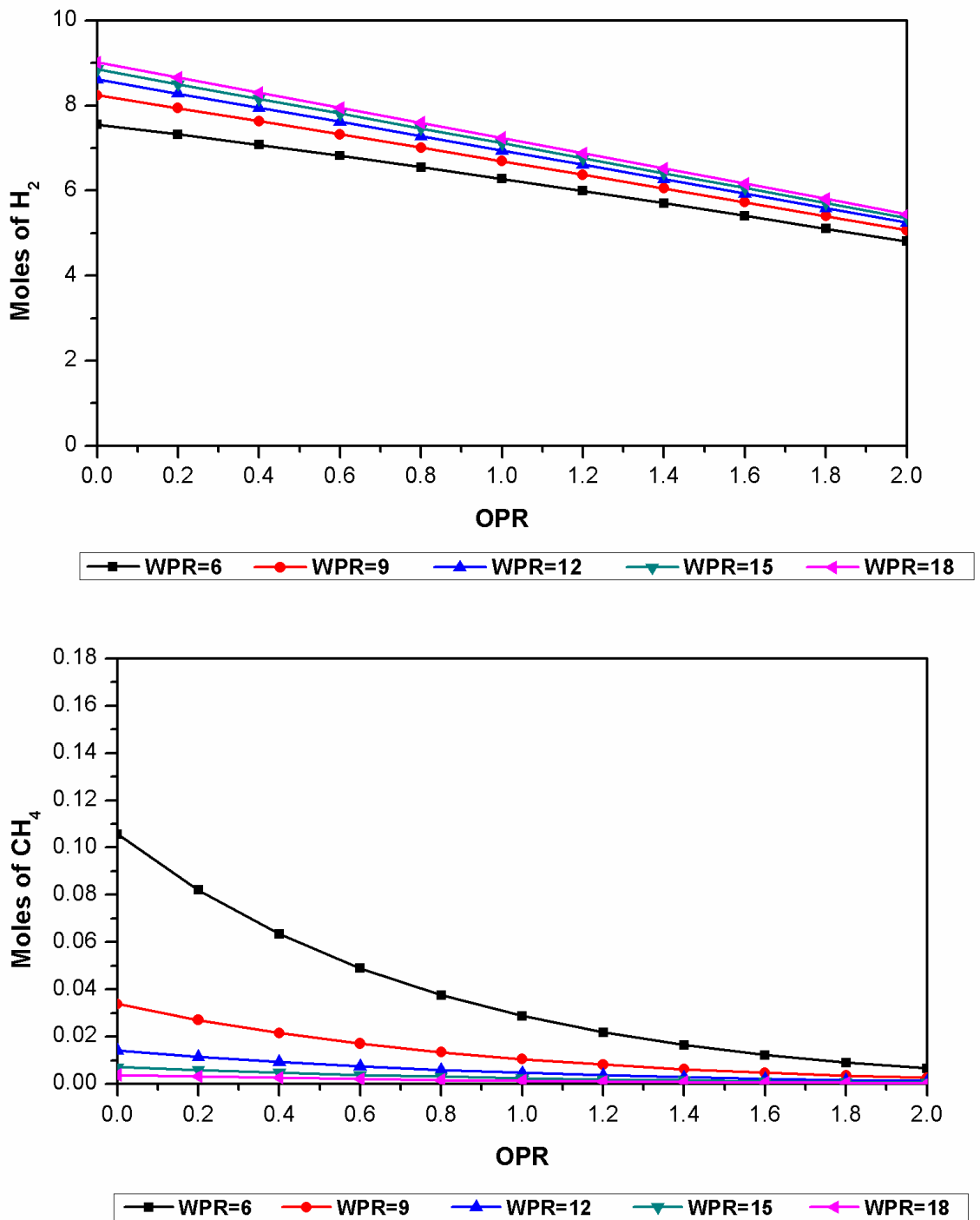
Fig. 4.7 Variation in H$_2$ and CH$_4$ production by OSRP with OPR and WPR at 1000K.
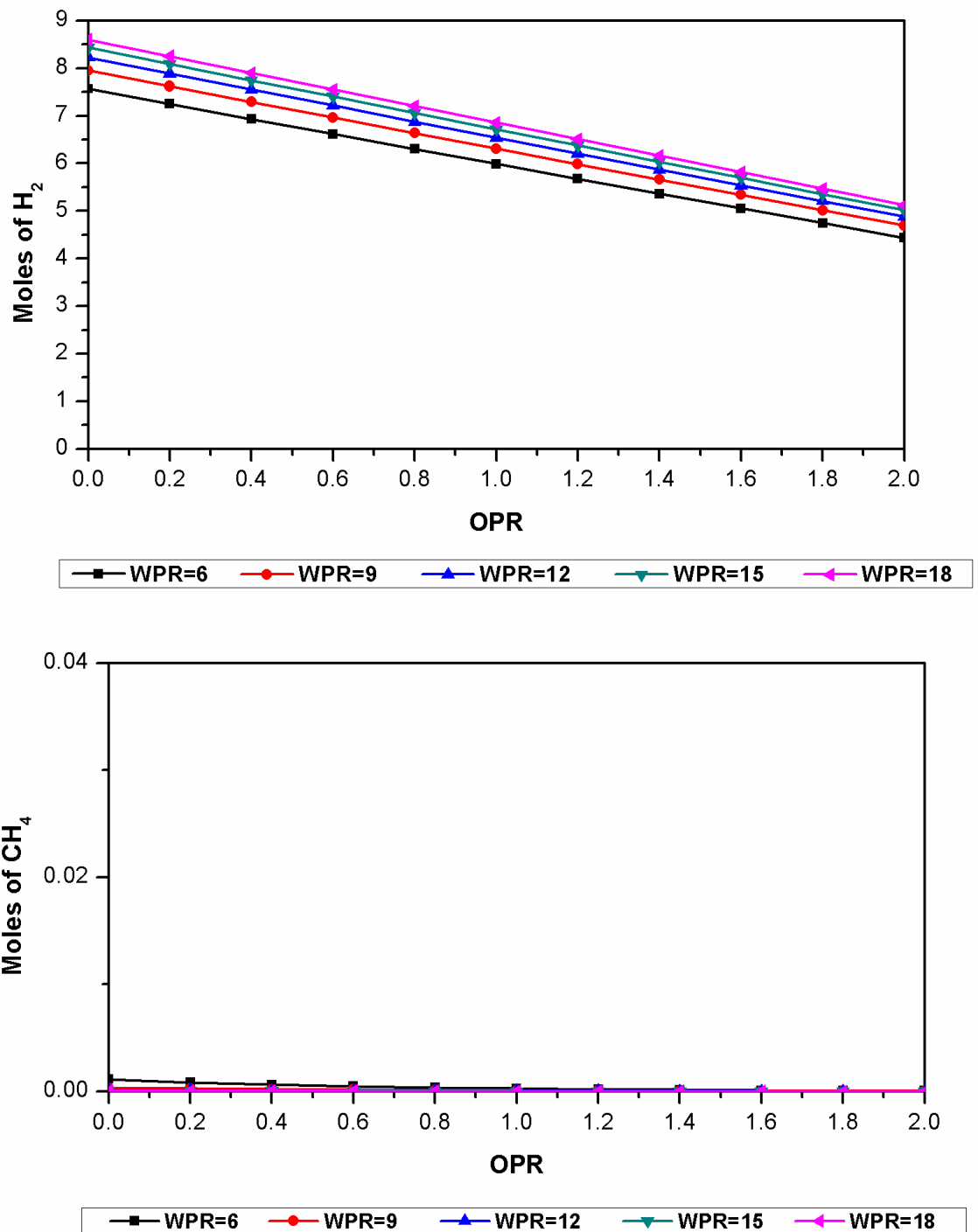
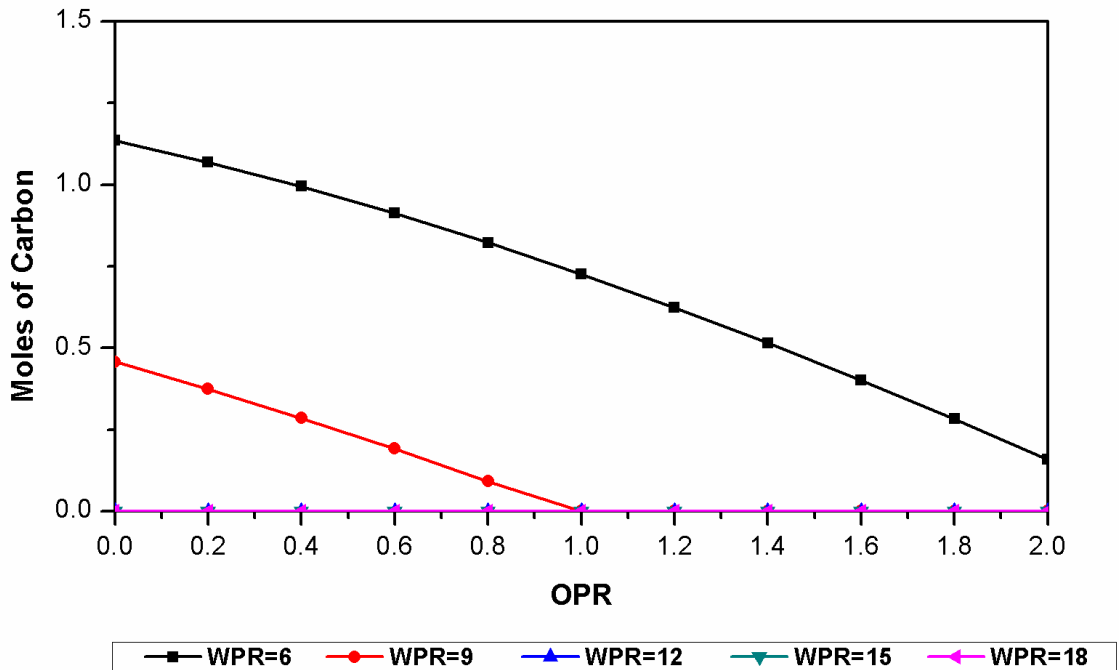**Fig. 4.8 Variation in H_2 and CH_4 production by OSRP with OPR and WPR at 1200K.**
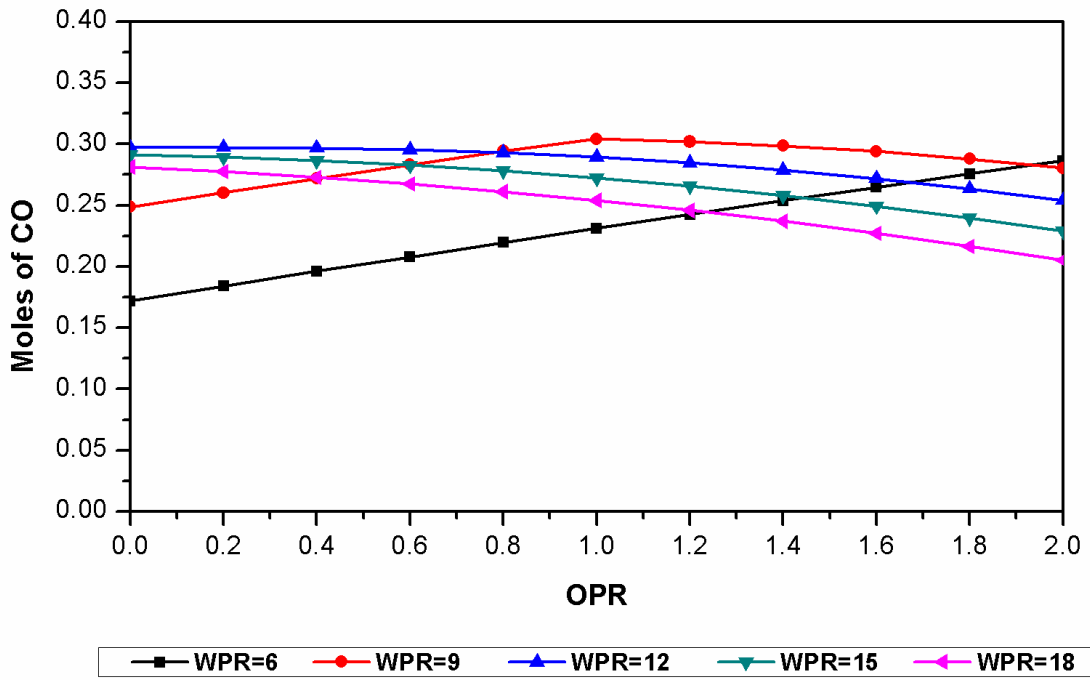
Fig. 4.9 Variation in CO and carbon production by OSRP with OPR and WPR at 800K.
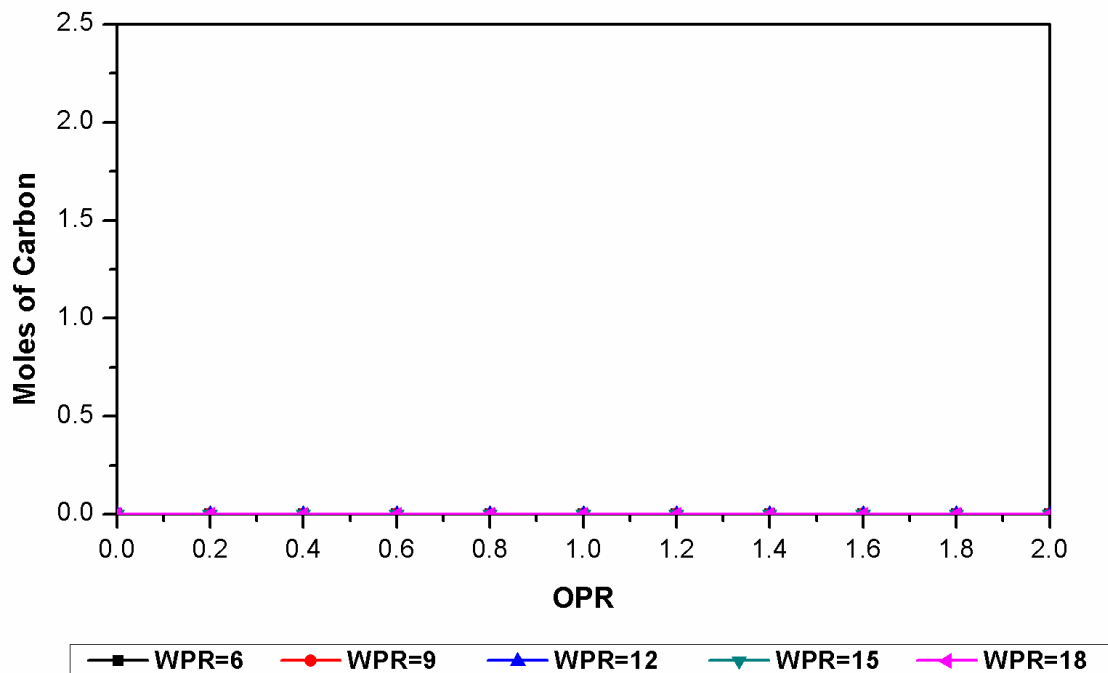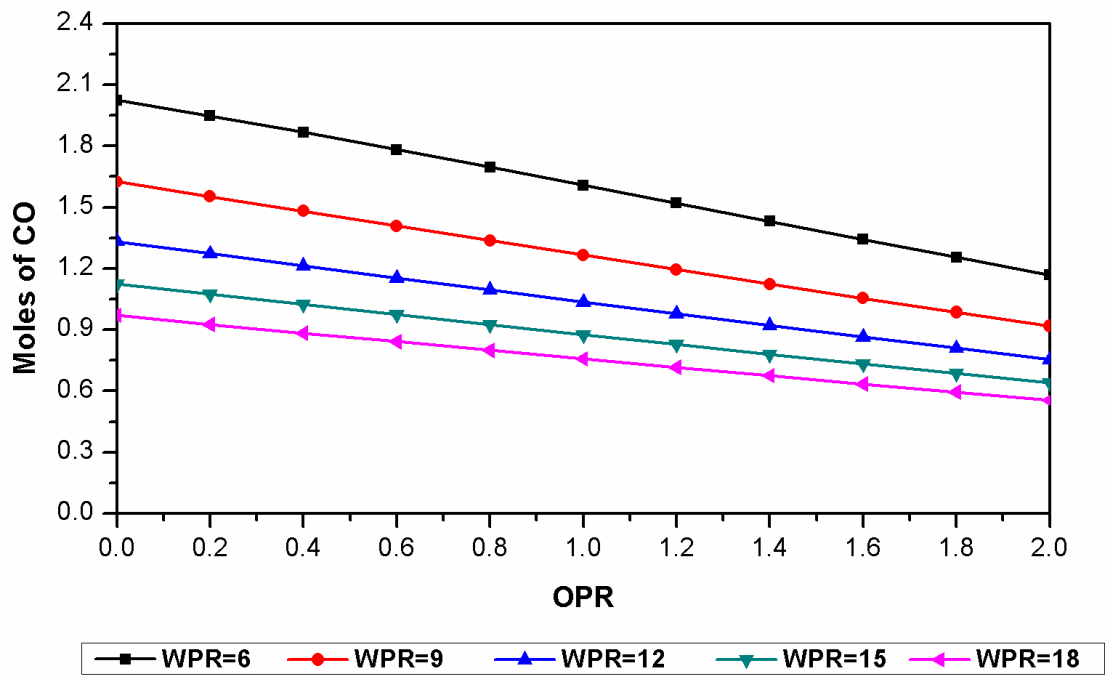
Fig. 4.10 Variation in CO and carbon production by OSRP with OPR and WPR at 1000K.
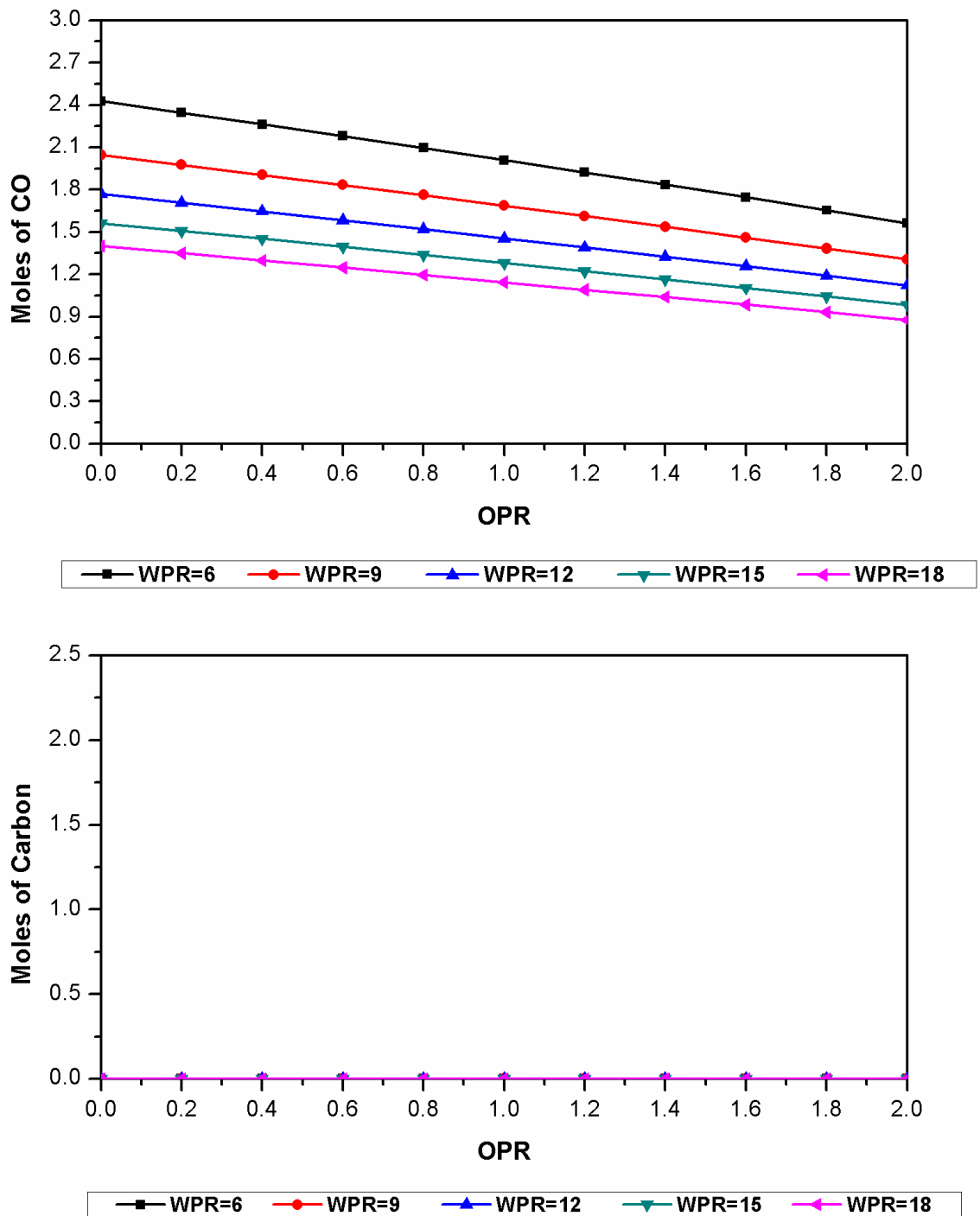
Fig. 4.11 Variation in CO and carbon production by OSRP with OPR and WPR at 1200K.

4.4 STEAM REFORMING WITH H_2 OR CO_2 REMOVAL

The oxidative steam reforming was analyzed with the aim of reducing the required heat energy to carry out endothermic steam reforming of propane. In the previous section, it can be viewed that co-feeding of O_2 with propane and steam reduces the CO, CH_4 and carbon to the great extent but at the expense of desired product H_2. Therefore in this section, the effects have been made to explore the possibility of enhancing the production of H_2 by incorporating thermodynamic concept of insitu fractional removal of H_2 or CO_2 from the product stream of reversible steam reforming reaction. The thermodynamic analysis is carried out at 1 atm pressure, WPR of 12, temperature range of 600-1100K, and fractional removal (f) range of 0-0.99) for both H_2 and CO_2 removal.

Figs. 4.12 and 4.13 depict the variation in H_2 and CH_4 production in SRP with insitu fractional removal of H_2 and CO_2 respectively. Since H_2 and CO_2 are the products, their removal shifts the equilibrium of steam reforming of propane towards more H_2 formation. As a result, moles of H_2 increases with increase in fractional removal and temperature. At 99% removal 9.93 moles of H_2 are produced at relatively low temperature of 750K. This production is very close to theoretical value of 10. Initially, without fractional removal of H_2, the maximum H_2 production of 8.62 (WPR=12) and 9.1(WPR=18) moles have been obtained at temperature of 950K by steam reforming. Thus by insitu fractional H_2 removal, enhanced H_2 production can be achieved at lower temperature and lower WPR value indicating lower energy requirement.

In Fig. 4.13, the effect of insitu CO_2 fraction removal on H_2 production is shown. The moles of H_2 certainly increase with increase in fractional removal and temperature. At 99% removal 9.89 moles of H_2 are produced at 950K and 8.79 moles of H_2 are produced at 800K. On comparing with steam reforming without CO_2 removal, it can be observed that maximum H_2 production of 8.62 (WPR=12) and 9.1(WPR=18) moles have been obtained at temperature of 950K by steam reforming. Hence 150K lower temperature is required for same amount of H_2 production by steam reforming with CO_2 removal.

On comparing results with SRP with CO_2 removal and with H_2 removal, it can be observed that maximum production of H_2 (9.89) moles are obtained at 950K and at 99% CO_2 removal. While 9.93 moles of H_2 are produced at relatively low temperature of 750K at 99% H_2 removal. Thus, it can be concluded that there is no significant advantage of fractional CO_2 removal in comparison to fractional H_2 removal on the production of H_2 as

far as energy required is concerned. The higher production at lower temperature in case of fractional removal of H_2 is caused by equilibrium shift of R1 and R2, whereas in case of removal of CO_2, it is caused by equilibrium shift of only R2 towards H_2 production.

Figs. 4.12 and 4.13 depict CH_4 which is highly undesirable product and highly thermodynamically feasible product, can be suppressed by insitu fractional removal of H_2 and CO_2. The temperature and f values promote the reduction in CH_4 production due to shifting of equilibrium of exothermic methanation reactions (R8 & R9). Although, the reduction in CH_4 with fractional removal of CO_2 is much larger than with fractional removal of H_2, it is apparent from Table 6 that overall production of CH_4 is highly reduced in case of 99% H_2 removal at higher temperature.

Figs. 4.14 and 4.15 illustrates the effect of insitu fractional removal of H_2 and CO_2 respectively on the production of CO and carbon by steam reforming of propane at various temperature, 1 atm pressure and WPR of 12. The CO production increases with temperature but decreases with increase in f values in both cases i.e fractional removal of H_2 and CO_2 . This reduction is attributed to the shifting of equilibrium of WGS (R7) reaction towards more production of H_2 and CO_2. The reduction in CO is quite high in case of fractional removal of CO_2 in comparison to the reduction in case of fractional removal of H_2. From these figures it is clear that CO production can be suppressed to a large extent by carrying out steam reforming reaction at lower temperature (say 700K) and higher fractional removal (99.9%) of H_2 & CO_2. As far as formation of carbon is concerned, higher temperature (>850K) in case of fractional removal H_2 removal, can be used to avoid carbon formation conversely, with fractional removal of CO_2, no carbon formation has been formed at all temperature and f values. The main chemical reactions responsible for carbon formation are given in Table 2. The fractional removal of H_2 and CO_2 suppresses R15 and R16 to produce carbon. Very low production of CO and CH_4 further reduces the carbon production through reactions R14 and R17.

Fig. 4.16 depicts the carbon formation boundaries at temperatures and WPR values during steam reforming of propane with and without fractional removal of H_2 & CO_2. These boundaries indicate the carbon formation and no carbon formation regions. Analyzing these figures, it is evident that coke formation can be avoided by increasing WPR and temperature, and by decreasing fractional H_2 removal with the exception at 99% H_2 removal. In case of fractional CO_2 removal, carbon formation can be avoided at higher

temperature, higher WPR and higher f values. At WPR of 12, no carbon is found at all temperature and fractional CO_2 removal.
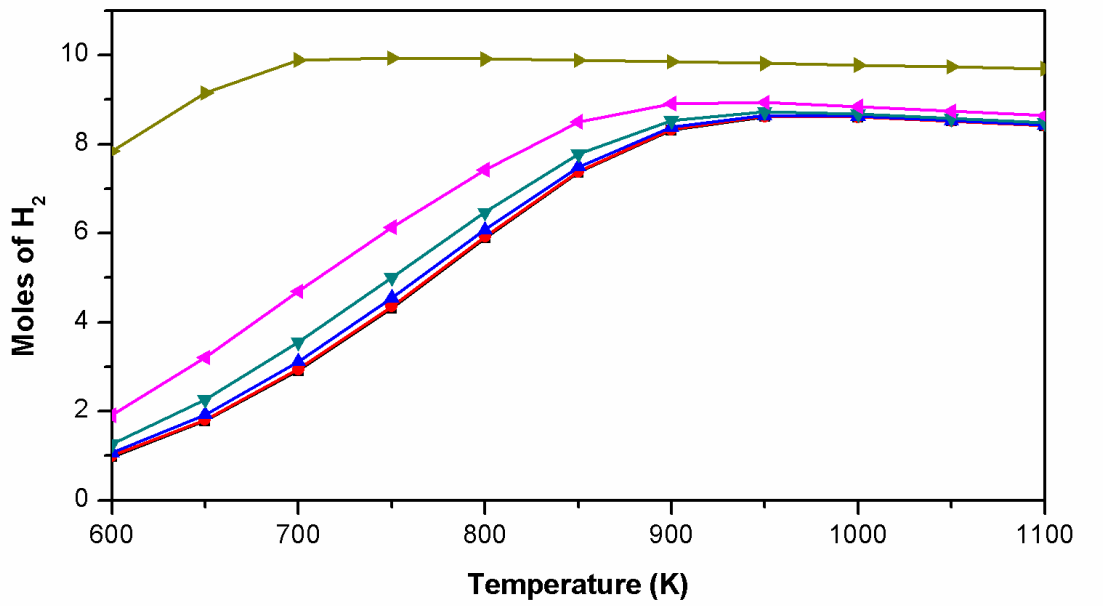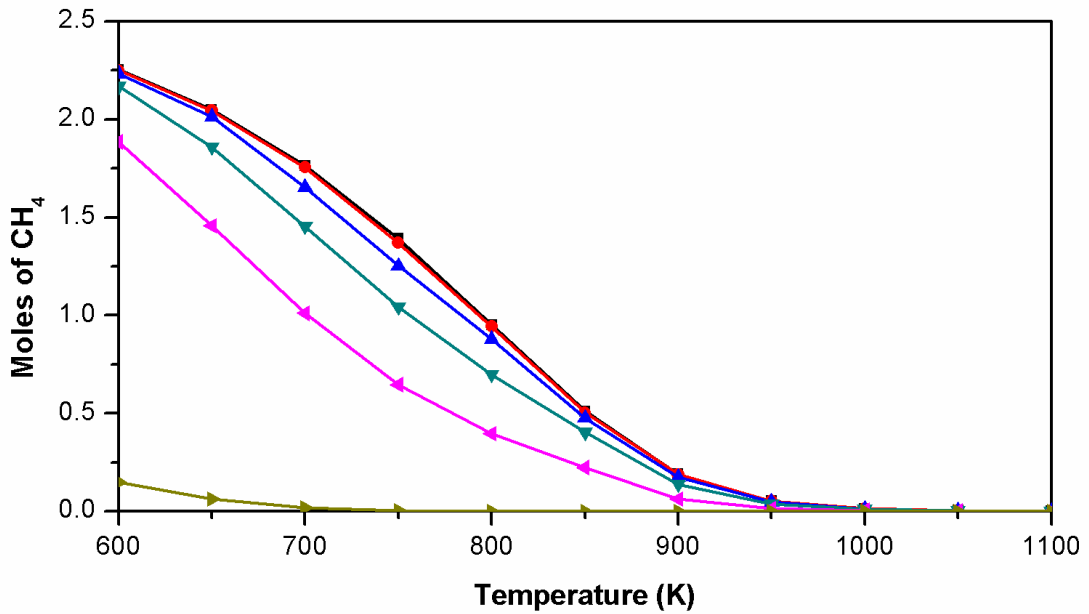
Fig. 4.12 H$_2$ and CH$_4$ production by SRP at WPR=12 with fractional removal of H$_2$.

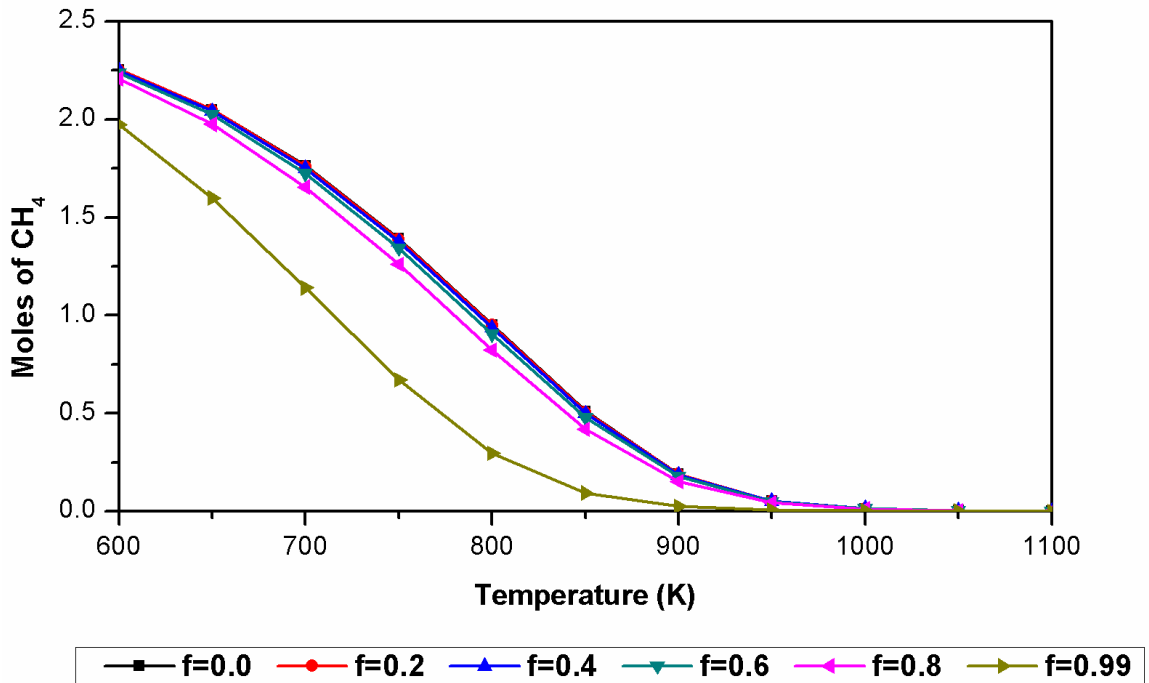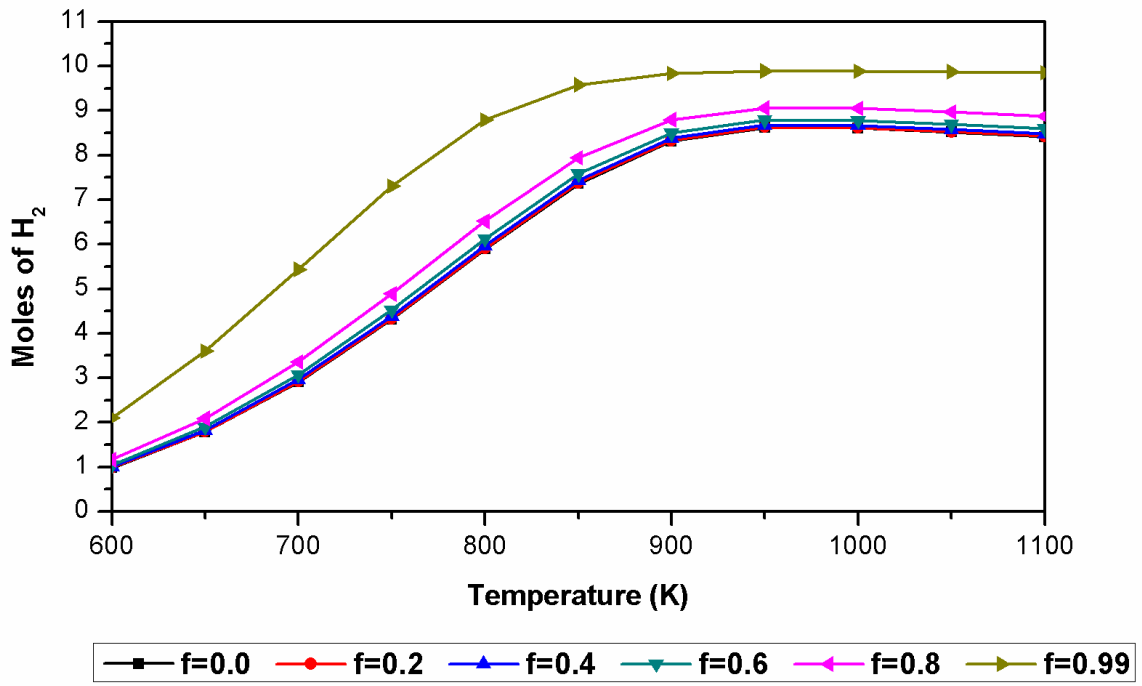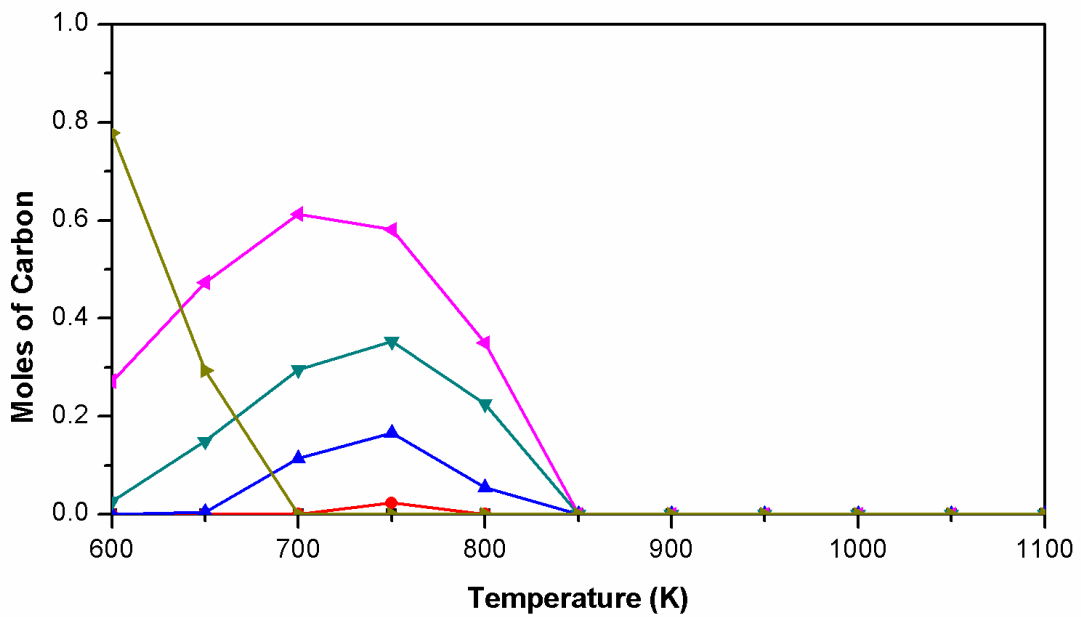**Fig. 4.13 H₂ and CH₄ production by SRP at WPR=12 with fractional removal of CO₂.**
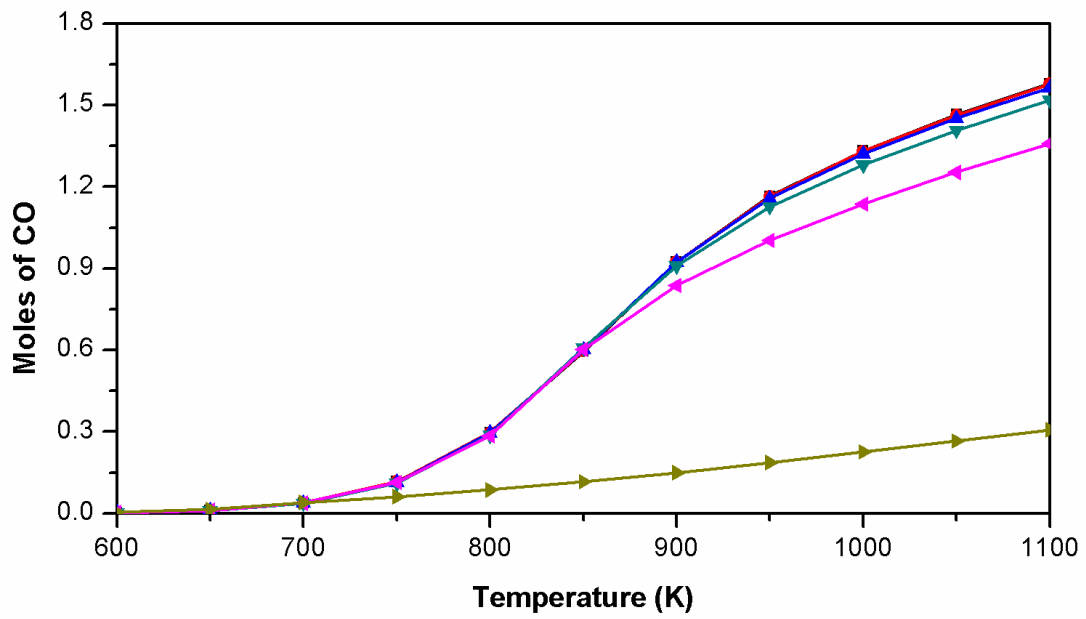
Fig. 4.14 CO and carbon production by SRP at WPR=12 with fractional removal of H$_2$.
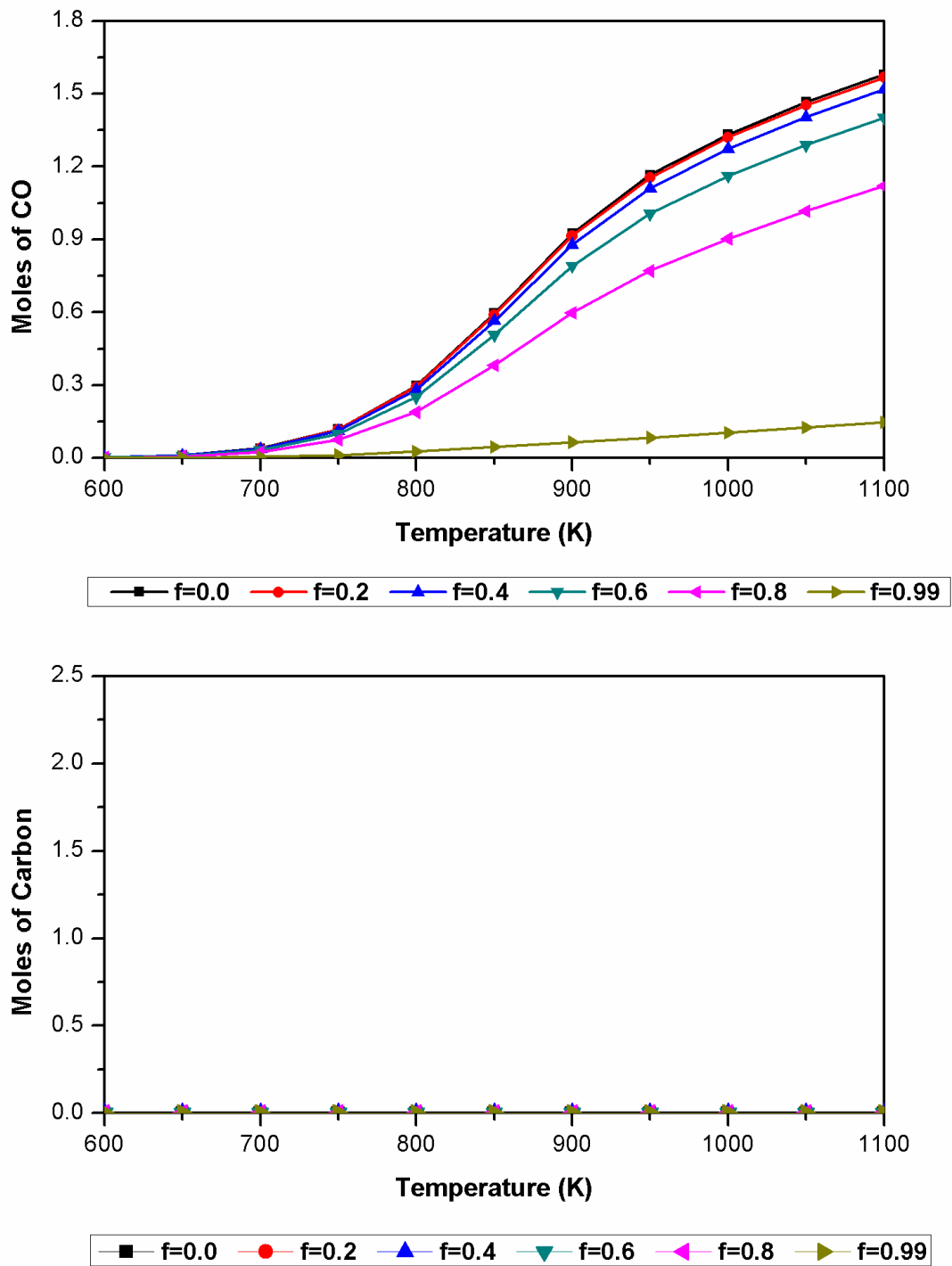
Fig. 4.15 CO and carbon production by DRP at WPR=12 with fractional removal of CO₂.
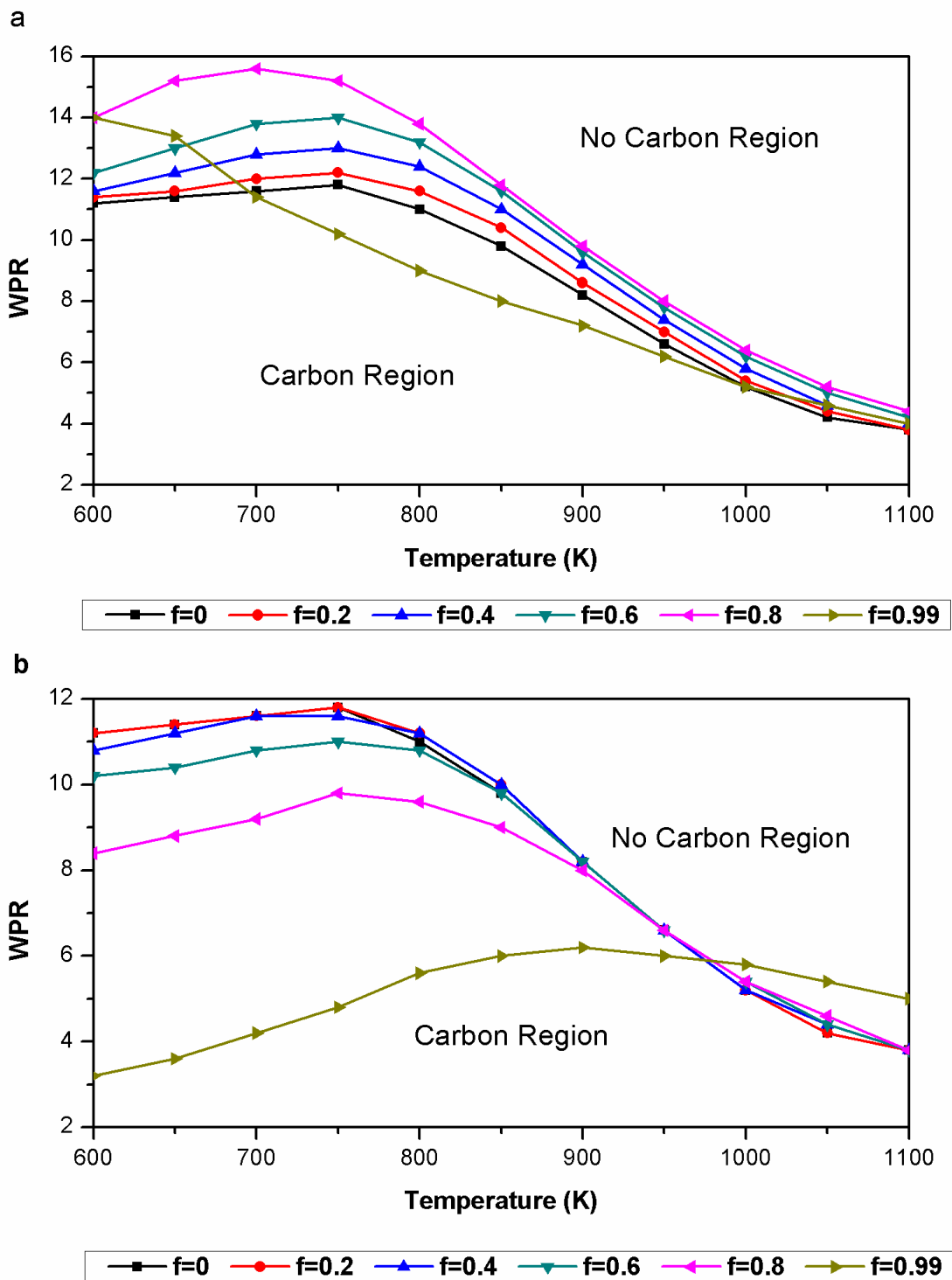
Fig. 4.16 Carbon boundaries for SR (a) with fractional removal of H_2 (b) with fractional removal of CO_2

4.5 DRY REFORMING WITH H_2 REMOVAL

Fig. 4.17 depicts the variation in H_2 and CH_4 production by DRP with insitu removal of H_2 as a function of temperature and fractional removal (f) at CPR=3 and 1 atm pressure. Since H_2 is a product of DRP reaction (R3), according to Le-chatelier's principle removal of one of the product shift the reaction in forward direction, hence removal of H_2 shifts the equilibrium of DRP towards more H_2 production. Moles of H_2 production increases with increase in temperature and fractional removal of H_2 (f). At 99% removal of H_2 and at 900K, 3.86 mol of H_2 can be produced in contrast with 2.56 moles of H_2 production by DRP without removal, at CPR=1, while at CPR=3, 2.16 mol of H_2 produced. At 1100K and for f=0.99, H_2 production reaches very close to theoretical amount of H_2 production i.e 3.97 moles (theoretical amount is 4 mole), Hence removal of H_2, enhances hydrogen production.

CH_4 production decreases in compare to DRP without fractional removal of H_2. For example at CPR=1 and at 600K, CH_4 production by DRP is 1 mol and 0.32 mol at CPR=3 and 600K. While in case of DRP with insitu removal of H_2, at 600K, CPR=3 and with 99% removal of H_2, CH_4 production reduces to 0.023 mol. CH_4 production decreases with increase in temperature and f values. The possible reason for this observation is the methanation reactions (R8 & R9) which are exothermic in nature and H_2 is one of the reactant. Hence high temperature and high f values promote the reduction in CH_4 production.

Fig. 4.18 illustrates the effect of insitu fractional removal of H_2 on the production of CO and carbon by dry reforming of propane at various temperature, 1 atm pressure and CPR=3. CO production increases with temperature at a given values of f and decreases with f value at a given temperature. Though reduction in CO production with f value at a given temperature is negligibly small. Comparing DRP with insitu removal, and DRP without removal, CO production is almost comparable and only slightly less for DRP with insitu removal than DRP without removal.

Carbon production decreases with increase in temperature and f values. At 99% removal of H_2, and at CPR=3, carbon production is less in comparison with DRP without insitu removal of H_2. The possible reason that at low temperature R15 & R16 dominates and since H_2 is one of the reactant, removal of H_2 shifts the reaction in backward direction. At higher temperature, carbon production is similar with DRP and DRP with insitu

removal of H_2. We can conclude that insitu removal of H_2 enhances H_2 production, suppress CH_4 and carbon production and almost does not affect CO production.
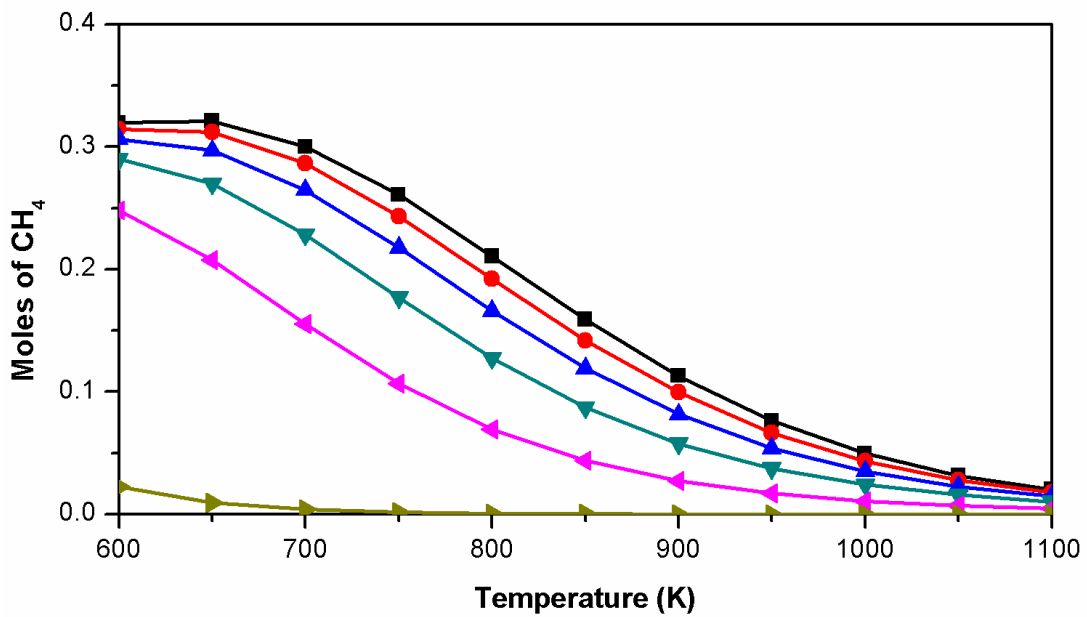
Fig. 4.17 H$_2$ and CH$_4$ production by DRP at WPR=12 with fractional removal of H$_2$.

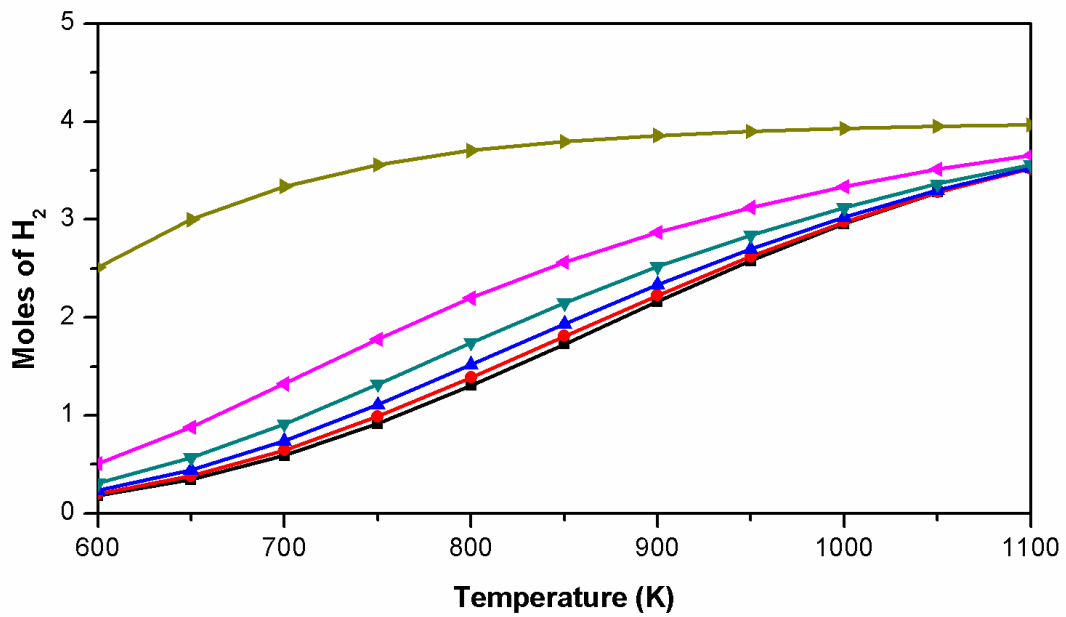**Fig. 4.18 CO and carbon production by DRP at WPR=12 with fractional removal of CO$_2$.**

4.6 SYNGAS

A widely used route to synthesize many chemicals is from syngas which is a blend of CO and H_2. The composition of syngas is expressed in terms of molar ratio of H_2 and CO which plays an important role in determining the product distribution during the reaction process [36]. In most of the synth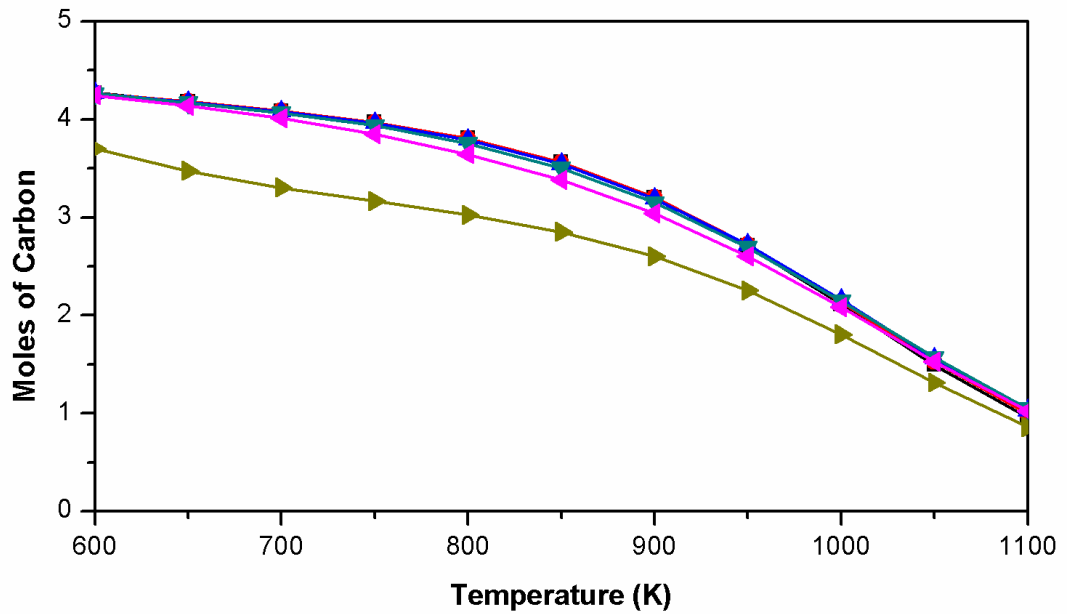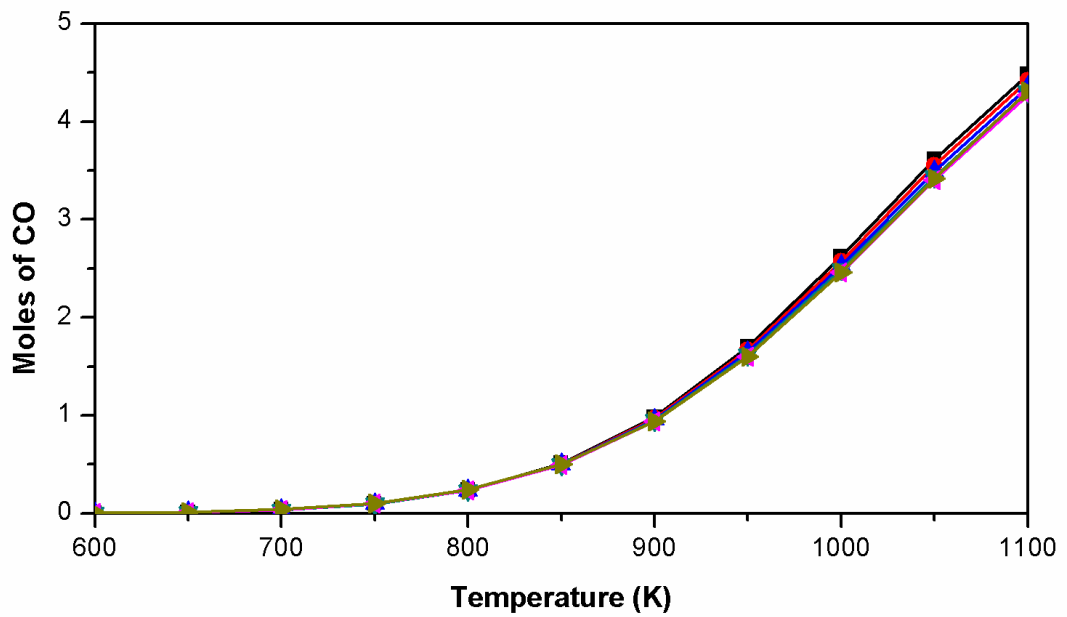esis of chemicals by syngas, the desirable H_2/CO ratio in syngas varies between 1-3 depending upon the desired product and processing technology [36, 37, 38]. Table 4.3 compiles the H_2/CO ratio in reformate gas for all steam and oxidative reforming systems at various operating conditions under consideration. This table provides the suitable range of operating parameter for syngas production.

In SRP, the increase in WPR value results in the higher production of H_2 and lower production of CO (Figs. 4.2 & 4.3) yielding higher value of H_2/CO ratio, low value of H_2/CO ratio can be achieved at higher temperature and low WPR values. For instance, H_2/CO ratio of 2.8 and 3.3 can be obtained at WPR of 3 and 6 respectively and temperature of 1100K. In case of fractional removal of H_2, Table 4.3 gives H_2/CO for retained amount of reformate gas. It can be seen that more H_2 removal and higher temperature are suitable operating conditions for syngas production with low value of H_2/CO ratio but at the expense of low amount of syngas. It is apparent from Table 4.3 shows that low fractional removal of CO_2 and very high temperature may produce syngas with low H_2/CO ratio. Very high temperature is not preferable in the reactor as it may result in hot spots in the reformer [36].

In case of DRP, the H_2/CO ratio is presented in Table 4.4 as a function of CPR, temperature and f values. Table 4.4 shows that the H_2/CO ratio decreases with increase in CPR and in increase in temperature. Main product of DRP is syngas, because it can produce syngas having H_2/CO ratio below 3 at reasonably low temperature and all value of CPR. Depending upon requirement, different value of H_2/CO ratio can be produced for different operating condition. For e.g. if H_2/CO ratio of 2 is required, then it can be achieved at CPR=3 and 900K or CPR=7 and 800K. If H_2/CO ratio=1 required then it can be achieved at CPR=3 and 1000K and CPR=7 and 900K. So, high CPR will fulfil the ratio demand at low temperature.

In case of DRP with insitu fractional removal of H_2, H_2/CO ratio decreases in retained gas with f values at a fixed temperature, but quantity of syngas will reduce. Hence

syngas having H_2/CO ratio below 3 can be obtained at low temperature, but at the expense of low amount of syngas.

Further, in case of OSRP, the H_2/CO ratio is presented in Table 4.5 as a function of WPR, OPR and temperature. The co-feeding of O_2 with propane produces H_2/CO ratio lower than that obtained from SRP. The increase in OPR value in the feed results in reduced production of H_2 and CO and higher production of CO_2 and H_2O which consequently gives lower values of H_2/CO ratio. The increase in temperature at one value of OPR and WPR decreases H_2/CO ratio. H_2/CO ratio less or approximately equal to 3 can be obtained at temperature of 1000K (WPR=3, OPR>0.2) and temperature of 1200K (WPR<9, OPR $\geq$ 0.2). These observations lead to the conclusion that high temperature $\geq$1000K, WPR $\leq$ 6 and OPR $\geq$ 0.2 are the optimum operating conditions for synthesis gas production with suitable H_2/CO ratio by SRP and OSRP reforming systems. Other operating conditions can be applied to produce high yield of H_2 with low yield of CO, CH_4 and carbon.

Table 4.3

H$_2$/CO ratio in syngas for steam reforming with and without removal of products.

SRP without removal				
	WPR			
Temperature (K)	3	6	9	12
600	738.17	483.27	395.89	388.26
700	139.87	94.36	79.21	74.61
800	32.41	22.89	19.75	19.84
900	9.58	7.13	7.05	8.99
1000	4.20	3.73	5.07	6.45
1100	2.81	3.33	4.33	5.32

f / T	SRP with H$_2$ fractional removal					SRP with CO$_2$ fractional removal				
	0.2	0.4	0.6	0.8	0.99	0.2	0.4	0.6	0.8	0.99
600	314.8	248.45	189.26	140.67	20.57	395.8	426.3	508.99	784.4	9203.9
700	60.06	48.68	37.31	24.11	2.49	75.87	80.98	94.79	139.9	1371.9
800	15.9	12.29	9.01	5.21	1.14	20.12	21.27	24.39	34.59	329.4
900	7.2	5.44	3.74	2.12	0.65	9.1	9.54	10.74	14.69	151.74
1000	5.17	3.92	2.71	1.55	0.43	6.52	6.8	7.55	10.02	95.39
1100	4.26	3.23	2.23	1.27	0.31	5.37	5.58	6.13	7.92	67.09

Table 4.4

H$_2$/CO ratio in syngas for dry reforming with and without removal of H$_2$.

Temperature(K)	Dry reforming of propane (DRP) Without removal CPR				
	1	3	5	7	9
600	346.45	61.97	30.16	19.59	14.44
650	154.69	30.99	15.71	10.37	7.71
700	74.65	16.61	8.75	5.88	4.41
750	37.93	9.37	5.13	3.50	2.65
800	20.10	5.51	3.12	2.17	1.66
850	11.23	3.39	1.98	1.40	1.08
900	6.73	2.20	1.31	0.94	0.73
950	4.43	1.51	0.92	0.66	0.52
1000	3.23	1.13	0.69	0.50	0.39
1050	2.61	0.91	0.55	0.42	0.35
1100	2.29	0.79	0.50	0.39	0.33

Temperature(K)	With removal of H$_2$ at CPR=3 Fractional removal (f)				
	0.2	0.4	0.6	0.8	0.99
600	55.17	48.74	42.31	34.45	7.60
650	27.39	23.88	20.21	15.43	2.40
700	14.54	12.47	10.22	7.26	0.86
750	8.10	6.82	5.40	3.58	0.34
800	4.71	3.89	2.98	1.86	0.15
850	2.86	2.32	1.73	1.03	0.08
900	1.83	1.46	1.06	0.61	0.04
950	1.25	0.99	0.70	0.39	0.02
1000	0.93	0.72	0.50	0.27	0.016
1050	0.74	0.57	0.39	0.21	0.012
1100	0.64	0.49	0.33	0.17	0.009

Table 4.5

H$_2$/CO ratio in syngas for oxidative steam reforming.

	Oxidative steam reforming of propane (OSRP)			
	1000 K			
	WPR			
OPR	3	6	9	12
0.2	3.73	3.76	5.11	6.51
0.4	3.06	3.83	5.20	6.60
1.0	2.60	3.90	5.29	6.70
1.4	2.62	3.98	5.38	6.80
1.8	2.70	4.07	5.48	6.90
2.0	2.73	4.12	5.53	6.95
	1200 K			
	WPR			
OPR	3	6	9	12
0.2	2.31	3.10	3.86	4.61
0.4	2.25	3.03	3.80	4.55
1.0	2.20	3.00	3.74	4.49
1.4	2.15	2.92	3.68	4.43
1.8	2.10	2.87	3.63	4.38
2.0	2.07	2.84	3.60	4.35

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

In view of aforementioned results and discussion, following conclusion are drawn.

- High temperature, high WPR favours H_2 production by SRP, and the optimum condition for H_2 production is 950K and WPR=12. Under this condition CH_4 and carbon production suppressed to negligible amount and the CH_4 being only impurity.

- 99% fractional removal of H_2 reduces 200K temperature for maximum amount of H_2 production and produce 1.31 more moles of H_2 at WPR=12 in compare to SRP without removal of H_2. At this condition CO, CH_4 and carbon production is negligible and almost pure hydrogen can be produced.

- 99% fractional removal of CO_2 reduces 150K temperature for almost same amount of H_2 produced by SRP without removal of CO_2. At 950K, 1.27 more moles of H_2 can be produced and this condition also minimizes CO, CH_4 and carbon at the expense of energy.

- In terms of H_2 production, fractional removal of H_2 is more beneficial than CO_2 removal because it can produce high amount of H_2 at low temperature.

- In case of OSRP , high temperature, high WPR and low OPR favours H_2 production. Low temperature, high OPR and high WPR are most suitable operating conditions for minimization of CO and high temperature, WPR & OPR values may reduce the undesired CH_4 and carbon formation to a great extent.

- DRP is not suitable for H_2 production since it produces only 3-4 moles of H_2 per mole of propane.

- The main product of DRP is syngas. It can produce different H_2/CO ratio in large range of temperature and CPR conditions. SRP with fractional removal of H_2 and CO_2 produce syngas having H_2/CO ratio below 3 but at the expense of low amount of syngas. In case of OSRP, high temperature, low WPR and high OPR are the optimum condition for syngas production with suitable H_2/CO ratio. At these conditions OSRP can produce high amount of syngas.

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5.2 RECOMMENDATIONS

The thermodynamic equilibrium calculations can be performed via two approaches: stoichiometric approach and non stoichiometric approach. Non stoichiometric approach has been used in this study. It has its own advantage over stoichiometric approach. However, stoichiometric approach has also its advantage over non stoichiometric approach. Apart from equilibrium compositions of species, stoichiometric approach also tells about the extent of each reaction. Hence it is recommended that thermodynamic analysis of propane should also be carried out by stoichiometric approach.

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