Review on Innovative Catalytic Reforming of Natural Gas to Syngas

Salwa A. Ghoneim*, Radwa A. El-Salamony, Seham A. El-Temtamy

Egyptian Petroleum Research Institute, Cairo, Egypt
Email: *Salwaghoneim70@yahoo.com

Abstract

Decreasing supplies of high quality crude oil and increasing demand for high quality distillates have motivated the interest in converting natural gas to liquid fuels, especially with the present boom in natural gas proven reserves. Nevertheless, one major issue is the curtailment of costs incurred in producing synthesis gas from natural gas, which account for approximately 60% of the costs used in producing liquid fuels. While there are three main routes to convert natural gas to syngas: steam reforming (SMR), partial Oxidation (POX) and auto-thermal reforming (ATR). Significant new developments and improvements in these technologies, established innovative processes to minimize greenhouse gases emission, minimize energy consumption, enhance syngas processes, adjust the desired H_2/CO ratio and change the baseline economics. This article reviews the state of the art for the reforming of natural gas to synthesis gas taking into consideration all the new innovations in both processes and catalysis.

Keywords

1. Introduction

In the last few years, natural gas, a non-renewable energy source of primary energy, has been utilized as a feed stock for several industrial high value-added productions and also as environmentally clean and easily transportable fuel due to its abundance and enormous surplus in remote areas and underground resources. The use of natural gas causes a rise in global concentration of green house gases [1]. According to the studies of Mackenzie and Mackenzie (1995), the contribution of CH_4 and CO_2 accounts for three quarters of the total greenhouse effect [2]. In this regard, therefore, extensive efforts are being made to convert greenhouse gases into high valuable products such as syngas and high purity hydrogen.

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*Corresponding author.

Searching for alternative energy sources to replace petroleum based fuels, natural gas has attracted the interest of many researchers and the large amount of methane contained in natural gas has been considered as an input in the production of other high-value products such as syngas and high purity hydrogen.

Syngas, a mixture of H_2 and CO, forms the feed stock in the chemical and petrochemical industries for the production of methanol, acetic acid, olefins, gasoline, MTBE, Oxo-alcohols, phosgene and synthetic liquid fuels, etc.

In some cases either H_2 or CO is utilized, for which H_2 and CO are acquired from synthesis gas. The hydrogen is used in fuel cells, in the production of urea and heavy water, etc. However, the biggest consumer of H_2 from syngas is ammonia synthesis. Recently it is being planned to utilize the hydrogen as a fuel for non-polluting vehicle. The carbon monoxide is used in the production of paints, plastics, pesticides, insecticides, acetic acid and ethylene glycol, etc.

For the production of clean fuel like hydrogen to be utilized in fuel cells from natural gas, it is first necessary to bring natural gas to a catalytic process called natural gas reforming. This catalytic process is also known as reforming of methane. Syngas can be produced from a variety of primary feedstock such as coal, petroleum coke, biomass, and natural gas. The lowest cost routes for syngas production, however, are based on natural gas [3]. The primary feedstock and reaction routes of syngas production determine the H_2:CO molar ratio of the syngas (also called syngas ratio), which is important as different end products require different syngas ratios. In general, for DME production, a syngas ratio of 1 is needed, whereas in the case of Fischer-Tropsch synthesis, the required syngas ratio varies from 1 to 2.1 depending on the catalyst and pressure used [4]. Natural gas reforming is based on a catalytic chemical reaction that aims to convert methane, the main constituent of natural gas, to a mixture of hydrogen and carbon monoxide. This mixture of gases (H_2 + CO), the product of natural gas reforming, is called syngas. Syngas is commonly used in the synthesis of important products.

Figure 1 shows the different indirect routes for the production of chemicals from methane via synthesis gas.

2. Reforming of Natural Gas

Natural gas reforming also known as reforming of methane can be accomplished by means of an exothermic or endothermic reaction depending on the chemical process selected to perform the catalytic reforming of methane.
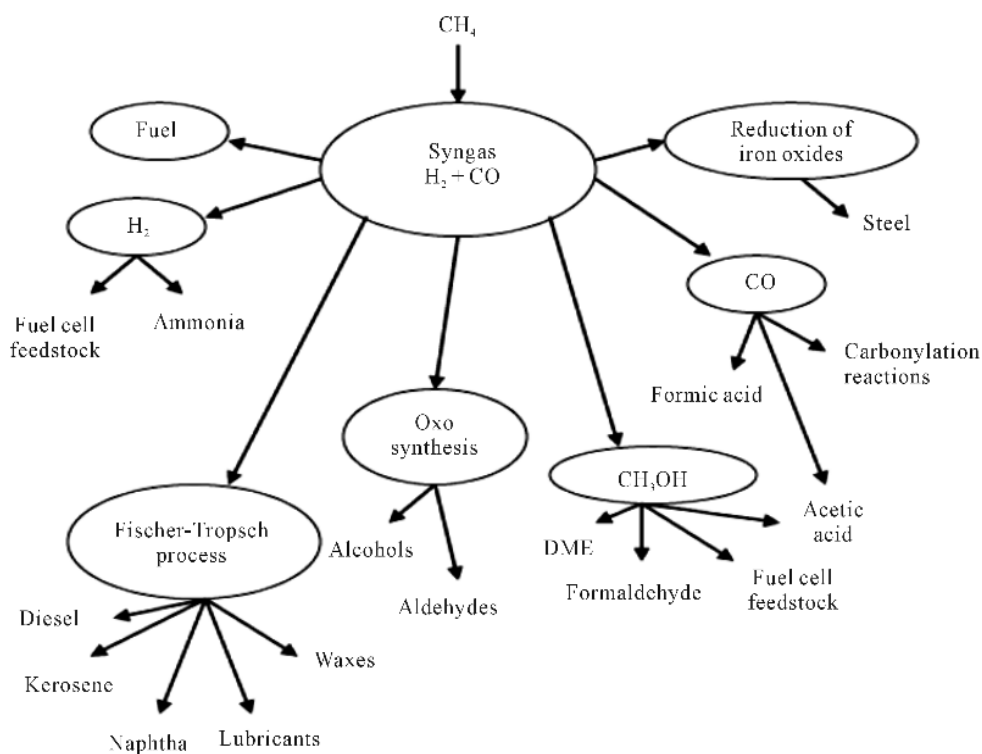
Figure 1. Various indirect routes for the production of useful chemicals from natural gas.

There are seven reforming processes available for the production of syngas from natural gas, whose major component is methane. These are:
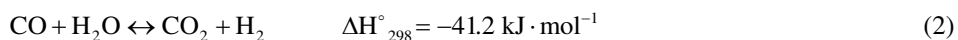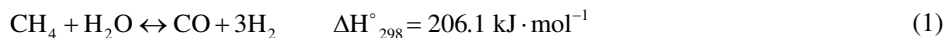
1) Steam Reforming (SMR),
2) Partial Oxidation (POX),
3) Auto Thermal reforming, (ATR),
4) Dry Reforming of methane (DMR),
5) Combined Reforming of methane (CMR),
6) Reforming with Membrane,
7) Tri-reforming of Methane (TMR).

While the top three methods are well established and are widely employed by industry the last four methods are innovations to minimize greenhouse gases emissions, minimize energy consumption and improve the reforming process yields. These methods differ in the composition of syngas produced *i.e.* their H_2/CO ratio as shown in **Figure 2**.
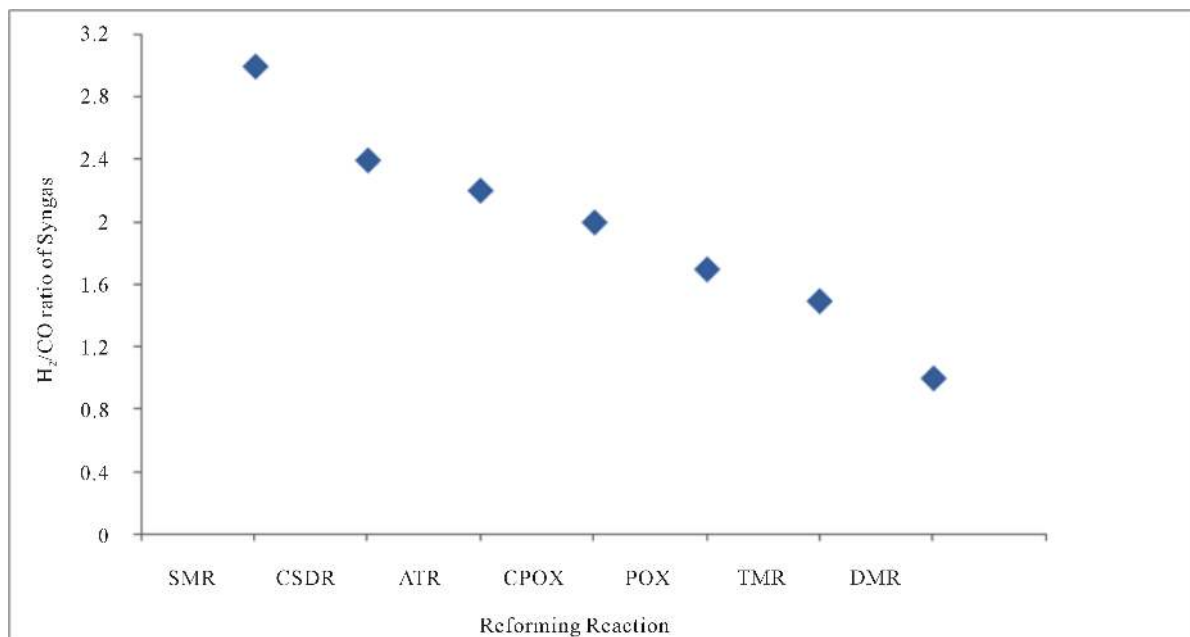
2.1. Steam Reforming

Steam reforming or steam methane reforming (SMR) is the reaction where steam and hydrocarbons, such as natural gas or refinery feed stock, react in a reformer at temperature of 800°C - 900°C and moderate pressure (around 30 bar) in the presence of metal based catalyst for the production of syngas [5]. Syngas reacts further to give more hydrogen and carbon dioxide via the water gas shift (WGS) reaction, which is a side reaction in steam reforming. Steam reforming of natural gas produces syngas with a H_2:CO molar ratio close to 3.

Figure 3 illustrates the tubular steam reformer of Linde Company [6].

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H°_{298} = 206.1 \text{ kJ} \cdot \text{mol}^{-1} \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H°_{298} = -41.2 \text{ kJ} \cdot \text{mol}^{-1} \tag{2}$$

Most SMR units include two sections, namely a radiant and a convective section. Reforming reactions take place inside the radiant section. In the convective section, heat is recovered from the hot product gases for preheating the reactants feeds and for generating superheated steam.

Because the process of steam reforming of methane is the reforming process that leads to obtaining syngas with the highest H_2/CO ratio, this type of reforming process is considered ideal to obtain a hydrogen gas flow of

Figure 2. H_2/CO ratio of syngas from various syngas generators.
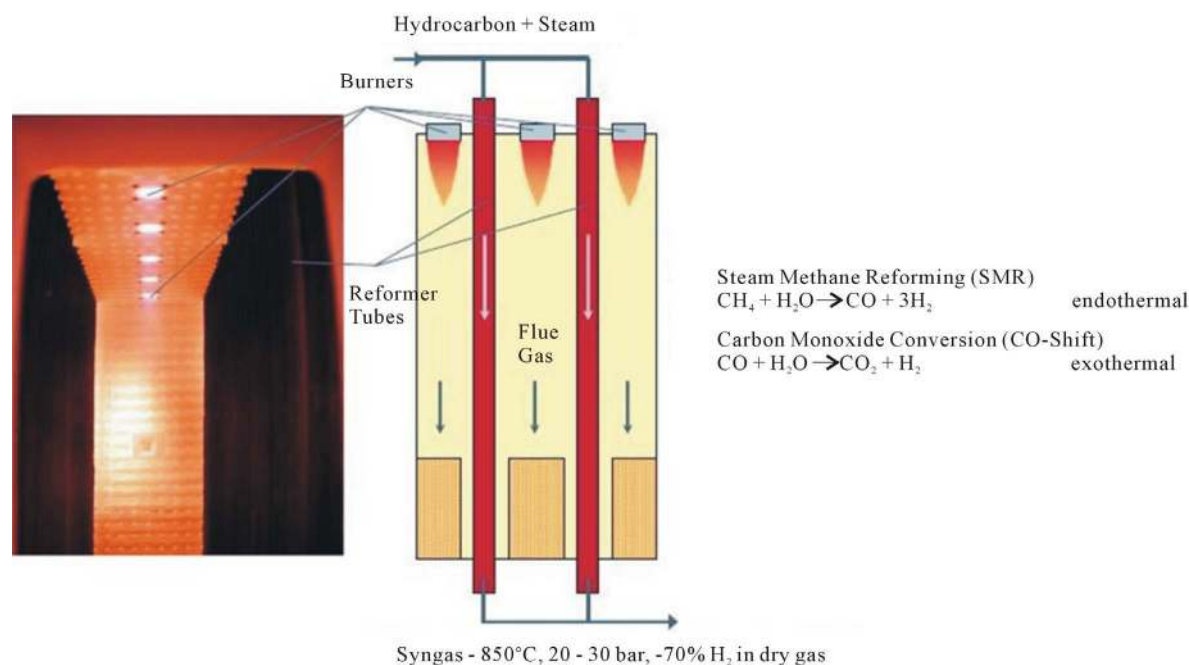
Figure 3. Tubular steam reformer [6].

high purity from syngas. It is the most widely applied method of producing syngas from natural gas and represents 50% of the global processes of conversion of natural gas for hydrogen production. This percentage reaches 90% in the U.S. Steam reforming of methane is an endothermic process and, therefore, requires very high temperatures, which makes this process very expensive.

Innovated Steam Reformer

Heat Exchange Reformers

Basically, a heat exchange reformer is a steam reformer where the heat required for the reaction is supplied predominantly by convective heat exchange. The heat can be supplied from flue gas or process gas or in principle by any other available hot gas. When the heat and mass balance on the process (catalyst) side only is considered, there is no difference between heat exchange reforming and fired tubular reforming, where the heat transfer is predominantly by radiation. This means that all process schemes using heat exchange reforming will have alternatives where the function of the heat exchange reformer is performed in a fired reformer. The process schemes differ "only", in the amount of heat in flue gas and/or process gas and in the way this heat is utilized.
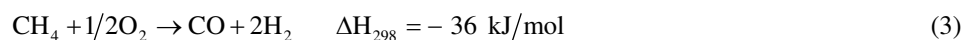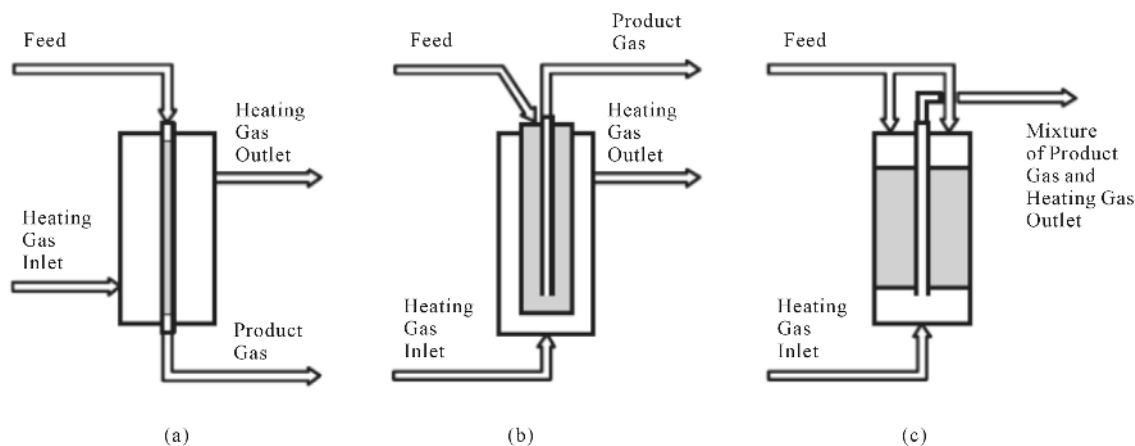
Types of heat exchange reformers

Three different concepts for heat exchange reformer design have been commercialized by various companies. The three concepts are illustrated in **Figure 4**.

Types A and B in **Figure 4** can be used with all types of heating gas, whereas type C can only be used when the desired product gas is a mixture of the heating gas and the reformed product gas.

2.2. Partial Oxidation POX and CPOX

It occurs when a sub-stoichiometric fuel-air mixture is partially combusted in a high temperature reformer [8], and it produces hydrogen rich syngas. Partial oxidation is an exothermic reaction and, thus, considered more economic than the processes of steam reforming or dry reforming, because it requires a smaller amount of thermal energy. On the other hand, the partial oxidation is considered an expensive process because it requires a flow of pure oxygen. Thus, there is a warning of danger inherent in the process of partial oxidation of methane, since the two reagents (CH_4 and O_2) can cause an explosion if the reaction is not conducted with the necessary care [9].

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad \Delta H_{298} = -36 \text{ kJ/mol} \qquad (3)$$

Figure 4. Different types of heat exchange reformer [7].

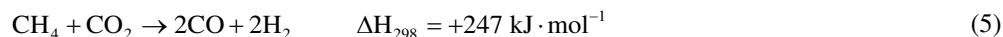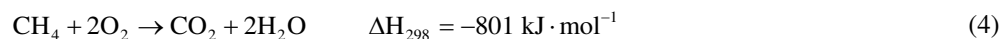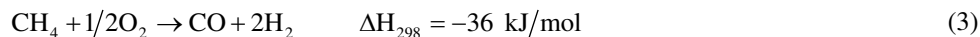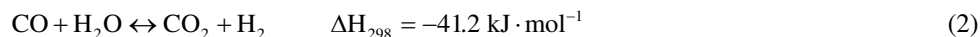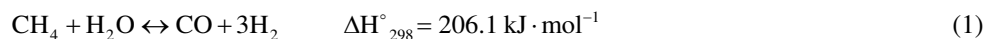The reactor design of POX and CPOX is presented as a scheme in **Figure 5**.

POX reactor simply comprises two zones, first the flame part where the hydrocarbons, oxygen, and possibly low amounts of steam react together and second a heat exchanger that recovers the excess heat after the reaction.

In non-catalytic partial oxidation, the production of syngas depends on the air-fuel ratio at operating temperature of 1200°C - 1500°C without a catalyst [10]. A non-catalytic partial oxidation process was developed by Texaco and Shell which results in high syngas yields at high temperature and pressures [11].

The use of catalyst in the production of syngas lowers the required reaction temperature to around 800°C - 900°C [10]. In the CPOX reaction, methane is converted with oxygen (or air) over noble metal (Pt, Rh, Ir, Pd) and non-noble metal (Ni, Co) catalysts to syngas in a single step process. CPOX has been studied extensively during the past decade. Many studies have focused on the reaction mechanism [13]; reactor configurations [14]-[16]; reactor simulations [17] [18] as well as novel catalyst synthesis [19] to improve the process efficiency.

Catalytic partial oxidation can be used only if the sulfur content of natural gas is below 50 ppm. Higher sulfur content would poison the catalyst, so non-catalytic partial oxidation should be used for such fuels.

Two reaction mechanisms have been proposed: one is the "*direct mechanism*" in which CH_4 and O_2 react on the adsorbed state on the catalyst surface to yield CO and H_2 (Equation 3); the second one is the so-called "*combustion-reforming mechanism*". In this latter mechanism, CH_4 and O_2 first form H_2O and CO_2 (Equation 4), and then dry (Equation 5) and steam reforming (Equation 1) reactions producing CO and H_2.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H^{\circ}_{298} = 206.1 \text{ kJ} \cdot \text{mol}^{-1} \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{298} = -41.2 \text{ kJ} \cdot \text{mol}^{-1} \tag{2}$$

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad \Delta H_{298} = -36 \text{ kJ/mol} \tag{3}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H_{298} = -801 \text{ kJ} \cdot \text{mol}^{-1} \tag{4}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H_{298} = +247 \text{ kJ} \cdot \text{mol}^{-1} \tag{5}$$

In addition to these reactions, other side reactions eventually occur. These include

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2 \tag{6}$$

and the formation of solid carbon by the Boudouard reaction

$$2CO \rightarrow C + CO_2 \tag{7}$$

Innovated Catalytic Partial Oxidation
Chemical-Looping Reforming and Combustion

Chemical-looping reforming is a novel process for partial oxidation of hydrocarbon fuel where oxygen is
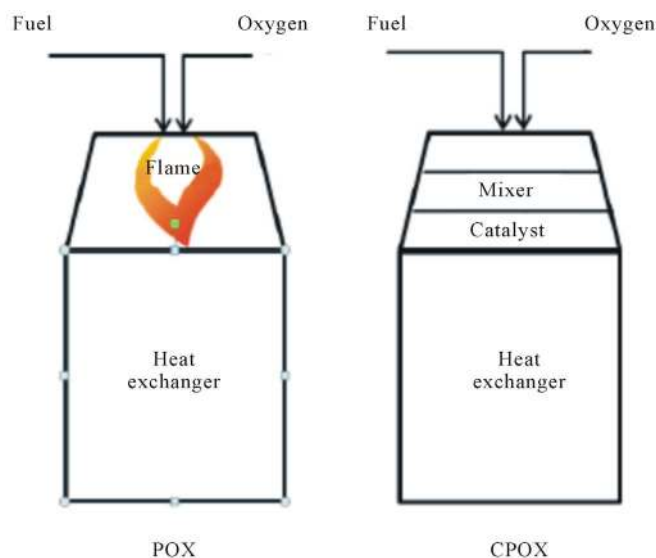
Figure 5. Reactor designs for POX and CPOX [12].

brought to the fuel by a solid oxygen carrier [20]. Chemical-looping reforming has been examined in a laboratory reactor consisting of two interconnected fluidized beds (**Figure 6**). Particles of NiO and $MgAl_2O_4$ were used as bed material, oxygen carrier and reformer catalyst. Natural gas was used as fuel. The reactor temperature was 820°C - 930°C. There was a continuous circulation of oxygen carrier particles between the fluidized-beds. In the fuel reactor the oxygen carrier was reduced by the fuel, which in turn was partially oxidized to H_2, CO, CO_2 and H_2O. In the air reactor the oxygen carrier was re-oxidized with air. Formation of solid carbon was noticed for some cases. Addition of 25 vol% steam to the natural gas reduced the carbon formation substantially. H_2 production by chemical-looping reforming with CO_2 capture has also been examined in a process study, where it was found that an overall efficiency of 81% including CO_2 sequestration is possible.

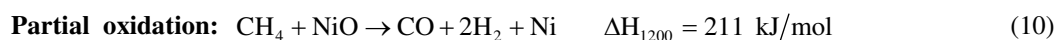**Figure 6** illustrates both chemical-loop reforming and combustion

MeO is the oxygen carrier in its oxidized form while Me is the reduced form.

Suitable oxygen carriers include metal oxides such as Fe_2O_3, NiO, CuO and Mn_3O_4.

If the fuel is CH_4, the oxygen carrier is NiO and the reactor temperature is 1200 K, reaction (8) occurs in the air reactor.

$$\textbf{Regeneration:} \quad Ni + 1/2\,O_2 \rightarrow NiO \qquad \Delta H_{1200} = -234 \;\; kJ/mol \qquad (8)$$

In the fuel reactor, reactions (equations 9, 10, 1 and 5) may occur, depending on the air ratio. Steam or CO_2 could be added to the fuel to enhance the relative importance of reaction (1) or reaction (5) respectively. This could be used to adjust the H_2/CO ratio in produced synthesis gas or to suppress formation of solid carbon in the fuel reactor. For chemical-looping combustion as much fuel as possible should be completely oxidized according to reaction (9).

$$\textbf{Oxidation:} \quad CH_4 + 4NiO \rightarrow CO_2 + 2H_2O + 4Ni \qquad \Delta H_{1200} = 136 \;\; kJ/mol \qquad (9)$$

$$\textbf{Partial oxidation:} \quad CH_4 + NiO \rightarrow CO + 2H_2 + Ni \qquad \Delta H_{1200} = 211 \;\; kJ/mol \qquad (10)$$

Chemical-looping reforming is similar to chemical-looping combustion, but complete oxidation of the fuel is prevented by using low air to fuel ratio. Hence chemical-looping reforming can be described as a method for partial oxidation of hydrocarbon fuels that is utilizing chemical-looping as a source of oxygen. This is a considerable advantage compared to conventional technology since the need for expensive and power consuming air separation is eliminated.

The Short Contact Time-Catalytic Partial Oxidation (SCT-CPO) Technology

Precise knowledge of the mechanism of CPOX reaction is of vital importance because of the different thermal effects, which indeed affect both the design and heat management of industrial units [21].
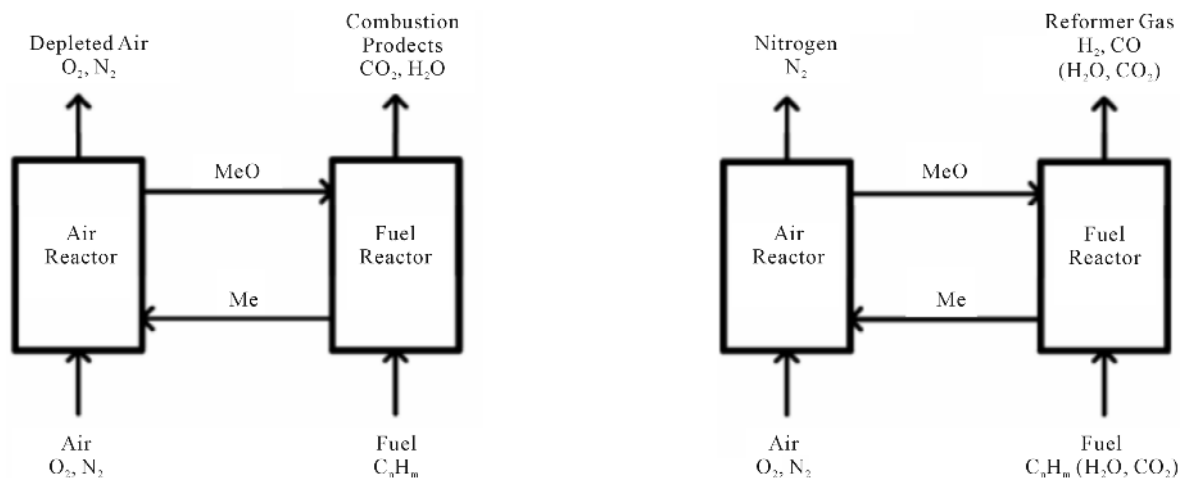
Figure 6. Schematic description of chemical-looping combustion (left) and chemical-looping reforming (right) [20].

Initial observation on the occurrence of short contact time hydrocarbon oxidation processes were reported in the years 1992-1993 [22]. These processes have been deeply studied since then, and the number of scientific articles published every year on this topic, is still high. Hickman and Schmidt [23] [24] demonstrated that near complete conversion of methane to mostly hydrogen and carbon monoxide could be achieved at reaction times as short as 1 ms, promising dramatic reduction in a reactor size and complexity, as compared to existing syngas production technologies.

The fast and selective chemistry that is originated is confined inside a thin (<1 mm) solid–gas inter-phase zone surrounding the catalyst particles. Here, the molecules spend 10 - 6 s at temperatures variable between 600˚C - 1200˚C. A key issue for the technological exploitation is in the possibility of avoiding the propagation of reactions into the gas phase that has to remain at a "relatively low" temperature. This condition favors the formation of primary reaction products (namely CO and H_2) inhibiting chain reactions. Indeed some experimental studies whose results have been partially described in literature [25]-[29] indicate that partial and total oxidation products are directly produced through parallel and competing surface reactions and that the formation of partial oxidation products is favored under SCT conditions due to the very high surface temperatures.

By proper choice of the operating conditions, surface temperatures are locally much higher than those predicted by thermodynamic equilibrium calculations assuming adiabatic reactors. The occurrence of the reactions in these local environments determines in some cases conversion and selectivity values higher than those predicted by the thermodynamic equilibrium at the reactor exit temperatures [30]. Moreover, the very high surface temperatures inhibit catalyst deactivation phenomena related to chemical poison effects [31] [32]. For these and other related reasons, this chemical process is carried out in very small reactors having a very high flexibility towards reactant flow variations. It has also been found that several hydrocarbon feed stocks, even containing sulfur and aromatic compounds can be fed to a SCT-CPO reactor for producing synthesis gas. Now a long term R&D effort is approaching the industrialization phase of a technology whose main advantages concern are:

i) Small dimensions technical and operational simplicity.

ii) Possibility of modular construction of pre-fabricated and skid mounted units.

iii) Flexibility towards feedstock composition & production capacity.

iv) Reduction of investment costs and energy consumption.

v) Reduction of CO_2 production and possibility of an almost complete CO_2 capture in case of H_2 production plants.

Figure 7 illustrates the main characteristics of SCT-CPO technology application devoted to H_2 production and CO_2 removal [33].

2.3. Auto-Thermal Reforming

Like other reforming processes of methane, the purpose of the auto-thermal reforming is the production of syngas. Although auto-thermal reforming is an old idea, to date there are only a few commercial sites. The H_2/CO
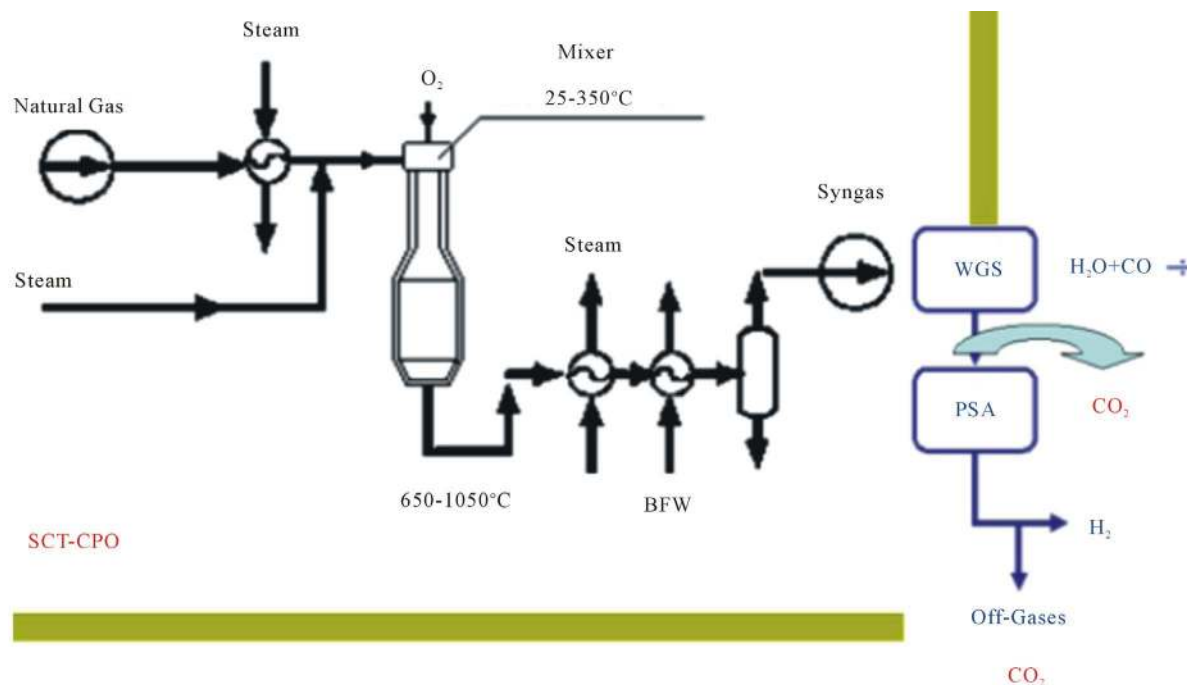
Figure 7. Main characteristics of SCT-CPO technology application devoted to H_2 production and CO_2 removal [33].

ratio of the syngas obtained in the auto-thermal reforming is a function of the gaseous reactant fractions introduced in the process input. Thus, the H_2/CO ratio can be 1 or 2 [34]. Natural gas is mixed at high temperature with a mixture of oxygen and steam and ignited in a combustion chamber (see **Figure 8**) originating sub-stoichiometric flames that can be represented with both equations:

Reactions carried out in the Combustion zone ≈2200 ˚K are given by Equations (4) and (6), and those carried out in the reforming zone 1200 - 1400 ˚K are given by Equations (1) and (5).

By proper adjustment of oxygen to carbon and steam to carbon ratios, the partial combustion in the thermal zone supplies the heat for completing the subsequent endothermic steam and CO_2 reforming reactions [36]. The product gas composition at the exit of the reactor results very close to the thermodynamic equilibrium of an adiabatic reactor, especially in large scale processes [37]. ATR is also utilized as a "secondary reformer" (for lowering the CH_4 residue) and it is placed after a primary SMR in syngas plants integrated with Ammonia synthesis reactors. In this case the "secondary" ATR is fed with the syngas produced from SMR and Air.

Innovation in Auto-Thermal Process
#### New Auto-Thermal Reactor (KBR)

KBRATR reactor contains a combustion zone at the top and a catalyst filled bed at the bottom. The feedstock is mixed with a sub-stoichiometric amount of oxidant and burned in the combustion zone. There is an intermediate conical recirculation section (see **Figure 9**), where the hot gases continue to react, but are far from equilibrium. The resultant gases are passed over the catalyst in the bottom section to achieve as close to an equilibrium mixture as possible.

ATRs are attractive when used in combination with a reforming exchanger. They are also suited for making large volumes of synthesis gas, especially with hydrogen/carbon monoxide ratios such as 1.5/1 - 3/1. These ratios are desirable for synthesis of higher molecular weight hydrocarbons. ATRs have limited commercial experience. One belongs to SASOL in South Africa, which uses ATRs licensed by Lurgi out of Germany. KBR-designed ATRs have been installed in ammonia plants in Kitimat, Canada and Liaohe, China [38]. There are a handful of other ATRs installed in commercial operation.
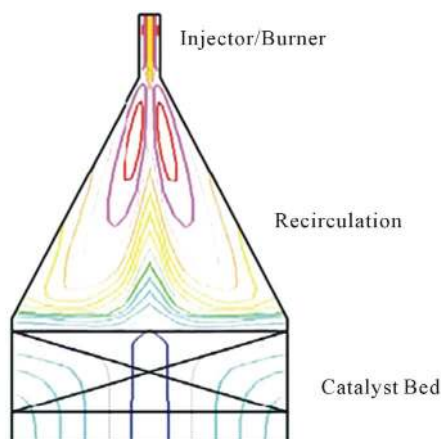
2.4. Dry Reforming

Since CO_2 is available in large quantities and at low costs, CO_2 can be used in place of steam for reforming.
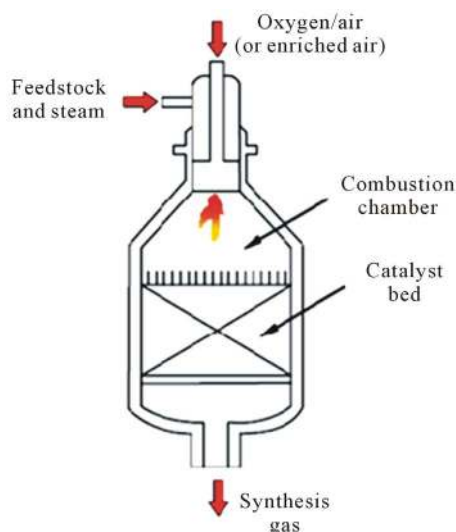
Figure 8. Diagram of an ATR reactor [35].

Figure 9. Schematic cross section of an ATR reactor vessel [38].

Therefore, the dry reforming which is reforming of methane with CO_2 seems to be a promising technology for the production of syngas. Dry reforming of methane (DMR) is a process that uses waste carbon dioxide to produce syngas from natural gas. The synthesis gas produced by steam reforming has high H_2/CO ratio which is not suitable for Fischer-Tropsch synthesis in the production of long chain higher hydrocarbons due to the excess hydrogen which suppresses chain growth and decreases the selectivity of higher hydrocarbons [39]. Conversely, methane reforming with CO_2 plays an important role in the industries due to the production of syngas with a low H_2/CO ratio (≈ 1.0) which can be preferentially used for production of liquid hydrocarbons in Fischer-Tropsch synthesis network specifically those based on iron catalyst [40].

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \text{RWGS} \quad \Delta H^\circ_{298} = 41 \ kJ/mol \tag{11}$$
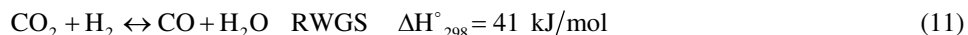
Dry reforming reaction (Equation (5)) is slightly more endothermic than steam reforming. It is favored by low pressure and high temperature [41]. The presence of CO_2 gives rise to more chances of carbon formation on catalyst surface due to production of CO and consumption of H_2 via RWGS reaction Equation 11.

The dry reforming of methane with CO_2 has received special attention in recent years due to two main reasons:

i) It produces syngas with a H_2: CO molar ratio that is suitable for products including F-T fuels and DME.

ii) The reaction consumes two types of greenhouse gases, CO_2 and CH_4 [42] [43].

The main disadvantage of dry reforming of methane is the significant deposition of carbon on the surface of the catalyst, which contributes to the reduction of its useful life. The main challenge for the industrial application of the reforming of methane with CO_2 is related to the development of active catalytic materials, but with a very low coke formation rate, either on the catalysts or in the cold zones of the reactor. The carbon formation in this process can be controlled by using a support that favors the dissociation reaction of CO_2 into CO and O, the last species being the responsible for the cleaning of the metallic surface [44].

2.5. Combined Methane Reforming

2.5.1. Steam and Dry Reforming

A few studies have been reported on simultaneous steam and dry reforming of methane Equation (12) [45]-[48]. Combined steam and CO_2 reforming of CH_4 has attracted interest from both industrial and environmental perspectives. Firstly, from an environmental point view, the two most abundant carbon containing greenhouse gases, methane and carbon dioxide, can be utilized effectively in this reaction and converted into useful chemical products. This is an important area of recent catalytic research. Secondly, from an industrial perspective, the reaction produces syngas (H_2/CO) with a ratio about 2, which is suitable for Fischere-Tropsch and methanol synthesis.

$$CH_4 + 1/3CO_2 + 2/3H_2O \rightarrow 4/3CO + 8/3H_2 \quad \Delta H^{\circ}_{298K} = +219 \ kJ/mol \quad (12)$$
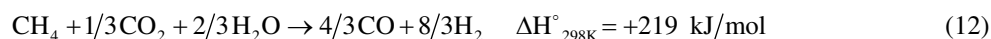
The current technology for syngas production requires an oxygen plant for partial oxidation (equation 3); whereas the proposed technology utilizes CO_2 using small installation (process intensification) and thus reducing operating and capital cost [49].

Process Overview

Figure 10 shows the simultaneous steam and CO_2 reforming process of methane to syngas. In this process, the syngas generated by steam reforming is transferred to a heat exchanger, where the syngas is cooled and passed through a CO_2 membrane separator. The CO_2 membrane separates CO_2 from the syngas mixture which initially contains CO, H_2, CO_2, H_2O and un-reacted CH_4. The CO_2-free syngas is sent to a two phase flash drum, where water is separated from syngas. The separated CO_2 is sent to the dry reformer where the methane reacts with CO_2 for increased production of syngas.

2.5.2. Combined Dry and Partial Oxidation Reforming

Combination of CO_2 reforming and partial oxidation of methane (Equations (3) and (5)) to produce syngas with different precursors

Catalytic dry reforming process is highly endothermic and hence, high energy consumption. Catalytic partial oxidation is an exothermic reaction, so it tends to form hot spots in catalyst beds. It is difficult to control, particularly in a large scale operation. The process of combination of CO_2 reforming and partial oxidation of methane (CDPOX) to produce syngas couples the advantages of DMR and POX and offsets the disadvantages of them, simultaneously [51]. Compared to POX and DMR, CDPOX is a green process and has the following advantages:

1) Energy coupling, 2) Controllable product ratio of H_2/CO according to the need of the post-process, and 3) A safer operating environment.

Múnera and co workers [52] studied the best oxygen concentrations (3% - 10%) in CDPOX reforming using Rh (0.6)/La_2O_3 as catalyst. They found that increasing the O_2 content enhanced the CH_4 conversion and at the same time drastically reduced the CO_2 conversion; the best results were obtained with 10% O_2, which corresponds to a CH_4/O_2 ratio of 3.3.

2.6. Reforming Using Membrane

2.6.1. Oxygen Membrane

Membrane reactors are non-porous multi component oxides suited to work at temperatures above 1000 K and have high oxygen flux and selectivity. These membranes are known as ion transport membranes (ITM).

In membrane reactors, the oxygen required to perform the CPO reaction is separated from air fed to one side of the membrane at temperatures around 300 K and moderate pressure (0.03 - 0.20 bar) and reacts on the other side with methane and steam at higher pressure (3 - 20 bar) to form a mixture of CO and H_2. Then this mixture
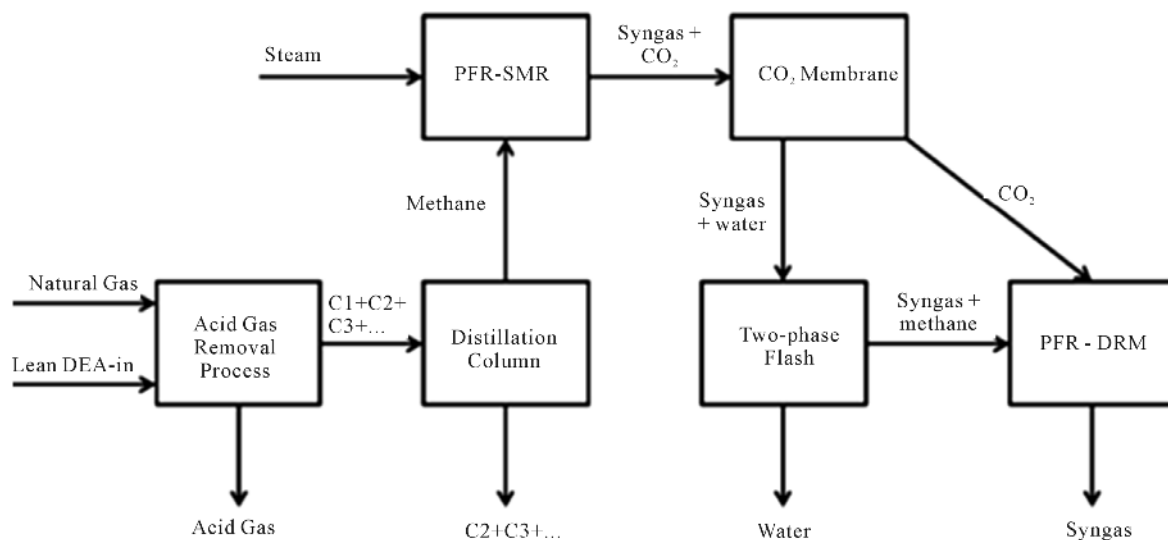
Figure 10. Schematic diagram of combined steam and dry reforming of methane [50].

can be processed downstream to produce H_2 or liquid fuels. The concept of the membrane reactor is depicted in **Figure 11** [21]. Among the different geometries employed for the ITM reactor, the flat plate system offers some advantages because it reduces the number of seals and thus makes safer operation. Among the ITM systems, perovskite structures remain prominent as they allow safe operation [53].
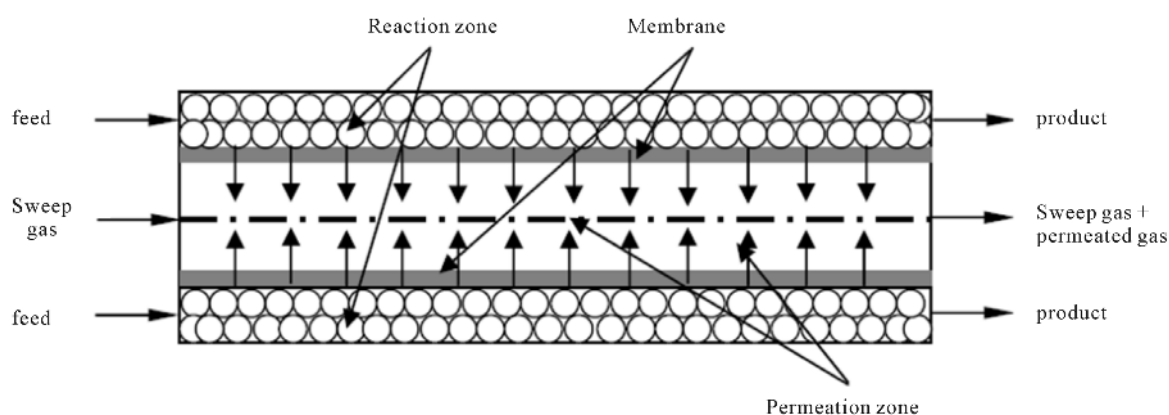
2.6.2. Hydrogen Membrane

Dense membranes are permeable to atomic or ionic forms of hydrogen. Pd-Pd alloy membranes offer high permeability only for hydrogen whereas zirconia and perovskites are highly selective only for oxygen. A schematic diagram of a tubular membrane reactor is presented in **Figure 12**. The catalytic membrane reactor is a cylindrical reactor equipped with a membrane. This membrane is inert with respect to chemical reaction and tubular in shape. The tubular membrane divides the reactor in two zones. The first zone is the shell side zone which a reaction zone is packed with catalyst particles. The reaction occurs in this zone. Second is tube side zone, also called permeate zone where the sweep gas is introduced co-currently with respect to feed to carry away the permeated gases from the permeate zone.

According to the low of mass action, and for reversible reactions, removal of one of the reaction products shifts the reaction to the RHS of the reaction equation. Therefore, removal of hydrogen from the reaction products DMR or SMR prevents the reversible reaction in Equations 5 and 1 as well as the RWGSR Equation 11, thus, increases conversion beyond the equilibrium conversion.

Membrane reactors for methane reforming reactions can be categorized according to the type of hydrogen separation membranes and the configuration of reactors and membranes. Dense metal membranes such as palladium and silver-palladium, which show complete perm selectivity toward hydrogen, have been used in hydrogen separation membranes for SMR reactions [55]. However, there are several problems with industrial applications of the dense membranes, including instability against acidic gases such as hydrogen sulfide (H_2S), high cost, adsorption of carbon monoxide that decreases hydrogen permeation, and formation of carbon alloys during SMR reactions [56]. Silica is another attractive material for hydrogen-selective membranes because of its amorphous structure in which the silica network allows the permeation of small molecules such as hydrogen. Recently, major progress in the preparation of porous membranes has made silica an alternative for use in hydrogen separation membranes for SMR. This has been achieved by either (CVD) chemical vapor deposition [57] or sol-gel processing [58], although the instability of silica in steam has been noted. Kanezashiand co workers [59] [60] succeeded in preparing hydrothermally stable silica membranes by doping metals such as Ni and Co into a SiO_2 matrix by sol-gel processing. A catalytic membrane having both catalytic activity and separation ability has attracted increased attention because it has a more compact configuration than other types of membrane reactors. One need with catalytic membranes is enhancement of catalytic activity, since only a limited amount of catalysts can be impregnated inside catalytic membranes [58].
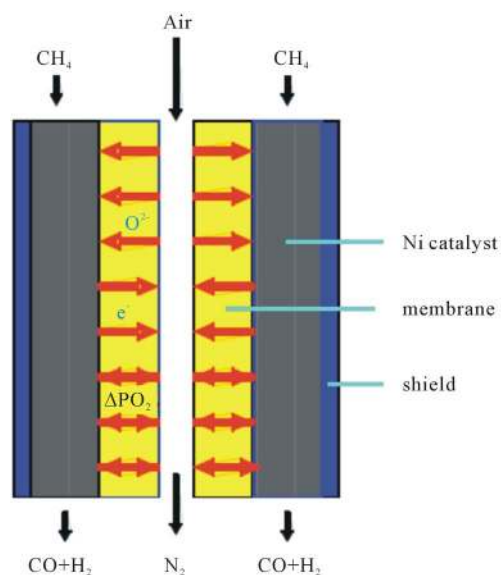
Figure 11. Sketch diagram showing the principle of oxygen membrane reforming [21].

Figure 12. Schematic diagram of a tubular membrane reactor [54].

A novel Multi-Channel Membrane Reactor (MCMR) was designed and built for the small-scale production of hydrogen via Steam Methane Reforming (SMR) [61]. The developed MCMR consists of alternate channels for catalytic SMR and Methane Catalytic Combustion (MCC) which provide the heat of reaction needed by the endothermic reforming reaction. A palladium-silver membrane inside the reforming gas channel shifts the reaction equilibrium, allowing lower operating temperatures, and producing pure hydrogen in a single vessel. Results showed that methane conversion reached 91% and a hydrogen purity in excess of 99.99% at 570°C and 15 bar.

Linde Engineering [6] developed a new small-scale reformer process based on palladium membrane tubes that can produce pure hydrogen without a separate purification unit. The composite palladium membranes comprise a porous metal support, a ceramic diffusion barrier layer and the final selective, thin and defect-free palladium layer. The chemical equilibrium of the reforming reaction shifts towards the products and the whole process can be operated at lower temperatures of 600°C - 650°C while delivering higher conversion rates.

2.7. Tri-Reforming (TMR)

It is a new process designed for the direct production of synthesis gas with desirable H_2/CO ratios by reforming methane or natural gas using flue gas from fossil fuel based electric power plants without pre-separation of CO_2. These flue gases are regarded as major source of CO_2 emission in the U.S. Generally the compositions of flue gases depend on the types of fossil fuels used in power plants. Flue gases from natural gas-fired power plants

typically contain:

8% - 10% CO_2, 18% - 20% H_2O, 2% - 3% O_2, and 67% - 72% N_2;

Flue gases from coal-fired boilers primarily contain:

12% - 14% CO_2, 8% - 10% H_2O, 3% - 5% O_2, 72% - 77% N_2, and trace amount of NO_x, SO_x, and particulates [62].

It is hypothesized that tri-reforming be a synergetic combination of CO_2 reforming (Equation 5), steam reforming (Equation 1) and methane oxidation reactions (Equation 3 and Equation 4). Therefore, tri-reforming is expected to encompass a number of unique features. One major feature is its ability to convert CO_2 in flue gas without CO_2 separation while avoiding the use of pure CO_2 and the severe problem of carbon deposition encountered in CO_2 reforming system [63]-[67]. Currently most of pure CO_2 is obtained from CO_2 separation processes (e.g. absorption, adsorption, and membrane separation) that are often energy-intensive and costly. Some separation processes could lower the power plant energy output as much as 20% [68].

Other features of tri-reforming include that there is no need to handle pure oxygen and it directly produces synthesis gas with a desirable H_2/CO ratio (e.g. H_2/CO = 1.5 - 2). Furthermore, oxygen in flue gas may help to ease the reaction energy requirement as encountered in CO_2 reforming alone or steam reforming alone. In general, the new tri-reforming process concept is consistent with the goals of **DOE** Vision 21 for power plants with respect to decreasing green house gas emission, improving power generation efficiency and co-producing fuels and chemicals [69].

It should be pointed out that the H_2/CO ratio in synthesis gas is important since synthesis gas with different H_2/CO ratios has different applications in industry. The current major application of synthesis gas (not hydrogen) includes methanol synthesis and Fischer-Tropsch (F-T) synthesis that require synthesis gas with a H_2/CO ratio close to 2. However, synthesis gas directly produced from CO_2 reforming of methane has H_2/CO ratio close to 1. Hence, this kind of synthesis gas (H_2/CO ratio ≤ 1) requires further treatment in order to be applied in methanol and F-T synthesis.

Similarly synthesis gas produced from steam reforming cannot be directly applied in methanol or F-T synthesis either since the H_2/CO ratio of synthesis gas produced from steam reforming is usually larger than 3. Although methane partial oxidation produces synthesis gas with a H_2/CO ratio of 2, methane partial oxidation is difficult to control due to its exothermic feature and is dangerous and expensive due to the handling of pure oxygen. Tri-reforming, however, is expected to readily produce synthesis gas with the desired H_2/CO ratios of 1.5 ~ 2 by manipulating tri-reforming reactant compositions under relatively mild reaction conditions.

The concept of tri-reforming using power plant flue gas was first proposed by [62] [70]. Before 1999, several papers were published on the study of combined CO_2 reforming and partial oxidation reaction [71]-[73] and simultaneous steam and CO_2 reforming of methane in the presence of oxygen [74]. The results in these papers have indicated that combined reforming is feasible. However, the new tri-reforming process still faces a number of challenges. The future challenges include, for example, effective conversion of CO_2 in the presence of O_2 and H_2O; the heat management; the minimization of the effect of SOx and NOx in flue gas on tri-reforming process; the management of inert gas N_2 in flue gas; and the integration of new process into power plants.

Tri reforming can also be used for converting and utilizing CO_2-rich natural gas [75] as some natural gas resources contain up to 50 vol% CO_2 which are not yet utilized commercially due to the high CO_2 concentration. Tri-reforming process concept was recently proposed and developed at the Pennsylvania State University [62] [75], and by independent studies on tri-reforming catalysts [76]-[79].

Figure 13 depicts the process concept.

2.8. Comparison between the Different Methods for Reforming of Methane

Steam reforming is the main reforming process of methane that is predominantly utilized because it has the greatest value for H_2/CO ratio, *i.e.*, the product of the reforming process is a gas flow considered ideal for the development of the catalytic process of obtaining a gas hydrogen flow of high purity. However, as the process of steam reforming is considered too expensive, the other types of catalytic chemical processes are considered as alternative processes for carrying out the reforming of methane and they were developed with the aim of making savings in thermal energy consumption required for the catalytic process to occur. The choice of process type to reforming of methane must take into consideration the economic viability of the process related to the destination to be given to the syngas produced.
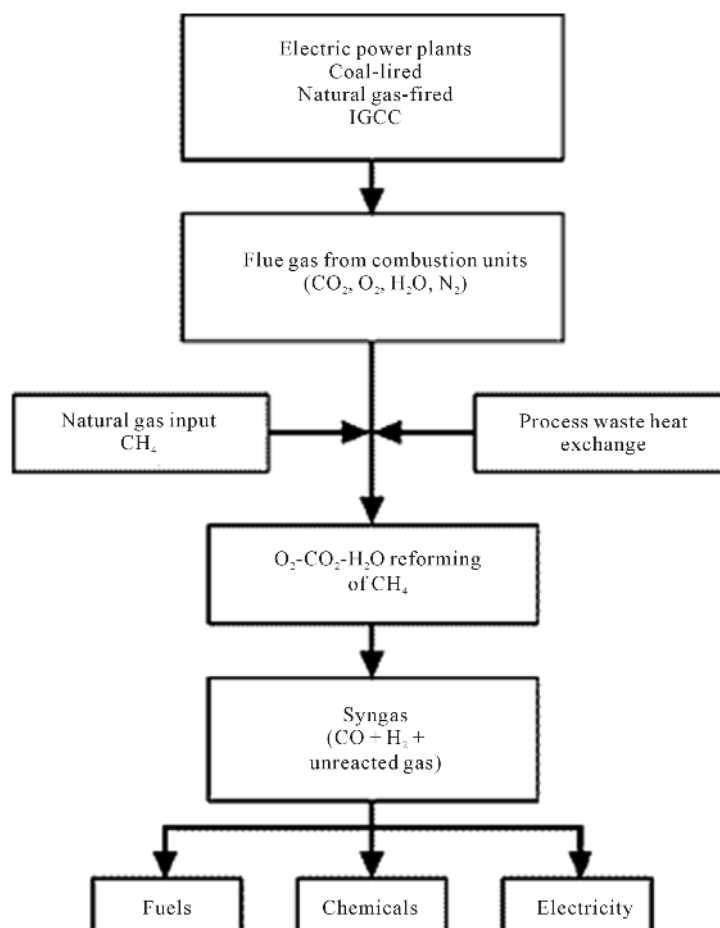
Figure 13. Process concept for tri-reforming of natural gas using flue gas from fossil fuel based power plants [62].

Partial oxidation and auto-thermal reforming are good choices to produce syngas when the value of H_2/CO ratio is adequate and especially when it comes to reduce the consumption of thermal energy, a most important factor. In short, it can be said that the selection of the type of catalytic chemical process of reforming of methane depends on the type of application of the syngas produced. A comparison of syngas generation technologies using natural gas as feed is shown in **Table 1**.

3. Catalysis

Generally, the catalysts used for the reforming reactions are categorized into two groups:
- Supported noble metals, and
- Non-noble transition metals.

Several investigations have been conducted to find the most suitable catalyst for the production of syngas using different processes. There has been extensive research work on steam reforming, catalytic partial oxidation and dry reforming catalysts including rhodium [80]-[82], ruthenium [83]-[85] and platinum [86]-[88], Palladium [89], Iridium [90] catalysts. Studies have proved that nickel based catalysts supported with metal oxides give the best conversion rate of methane [91]. Although noble metals-based catalysts are more active and usually less prone to deactivation by carbon formation or oxidation, owing to their low cost (100 - 150 times less expensive than noble metals [92]), nickel based catalysts are more widely used in industrial applications. However, their stability is poor due to carbon deposition. Therefore, the inhibition of carbon deposition for non-noble metal catalysts became the most important topic for reforming of methane especially in dry reforming. The strategies, which were exploited to inhibit carbon deposition, are to control particle sizes of active components and to in-

crease the surface basicity of catalysts. Several approaches were developed to control the metal particle sizes, including the enhancement of metal-support interaction, the formation of solid solutions, and plasma-treatments. To increase the surface basicity of catalysts, basic metal oxides were employed as support or promoter. Several authors have resulted in improved catalysts and processes, leading to improved overall efficiency and environmental performance [93] [94]. In general, we can say that the group VIII (except Osmium) metals are highly active in the reforming reaction, each of them showing their own characteristics.

The effect of the support has also been investigated in other active metals, and the tendencies are not the same in all cases. Bitter *et al.* [95] found that the trend in stability on supported platinum was $ZrO_2 > TiO_2 > Al_2O_3$. This trend was different in supported nickel, Al_2O_3 supported nickel being more stable than the corresponding TiO_2 supported catalyst [96]. It has been reported that $Pt/Ce_xZr_{1-x}O_2$ catalysts are more active, stable and selective than the CeO_2 and ZrO_2 supported counter parts. The higher reducibility and oxygen storage/release capacity of $Pt/Ce_xZr_{1-x}O_2$ catalysts promotes the continuous removal of carbonaceous deposits from the active sites, which takes place at the metal-support interfacial perimeter [97].

3.1. Promoters

Zirconia [98], lanthana [99] [100], ceria [101] and ceria-zirconia [102] [103] oxides have been recently reported as promoters of methane reforming reactions. Incorporation of a 5 wt% ZrO_2 to a base Ni/SiO_2 catalyst resulted in excellent performance for the CPOX reaction O_2 mixture in a fluidized-bed reactor. Chawla *et al.* [104] prepared Nickel catalyst by impregnation method using support-Al_2O_3 and different types of promoters to improve activity, stability and selectivity in order to reduce coke formation and to achieve long-term operation. Nickel catalysts promoted by the ZrO_2 shows higher dispersion of the metal particle on the surface of the support than the un-promoted catalysts [105]. It has been found that the ZrO_2, CeO_2, K_2O and MgO promoted 10% $Ni/-Al_2O_3$ catalysts exhibited good activity, stability and long-term operation as compared to the un-promoted catalysts.

Iron has also been used as a promoter. Park *et al.* [106] prepared a set of mesoporous nickel-iron-alumina xerogel catalysts with different iron loadings. The catalyst formula "20Ni$_4$FeAl" reviled the finest nickel dispersion, the highest nickel surface area and the best catalytic performance in the steam reforming of LNG.

3.2. Perovskite Precursors

Perovskite oxides have also been extensively used as precursors of supported metal catalysts. Perovskites are mixed oxides with a general stoichiometry of ABO_3, where A and B can be partially substituted by other metals.

Table 1. Comparison of syngas generation technologies with natural gas feed [5].

Technology	Advantages	Disadvantages	Developers/Licensors
POX	Feed stock desulfurization not required	Very high process operating temperature Usually requires oxygen plant	Texaco Inc. and Royal Dutch/Shell
SMR	Most extensive industrial experience Oxygen not required, lowest process operating temperature Best H_2/CO ratio for production of liquid fuels.	Highest air emissions More costly than POX and auto-thermal reformers Recycling of CO and removal of the excess hydrogen by means of membranes	Haldor Topsoe AS, Foster Wheeler Corp, Lurgi AG, International BV, Kinetics Technology and Uhde GmbH
ATR	Lowest process temperature requirement than POX. Syngas methane content can be tailored by adjusting reformer outlet temperature	Limited commercial experience Usually requires oxygen plant	Lurgi, Haldor Topsoe
DMR	Green house gas CO_2 can be consumed instead of releasing into atmosphere Almost 100% of CO_2 conversion	Formation of coke on catalyst. Additional heat is required as the reaction takes place at 873 K	Carbon Sciences
CSDR	Best H_2/CO ratio for production of liquid fuels Coke deposition drastically reduced.	Separation of un-reacted methane from SMR syngas. Project installation cost.	Midrex Process
TMR	Directly using flue gases, rather than pre separated and purified CO_2 from flue gases. Over 95% of methane and 80% CO_2 conversion can be achieved	Usually requires oxygen plant. Low H_2/CO ratio ratios limit its large-scale application for F-T & MeOH synthesis	Haldor Topsoe AS

Most of the perovskites studied have a lanthanide and/or alkaline earth metal in the A site, and the active metal in the B site. After reduction, a highly dispersed metal supported in the lanthanide or alkaline earth oxide is obtained [107]

Perovskite structures of the type $CaTiO_3$, $SrTiO_3$, $BaTiO_3$ and $LaAlO_3$ have been used as supports by [108] to prepare supported nickel catalysts. All these supported Ni catalysts showed better performance than Ni/Al_2O_3 reference catalyst. Specifically, the Ni/ $LaAlO_3$ was the most active catalyst which suppressed the hot spot formation at the catalyst inlet. It has been shown that the $LaNiO_3$ perovskite renders small Ni particles deposited on a La_2O_3 substrate upon reduction. The resulting catalyst exhibited over 90% CH_4 conversion at 800°C with H_2 and CO production at a ratio close to 2:1 [109]. Traditional catalyst preparation methods involve the precipitation and/or impregnation techniques; the latter has broadly been used for the preparation of Ni-supported catalysts for different areas of catalysts preparation methods [110]. However, the conventional impregnation method does not provide adequate control over the final size, morphology and dispersion of active metal particles. In the literature several other preparation methods such as surfactant assisted route to reduce the particle size of the support material, sol-gel, mixed oxides solid solution micro emulsion and combustion synthesis were investigated as alternatives to traditional methods [111].

3.3. Nano Catalysts

On conventional reforming catalysts, discrete metal nano crystals (typically 1.15 nm) are dispersed on support particles that are one to several orders of magnitude larger than the supported metal nano particles. However, when the particle sizes of an oxide support are reduced to such an extent that they become comparable to that of the active metal particles, the oxide may deviate dramatically from its function as a conventional catalyst support. Such metal/oxide catalyst with size-comparable metal and oxide nano crystals may be better called a metal/oxide nano composite rather than an "oxide-supported" metal catalyst [112].

When the sizes of zirconia particles become smaller than 25 nm, the oxide forms nano composite catalysts with size-comparable Ni-metal nano crystals (10 - 15 nm). The nano composite catalysts show extremely stable catalysis, which is in strong contrast with the deactivating Ni catalyst supported on bigger zirconia particles (>25 nm). Energy dispersive analysis of X-rays focused on individual particles showed little contamination between Ni-metal and zirconia nano crystals. This raises the possibility of tailoring the catalytic behavior of oxide-supported metal catalysts by reducing the particle size of oxide to make high performance nano composite catalysts [112].

The reason for high stability of nanoco mposite Ni/ZrO_2 remains unclear. It could be due to the enhancement of oxygen transfer ability of zirconia particles smaller than 25 nm or by formation of nano composite with high percentage of metal/oxide boundary or perimeter CO_2, which in turn increase oxidative removal of carbon atoms to produce CO [112].

Application of the MgO nanocrystals for support of nickel catalyst was also successful and gave promising results for highly active as well as very stable Ni/MgO catalysts for the dry reforming of methane [113]. The work of Ruckenstein and Hu, [96] showed that NiO/MgO catalysts prepared by impregnation of nickel nitrate onto MgO powders containing 7 - 10 nm nano crystals developed stable activities for the reforming reaction after reduction at 1063 K.

Mesoporous materials when used as the support could control the size of nano particles by the diameter of their pores [111] [114]. It has been found that appropriately prepared mesoporous, nano crystalline pure tetragonal zirconia could result in an active and stable nickel based catalyst for dry reforming reaction [115]. Under relatively low temperatures and low carbon dioxide to methane ratios which thermodynamically favors coke formation, long-term stable performance was observed over 5% Ni catalyst. The addition of CeO_2 to the support was found to increase the surface area of the resulting zirconia powder [116]. The use of alkaline promoter [117] as well as CeO_2 and La_2O_3 [118] further improved the stability and activity of the resulting catalysts under conditions otherwise coke formation is extensive.

3.4. Innovated Multi Component Thermo-Neutral Reaction (TNR) Catalyst

Most recently, an innovative steam- and/or CO_2-reforming designated as Thermo-Neutral Reforming (TNR) has been introduced by [119] after several years studies on ultra-rapid catalytic reactions. The reformer can be reduced two-order magnitude compared with traditional steam reformers, because the large endothermic heat of

reforming is compensated by the large exothermic heat of complete combustion on the same catalyst surface without supply of heat from outside of the reactor.

By applying the extremely compact size of the TNR system to the successive syngas converters packed newly developed catalysts, highly effective ultra clean fuels such as MeOH, DME, and sulfur-free & non-aromatic high octane number gasoline can be produced effectively with non-expensive costs.

Recent advances in the steam reforming catalyst have been done through the CO_2 reforming associated with the CO_2 mitigation against the global warming crisis [119]. The common sense of the steam reforming has been that the excess steam is necessary to prevent coke formation by the reaction between deposited carbon and steam to convert to carbon mono oxide and hydrogen, while in case of dry reforming with CO_2 there is no opportunity to avoid coke formation. Inui [120] investigated a novel catalyst to avoid coke formation even under the reaction condition of CO_2 reforming. As criteria to develop this ideal catalyst; the following performances have been required:

- No coke formation,
- High sulfur tolerance,
- Ultra-rapid reaction rate,
- High-temperature resistance,
- Low temperature start-up in a very short time,
- Non toxic, and
- Low production cost.

This novel catalyst has both catalytic functions of combustion and steam reforming for hydrocarbons, the **thermo-neutral reactions** (TNR) on the same catalyst surface could be realized [120]. As the result, the reactor size could be reduced to two-orders of magnitude that of traditional hydrocarbon steams reforming (HSR) method [121]. Catalyst composition of the four-component catalyst (wt%): 10Ni-6.0Ce$_2$O$_3$-1.0Pt-0.2Rh. The synergistic effect of the four-component catalyst on CO_2 reforming of methane is shown in **Figure 14** [122].

4. Conclusion

From the above review we can conclude that each reforming method has its particularities and the preference of one method over another depends on the final application of the syngas produced. If we need maximum hydrogen production e.g. for the case of ammonia synthesis then steam reforming is the traditional choice. On the other hand, if the syngas produced is to be utilized in the production of liquid hydrocarbon fuels then ATR and POX or more recently SCT-CPO reforming would be the proper choice where H$_2$/CO ratio can be adjusted to the required ratio. New comers like dry reforming and tri-reforming will certainly occupy their proper place with the increased climatic awareness where CO_2 is utilized as a raw material. Nickel catalysts supported on alumina or silica are the most used catalysts in the reforming of methane because of their low cost compared to noble metals. It must be emphasized that the method of preparation affects the final structure of the catalyst and therefore its activity. Nano catalysts are gaining grounds in the reforming process. Future challenges include the development of better catalysts that have longer life time and enhance conversion at moderate operating
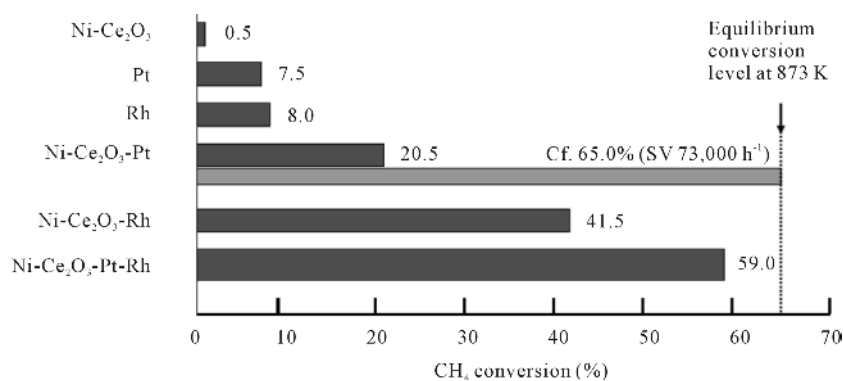
Figure 14. Comparison of the catalytic performance in CO_2 reforming of methane for various catalyst components-Synergy appeared by proper combination of catalyst components [122].

conditions to reduce the operating cost as well as the development of more compact reactors (Process Intensification) e.g. membrane reactors to lower the capital cost.

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List of Abbreviations

ATR	Auto-thermal Reforming
BFW	Boiler Feed Water
CDPOX	Combined Dry Reforming and Partial Oxidation
CPOX	Catalytic Partial Oxidation
CSDR	Combined Steam and Dry Reforming
CMR	Combined Methane Reforming
CTL	Chemicals to Liquid Fuels
DME	Di Methyl Ether
DMR	Dry Methane Reforming
F-T	Fischer-Tropsch
GHSV	Gas Hourly Space Velocity, h^{-1}
GTL	Gas-to-Liquid
HR-TEM	High Resolution Transmission Electron Microscopy
HT	Heat Transfer or Heat Exchange
IGCC	Integrated Gasification Combined Cycle
ITM	Ion Transport Membrane
KBR	Kellogg Brown & Root Company
MCC	Methane Catalytic Combustion
MCMR	Multi-Channel Membrane Reactor
MTBE	Methyl Tertiary-Butyl Ether
POX	Partial Oxidation Method
PSA	Pressure swing adsorption
RWGS	Reverse Water Gas Shift
SCT- CPO	Short contact time-catalytic partial oxidation
SMR	Steam Methane Reforming
TGA	Thermal Gravimetric Analysis
TNR	Thermal Neutral Reaction
TMR	Tri Reforming
WGS	Water Gas Shift
WHSV	Weight Hourly Space Velocity cc $g^{-1} \cdot h^{-1}$
YSZ	Yttria-Stabilized Zirconia