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Recent advances in the methanol synthesis via methane reforming processes

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ABSTRACT:

Depleting fossil fuel resources and continuously degrading environment due to greenhouse gases demands an immediate search for alternative energy resources on an emergency basis to develop a sustainable and green environment. The utilization of coke oven gas, biogas and flue gases from fossil fuel power plants to produce synthesis gas, which is a major feedstock for the production of liquid fuels (methanol), is beneficial both from economical and environmental aspect. In this review paper, our aim is to discuss the applicability of these sources in different reforming processes to produce suitable syn-gas ratio (~2) for methanol production. The feasibility, suitability and applicability of each source have been discussed in detail accompanied with their environmental impact and detailed economic analysis. Moreover, the influence of different supports, promoters and preparation methods on the catalyst properties to minimize carbon deposition has also been described. This review will summarize all the recent advances in the area of syn-gas production for methanol synthesis.

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1. Introduction

Fossil fuels (oil, natural gas and coal) are the major source of energy and have been utilized as a feed stock for a number of man-made materials such as: gasoline, diesel oil and various petrochemicals, plastics and pharmaceuticals. During the 19th century, the rapid industrialization and urbanization has led to the increased consumption of fossil fuels. Therefore, it is necessary to search for alternative energy

sources on an emergency basis due to the increased costs of fossil fuels and depletion of energy sources. It is estimated that the current population (6 billion) will jump to 9-10 billion by mid-21st, whereas, the current estimated oil reserves (200 billion metric tons) will only last for 40 years with the current consumption rate. Therefore, to meet the energy demand in the coming years it is advisable to look for alternative and efficient energy sources and one way to meet the challenge is to produce efficient manmade hydrocarbons.[1] Methanol is considered to be one of important raw material for the production of biodiesel and as an alternative fuel.[1-4] Another feature of methanol is that it can be blended with gasoline, even though it processes half of the volumetric energy density of diesel or gasoline.[1-4] Methanol belonging to alcohol family is considered as the simplest of all alcohols and the global annual production of methanol in 2007 was 38 million metric tons.[5] Besides its utilization for the production of biodiesel, it is widely utilized in the synthesis of formaldehyde, acetic acid and man-made materials such as: polymers and paints. Moreover, it has been regarded as a clean, convenient energy-storage material and a bridge to the renewable energy future.[1] Furthermore, the production of methanol has several advantages such as: low toxicity, easy to handle and lower risks associated with its transportation. Methanol can be consumed directly into the existing internal combustion engine and fuel cells. Moreover, the storage of methanol does not require high pressure at room temperature, as in the case of H_2 storage.[1,2] Methanol has several advantages over currently highly consumable gasoline, as the latent heat vaporization of methanol is 3.7 times higher than gasoline, which allows it to adsorb more heat from the system as it changes from liquid to gaseous state. This special feature of methanol allows it application for air-cooled radiators instead of

the currently heavier water-cooled system. Methanol-powered vehicles will provide smaller, lighter engine block, reduced cooling requirements and better mileage. The consumption of methanol as fuel is safer compared to gasoline and diesel as its combustion will produce lower emissions of noxious gases (NO_x, SO_2 and certain hydrocarbons).[6]

Natural gas (NG) consists of a major component of methane and low balances of other hydrocarbons comprised on ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}). NG also contains inert diluents such as molecular nitrogen (N_2) and carbon dioxide (CO_2).[7] Large numbers of NG reservoirs are located far from industrial complexes and often produced offshore. The transportation of NG to potential market by pipelines may not be available and liquefaction for shipping by an ocean-going vessel is expensive.[8] In 2011, large volume of NG (140 billion cubic meters, (BCM)) has been flared globally[9]; moreover two disadvantages occurred from flaring, first: the wastage of an important hydrocarbon source worth billions and second: global warming by the production of GHG.[10] The conversion of natural gas into liquid fuel has been a great challenge and two possible routes have been considered called as direct conversion and indirect conversion. However, the direct conversion of natural gas to methanol by partial oxidizing methane is far from being feasible because the products from this route are more reactive than the starting feedstock (CH_4).[11] Although this route may have higher selectivity (~ 80%) but the major problem lies in its lower conversion per pass (~ 7). This route requires large recycle ratio and the lower partial pressure of the products create problems in the separation. Therefore, indirect conversion is considered as an efficient way to produce methanol although it require high capital investments.[12]

Methanol is produced by the gaseous reaction of synthesis gas (syn-gas) and the required ratio of syn-gas (H_2/CO) for methanol synthesis is two, as described in the following equation 1.

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H_{298K} = -91 \text{ kJ/mol} \qquad (1)$$

The production of syn-gas from natural gas (NG) is an important technology in the chemical industry, as syn-gas is a building block for valuable liquid fuels and chemicals such as Fischer-Tropsch oil, methanol and dimethyl ether.[8,13-15] The processes that draw industrial attention are steam reforming of methane (SRM), partial oxidation of methane (POX) and dry reforming of methane (DRM).[16] However, the choice of reforming technology depends on its suitability for the production of suitable syn-gas ratio and scale of operation for methanol production.[12]

Stoichiometric SRM (H_2O:CH_4 = 1:1) produces a higher syn-gas ratio (H_2/CO = 3)[17] compared to that required for methanol synthesis (H_2/CO = 2).[18-20] The presence of water in the feed leads to the occurrence of water gas shift (WGS) reaction to produce hydrogen and carbon dioxide (equation 3). WGS reaction is slightly exothermic reaction and stoichiometry of the reaction (equal number of moles of reactants and products) drive us to conclusion that this reaction is independent of pressure and will be favored at low temperatures. Therefore, the overall SRM reaction followed by WGS reaction is regarded as global SRM reaction (equation 4) having high syn-gas ratio (H_2/CO = 4).[21] However, the application of SRM produced syn-gas with such higher ratios is not suitable for liquid fuels (e.g., methanol).

SRM: $CH_4 + H_2O \rightarrow CO + 3\ H_2$ $\Delta H_{298K} = 225.4$ kJ/mol (2)

WGS: $CO + H_2O \rightarrow CO_2 + H_2$ $\Delta H_{298K} = -41$ kJ/mol (3)

Global SRM: $CH_4 + 2H_2O \rightarrow CO_2 + 4\ H_2$ $\Delta H_{298K} = 165$ kJ/mol (4)

Therefore, it was suggested that the desired syn-gas ratio (~ 2) can be achieved only at very low steam/methane (S/C) ratios. The operation of process at such reaction conditions will produce smaller amounts of CO_2 and also requires lower amount of gas to be recycled. As high recycling demands high energy consumption and higher content of carbon dioxide in purge gas means less carbon yield and large syngas unit. However, this process is only suitable for lower methanol production units around 1000-1500 metric tons per day (MTPD).[12] Moreover, SRM is energy intensive process due to the endothermic nature of reaction and requires high investments of capital.[22] SRM process faces corrosion issues and requires a desulphurization unit.[23,24] The source of carbon deposition in the SRM is believed to be either methane decomposition reaction (equation 5) or CO disproportionation reaction (also referred as Boudard reaction) as described below in equation 6.

$CH_4 \rightarrow C + 2\ H_2$ $\Delta H_{298K} = 75$ kJ/mol (5)

$2CO \rightarrow CO_2 + C$ $\Delta H_{298K} = -172$ kJ/mol (6)

Whisker carbon formed due to the decomposition of adsorbed methane on the metal surface to produce adsorbed carbon atom and regarded as a major contributor in carbon formation. Even though the desired syn-gas ratio can be obtained by working at

lower S/C ratios, the application of lower S/C ratio leads to the sever carbon formation over Ni-based catalysts because in the presence of excess S/C ratios the deposited carbon can be removed through steam gasification.[25]

Partial oxidation of methane (POX) draws industrial attention due to exothermic nature of reaction, which requires lower energy consumptions (equation 7). The advantages of this process are high conversion rates, high selectivity and very short residence time.[26] However, exothermic nature of reaction induces hot spots on catalyst surface due to poor heat removal rate and makes operation difficult to control.[16,23]

$$CH_4 + 1/2\ O_2 \rightarrow CO + 2H_2 \qquad \Delta H_{298K} = -22.6\ kJ/mol \qquad (7)$$

The major drawback of this process is the high cost affiliated with the air separation unit that accounts up to 40% of the total cost of the synthesis gas plant. Therefore, to overcome this problem routes based on air were considered eliminating the requirement of cryogenic air separation plant. However, the use of air in POX process is limited to the once-through synthesis scheme to avoid huge accumulation of nitrogen.[27] Moreover, the application of syn-gas containing high nitrogen content will have an adverse impact on methanol conversion.[28] The application of air in synthesis gas plant leads to big gas volumes and consequently will demand big feed/effluent heat exchangers and compressors. This kind of setup is not feasible for large scale plants. The availability of oxygen at a lower cost can be a vital factor to reduce the cost of synthesis gas manufacture. One such approach is the application of a reactor concept with oxygen additives through a membrane. The reported oxygen ion diffusivities make

a syn-gas unit possible but the feasibility of the scheme is yet to be demonstrated. Moreover, the membrane separation setup which utilizes less energy remains expensive mainly due to the challenges associated with its fabrication, installation and integration.[29] Another problem with such setup is that it cannot fully separate oxygen from air; however it can only be used to increase oxygen concentration in the feed stream with the possible passage of nitrogen through the membrane.[30]

On the other hand, DRM offer valuable environmental benefits such as: utilization of biogas having considerable amounts of GHG (60-65% methane and 40-35% carbon dioxide) [31,32] and conversion of NG with high CO_2 content to valuable syn-gas.[8,20] Although, DRM has interested aspect of utilizing GHG, it yielded a lower syn-gas ratio ($H_2/CO = 1$), which was not suitable for the production of methanol.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H_{298K} = 247 \text{ kJ/mol} \qquad (8)$$

Therefore, in this study combination of different reforming process (DRM or SRM or POX) will be investigated for their influence to minimize carbon deposition with the addition of steam and O_2 in the system and the effect of H_2O/CH_4 and O_2/CH_4 ratios to control syn-gas ratio. Moreover, various possible feed sources such as: coke oven gases, biogas and flue gases, to produce suitable syn-gas ratio ($H_2/CO = 1.5$-2.0) by the combination of the any of the two reforming process (SRM, POX or DRM) or combination of all three processes regarded as tri-reforming process will be described. Furthermore, different types of catalysts investigated for reforming process will be described in detail.

2. Methanol synthesis via CO_2 hydrogenation

Two major routes are considered for the methanol synthesis via syn-gas and CO_2 hydrogenation. This review paper is focused on the methanol synthesis via syn-gas; however, it will be necessary to discuss the brief overview of CO_2 hydrogenation. There are number of review papers published in the recent years describing the thorough background of the process and detailed information on the recent advances.[3,33-43] CO_2 is a cheap, nontoxic and abundant C1 feedstock and its chemical utilization is a challenge and important topic. CO_2 activation by heterogeneous catalytic routes was still limited and efforts have been made towards the synthesis of dimethyl carbonate, cyclic carbonates and syn-gas as well as methanol synthesis.[34] CO_2 is a kind of potential carbon raw materials and also regarded as a major greenhouse gas.[44] Therefore, utilization of greenhouse gas in the synthesis of chemicals made by the hydrogenation of CO_2 is the most economical way to deal with the crisis of global warming and greenhouse gas issue.[2,45] The major reactions in the methanol synthesis are CO_2 hydrogenation (equation 9) and a side reaction referred to as reverse water gas shift (RWGS) reaction (equation 10).

CO_2 hydrogenation: $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$ $\Delta H_{298K} = -49.50$ kJ/mol (9)

RWGS: $CO_2 + H_2 \rightarrow CO + H_2O$ $\Delta H_{298K} = 41.19$ kJ/mol (10)

Thermodynamic analysis of methanol synthesis reaction indicated the exothermic nature of reaction and reduction of reaction molecular number. Therefore,

this reaction was favored at low temperature and high pressure.[34] The major challenge faced during the catalytic synthesis of methanol is the higher production of water from both the reactions that had an inhibiting effect on the metal activity during the process.[34,46] Therefore, to diminish the negative influence of water production on the methanol synthesis process, it was suggested to enhance hydrophobic characteristics of the catalysts to achieve better catalytic activities. The occurrence of RWGS leads to the consumption of hydrogen and in result lower the methanol formation. There are many studied focusing on the promotion of catalysts, however, it is suggested that the application and synthesis of novel catalysts should be encouraged which can directly convert CO_2 and remain inactive in RWGS reaction.[47]

The most commonly studied catalyst for methanol synthesis via hydrogenation route is the combination of Cu/Zn system [34,48]; moreover, the application of various metal (Zr, Ga, Si, Al, B, Cr, Ce, V, Ti, etc)[49-52] and metal oxides (ZrO_2, Ga_2O_3 and SiO_2) additives are also studied over Cu-Zn system.[53] The mechanistic study of CO_2 hydrogenation reveals that CO_2 adsorbs on Cu and H_2 adsorbs on Zn and the reaction takes place on the surface of the catalyst. Based on various studies, it was deduced that the high Cu/Zn dispersion is a key factor for high methanol yield and selectivity for methanol synthesis.[48] Sloczynski et al.[54] investigated the addition of Mg and Mn oxides on $Cu/ZnO/ZrO_2$ catalyst and reported the significant influence of MnO promoter on methanol yield and catalytic activity. Another study reported the influence of various active metal (M = Cu, Ag, Au) supported on $3ZnO.ZrO_2$ system and the study reported higher catalytic activity for Cu/ catalyst compared to Ag and Au-based catalyst. This can be dedicated to the strong synergy between Cu and ZnO or ZrO_2.[55] The promotional

influence of various metal oxides of B, Ga, In, Gd, Y, Mn, and Mg was studied on $Cu/ZnO/ZrO_2$ catalyst prepared by two methods: first, by the co-precipitation of basic carbonates and second by complexing with citric acid. It was reported that the addition of metal oxides has strong influence in the enhancement of catalytic activity, stability, dispersion of Cu, modifying surface composition of the catalyst and among all the metal oxides Ga_2O_3 was the more effective and efficient one.[56] Sami et al.[57] investigated the addition of small amount of silica (0.6 wt%) to $Cu/ZnO/Al_2O_3$ catalyst prepared by co-precipitation. The addition of SiO_2 leads to high surface area, pore volume, smaller crystallite size and dispersion of Cu. Moreover, the addition of SiO_2 leads to the suppression of crystallization of Cu occurred due to the products of water produced during methanol synthesis and inhibited sintering. The application of ZrO_2 as carrier or additive for Cu-based catalysts exhibited higher performance due to its excellent ion exchange capacity and abundant oxygen vacancy surface. Zhang et al.[58] investigated the application of ZrO_2 modifier on $Cu/\gamma\text{-}Al_2O_3$ catalyst and reported that addition of Zr enhances the dispersion of CuO species and produced better catalyst performance.

Furthermore, it was proposed that an industrial CO_2 hydrogenation process should be operated at low reaction temperatures. However, a conventional Cu/Zn/Al that was active for methanol synthesis from syn-gas[59] is not as active and selective for the same purpose from a H_2/CO_2 mixture at temperature below 250 ^oC.[60] Therefore, there was a need to synthesize novel catalysts with high catalytic activity at lower reaction temperatures and selectivity for CO_2 hydrogenation. Two major routes are considered to achieve this goal: first is the adoption of complicated preparation procedures to develop catalysts with desired properties and second is the addition of certain metal and metal

oxides other than Al on Cu/Zn crystallites or Cu/Zn/Al composites. A novel fibrous Cu/Zn/Al/Zr was prepared and exhibited higher catalytic activity compared to Cu/Zn/Al, Pt-Ca/C or Cu/Zr based catalysts. The application of Cu/Zn/Al/Zr catalyst exhibited higher CO_2 conversion and methanol yield.[48,60] Cu-based catalysts are usually prepared by co-precipitation method which requires precise pH control and longer aging time for the suspensions.[61] Several other methods such as hydrothermal[62], sol-gel[63,64] and reverse emulsion techniques[65] have also been developed to prepare Cu-based catalysts. These described methods also require longer period of time, complex procedure and in some cases require expensive starting materials.[66] Therefore, Xin et al.[67,68] developed a novel catalysts synthesis procedure regarded as solid-state synthesis approach in which solid-state metathesis reaction occur between hydrate transition metal salts and organic ligand to yield metal complexes, metal clusters or oxides with uniform sizes and shapes. Similar results were reported by Guo et al.[61] for the preparation of $Cu/Zn/ZrO_2$ catalyst with this approach exhibiting better catalytic activity and selectivity for methanol synthesis. Another study reported the application of vertically aligned carbon nanotubes (CNTs) with metal nitrates to form long CNTs intercrossed Cu/Zn/AL/Zr catalyst and reported an enhance effect on methanol yield from 0.94 to 0.28 ($g/g_{cat}.h$) compared to Cu/Zn/Al/Zr catalyst alone without CNTs. This can be dedicated to the phase separation, ion doping, hydrogen reversibly adsorption; moreover, the high thermal conductivity of CNTs improved the stability of the catalyst owing to the fact that CNTs are a good promoter for the Cu/Zn/Al/Zr catalysts.[69]

Noble metal catalysts especially Pd-based catalysts are the most effective catalysts exhibiting significant catalytic activity and selectivity for CO_2 hydrogenation.

Collins et al.[70] investigated the application of β-Ga_2O_3 as a support for Pd active metal and compared the results with pure β-Ga_2O_3. It was reported that Pd-based catalyst exhibited higher conversion rates for feed gas, which was dedicated to the strong metal-support interaction and spillover of atomic hydrogen from active metal Pd to β–Ga_2O_3. Fan et al.[71] studied the application of Pd/CeO_2 for CO_2 hydrogenation and reported higher catalytic activity and stability. Bonivardi et al.[72] investigated the promotional effect of Ga on Pd/SiO_2 and reported enhanced catalytic performance, which can be dedicated to the closeness of Ga_2O_3-Pd functions and hydrogen spillover onto the SiO_2 support. Liang et al.[73] investigated the application of multi-walled carbon nanotubes (MWCNTs) as a support for Pd-ZnO catalyst and reported higher catalytic activity and TOF (1.15×10^{-2} s^{-1}) for 16%$Pd_{0.1}Zn_1$/MWCNTs under reaction conditions of 3.0 MPa and 523 K. The catalytic activity exhibited by CNTs supported catalyst was high compared to 35%$Pd_{0.1}Zn_1$/AC and 20%$Pd_{0.1}Zn_1$/γ-Al_2O_3. However, the high cost of noble metals restricts their application on industrial scale and Cu-based catalysts are commonly used for this purpose. The industrial methanol synthesis process using copper-zinc catalysts is thus the starting point for implementation of methanol chemistry in a future energy scenario.

The capital investment required for a methanol synthesis plant using H_2/CO_2 mixture was estimated to be about the same as that of a conventional syn-gas based plant. The key factor for the large scale production of methanol is the availability of the raw materials (CO_2 and H_2).[3] It was estimated that around 25 billion tonnes of CO_2 yearly added to the atmosphere by the anthropogenic activities.[3] In the present scenario, CO_2 sequestration is employed to reduce the CO_2 associated global warming problems;

however, regarded as an expensive process. Therefore, the better option is to utilize captured CO_2 from various sources such as industrial and natural sources and this concept is regarded as chemical recycling of carbon dioxide to valuable chemicals (methanol and DME), which provides a renewable, carbon-neutral and inexhaustible source for efficient transport fuels.[3] Several technologies have been employed to efficiently capture CO_2 absorption into a liquid solution, adsorption, cryogenic separation and permeation through membranes.[74] A newly introduced material for the purpose of CO_2 capture is the application of metal-organic frameworks (MOF), which are described as a highly porous material with high surface area. Such example of a material is MOF-77 containing zinc clusters joined by 3,5-benzenetribenzene units with a surface area of 4500 m^2/g and have a storage capacity of 1.47 g of CO_2 per g of MOF at 30 bar.[3] Moreover, the requirement of pure CO_2 demands more efficient CO_2 separation method such as the application of novel CO_2 "molecular basket" adsorbent,[75] which can selectively capture CO_2 for the separation of CO_2 from simulated flue gas.[76,77] The recent studied showed the successful application of CO_2 molecular basket to the separation of CO_2 from natural gas fired and coal fired boiler flue gas.[78,79]

Furthermore, the sustainable and cost-effective production of the other primary raw material (H_2) is major challenge.[33,80] The current commercial route to produce H_2 is steam reforming of methane, coal gasification and partial oxidation of light oil residues.[80] Methanol production from H_2 and CO_2 will be considered an environmentally benign process if it utilizes more CO_2 than the one produced during H_2 manufacturing. The other routes adopted for H_2 production are dry reforming of methane and electrolysis of water; however, these processes have their own limitations

due to the high CO content and high electricity cost. Another attractive possible way is the thermo-chemical route as the energy required for water splitting will be supplied by atomic energy or solar energy. The attractiveness of this route is the absence of carbon source (e.g., fossil fuel or biomass origin) for the production of H_2.[33]

A lot of research work is focused on the commercial application of CO_2 hydrogenation; however, the certain challenges hindering its application are stable nature of CO_2 molecule, economical and feasible availability of raw materials (CO_2 and H_2) for large scale plants. Moreover, if renewable sources such as solar energy or electricity produced from sunlight are employed to meet the energy requirements for CO_2 reduction processes; it comes out to be an attractive option and can enhance the attractiveness of the process. Extensive research priority has been given to the utilization of solar energy for CO_2 hydrogenation; with the aim of mitigation of CO_2 associated global warming problems, creation of highly sustainable and renewable energy source and the production of valuable liquid fuels.[41] Therefore, the scale up of these technologies and further improvements are necessary to capture CO_2 efficiently and economically to combat the issue of global warming and to synthesis valuable liquid fuels from problematic greenhouse gas.

3. Methanol synthesis via syn-gas route

In this section, methanol synthesis via syn-gas route and combination of different reforming processes will be investigated with the aim of reducing energy requirements, lower carbon deposition and to enhance attractiveness of reforming processes. Moreover, various sources are considered for their utilization in reforming process such as coke oven gas, biogas, flue gases from power plants based on NG and coal. The composition of biogas depends upon its source such as: sewage digesters usually contain 55% to 65% CH_4, 35% to 45% CO_2 and 1% N_2; from organic waste digesters usually contains 60-70% CH_4, 30-40% CO_2 and 1% N_2. Landfill gases by anaerobic digestion of municipal solid waste have 45-55% CH_4, 30-40% CO_2 and 5-15% N_2.[81] Reforming of biogas not only reduces the concentrations of two major GHG (CH_4 and CO_2) but also enhance recyclability and usability of the GHG to produce useful syn-gas. Furthermore, the addition of various constituents such as oxygen (O_2) and steam (H_2O) will be studied also based on the requirements of the process.

3.1. Methanol synthesis via coke oven gas

Coke oven gas (COG) is regarded as a by-product from coking plants and the composition of COG is: H_2 (55-60%), CH_4 (23-27%), CO (5-8%), N_2 (3-5%) and a lower quantity of several hydrocarbons. COG has been utilized as a fuel in the coke ovens, however, there is a certain amount of COG, which was still available even after its consumption in coke ovens, and this surplus gas is utilized in other plant processes or

sent to torches for flaring.[82-86] However, to make use of COG for methanol synthesis, syn-gas ratio should be around 2 and the acceptable range of R parameter (dimensionless) should be around 2.03-2.05 as described by the previous studies[1,87,88], and the value of R is determined by equation 11.[89-93]

$$R, \text{dimensionless} = (H_2 - CO)/(CO + CO_2) \quad (11)$$

Bermudez et al.[94] studied the production of syn-gas based on CO_2 reforming of COG (DR-COG) and conventional process (combination of SRM and POX). The comparison of both models was done on the basis of four parameters such as: energy consumption, CO_2 balance, carbon and hydrogen yields and their investigations were based on the simulation software ASPEN PLUS®. They concluded that DR-COG is suitable and feasible alternative to produce suitable syn-gas ratio ($H_2/CO = 2$) compared to conventional process. This conclusion was drawn on the basis of low energy consumption, sustainability of the DR-COG process and higher H_2 yields (83.9%) compared to conventional process (H_2 yield: 73.2%). Moreover, the methanol produced from DR-COG will not require further processing and can be utilized as fuel straightaway. However, this was not the case for conventional process, which will produce low purity methanol and further purification will be required. DR-COG process (Fig. 1) requires one reactor; however, to achieve suitable syn-gas ratio there is a double loop system: one for the recirculation and the other for the recovery of untreated H_2. However, conventional process exhibited a higher potential for energy recovery compared to DR-COG despite of its low purity methanol and complex system

requirements. Therefore, an efficient energy integration system will play a decisive role to turn favor for one process over another.

Fig.1. Block diagram of DR-COG process.[94]

Another study investigated the influence of different parameters such as: temperature (800, 900 and 1000 ^{o}C) and volumetric hourly space velocities (VHSV, 0.75 - 9.30 h^{-1}) on the syn-gas production in the presence of Ni/γ-Al_2O_3 catalyst.[92] In this study, the feed consists of 54% H_2 and 23% CO_2 and CH_4 (denoted as gas ternary mixture, (GTM)), moreover, the effect of H_2 addition in the system was compared with the conventional DRM process (CH_4 and CO_2 = 1:1). The presence of H_2 will have two important effects (i) the shift of equilibrium to the left side (reactants), which will lead to the lower reactants (CH_4 and CO_2) conversion and (ii) the RWGS reaction (equation 10) may have more influence on the process leading to the increased consumption of CO_2 and H_2 and in turn more water produced and a decrease of H_2/CO ratio will occur. The comparison of CO_2 reforming of methane and CO_2 reforming of GTM is presented in Fig. 2.

Fig. 2. The comparison of (a) CO_2 reforming of methane and (b) CO_2 reforming of GTM.[92]

It was reported that the increase of reaction temperature (from 800 to 1000 ^{o}C) assisted in the reduction of water production exhibiting the absence of RWGS reaction

and dominance of DRM at high temperatures. At 1000 ^{o}C, there was no water formed and the occurrence of RWGS was avoided, which will lead to higher hydrogen productivity and selectivity. These results are consistent with thermodynamics of reaction since DRM reaction is more endothermic than RWGS, hence, an increase of temperature will lead to the higher impact on dry reforming reaction and in turn higher CH_4 conversion, higher H_2 production and lower water formation. The lower water content has significant influence on methanol synthesis as the water has deactivating effect on $Cu/ZnO/Al_2O_3$ catalyst widely used for this reaction.[95] Moreover, the study of VHSV effect on the reaction indicates that it has a significant influence over the syn-gas ratio, R parameter and selectivity. In case of syn-gas ratio, VHSV was pointed out to be a critical factor with prominent effect (5% variation with the increase of VHSV from 0.75 to 9.30 h^{-1}) compared to the temperature, which has very little effect (only 0.5% from 800 to 1000 ^{o}C). The production of higher syn-gas ratio (> 2) indicated that COG is suitable way to produce methanol. However, the influence of carbon monoxide (CO) addition was not considered in this study, which is present in the COG in the range of 5–8% and will be interesting to study its influence.

Therefore, another study by Bermudez et al.[91] investigated the influence of CO addition over the process performance. This study was focused on the CO_2 reforming of COG with Ni/Al_2O_3 catalyst mixed with activated carbon (AC), performed at 800 ^{o}C with different feed compositions, such as: GTM consists of 54% H_2, 23% CO_2 and CH_4 and GQM (gas quaternary mixture) consist of 52% H_2, 22% CO_2 and CH_4 and 6% CO. It was proposed that the production of syn-gas can take two routes (i) DRM in which decomposition of methane (equation 5) leads to the production of solid carbon and H_2

and in the second step the deposited carbon was gasified with CO_2 to produce CO referred as reverse Boudouard reaction.

$$CO_2 + C \leftrightarrow 2CO \qquad \Delta H_{298K} = 172 \text{ kJ/mol}$$

However, the presence of water in the outlet indicates another possible route, which is the occurrence of RWGS reaction (10) followed by the SRM (equation 2).The syn-gas ratio for all the catalysts was above 2 and hence, suitable for the production of methanol. However, R parameter value is also essential to justify its application for methanol production. This study showed that certain catalysts (50AC/50Ni, 33AC/67Ni and 100 Ni) are suitable for further applications even though the value of R still was just below 2. However, this problem can be overcome by the addition of H_2 in the system, which was unreacted after the methanol synthesis. The addition of CO in the system produced similar effect as explained in the above study for H_2 addition, which is the shift of equilibrium to the left side (reactants) and in turn will exhibit lower reactants conversion.[89,96] The addition of CO produced lower amounts of water by shifting the RWGS equilibrium to the left and enhanced selectivity of the process. However, the lower water production would have a negative impact on the system as there will be less water available to react with methane (SRM). However, in this study different catalyst for CO_2 reforming of COG responded differently with the addition of CO, pure AC catalyst exhibited a slight increase in reactants conversion and opposite was observed for Ni/Al_2O_3. However, for the mixture of AC and Ni, it was concluded that if AC

content in higher than that of Ni/Al_2O_3 there is a small increase in conversion of reactants and opposite occurs in the case of high Ni/Al_2O_3 content.

The discussion above focused on the production of syn-gas with COG; however, there are few studies which focus only on the methane part in COG. Shen et al.[84] studied the POX based on the COG source to produce syn-gas. Their experimental setup was composed of three systems such as; COG purification, membrane separation and CH_4 conversion. In COG purification and membrane separation system, the aim was to separate CH_4 from its components and then executed POX ($CH_4/O_2 = 1$) to produce syn-gas. However, the disadvantage of this process was the lower syn-gas ratio ($H_2/CO = 0.4$), which was not suitable for the production of methanol. Moreover, it requires complex system to separate and recover methane from COG, which makes this process less attractive and expensive. In the above section, the feasibility of COG to produce suitable syn-gas ratio was investigated with H_2 and CO addition and a detailed study leads to the conclusion that COG can be utilized to produce syn-gas for the production of methanol owing to its suitability to the current system without further purification and extra cost. However, it will be interesting to study the influence of different catalysts on the reforming of COG, as most of the studies were focused only on different feed ratios (effect of H_2 and CO addition). Further study on economic analysis of the COG reforming process will highlight the attractiveness and feasibility of this process to adapt on industrial scale.

3.2. Methanol synthesis via bi-reforming

There is an always increasing demand and extensive research going on to produce alternative energy sources with less or minimal environmental impact. There is a process termed as "Carnol Process" which is regarded as a combination of two industrial based chemical reactions. The first chemical reaction is methane decomposition reaction producing deposited carbon and gaseous H_2. This chemical reaction is thermodynamically favorable at high reaction temperatures. Furthermore, the produced H_2 is reacted with captured CO_2 from fossil fuel burning power plants and other industrial flue gases.[97,98] This process was develpoed by Brookhaven National Laboratory. The major advantage of this process is the utilization of recovered waste CO_2 from the coal burring plant, which results in the decrease of around 90% net CO_2 emission compared to the conventional SRM for methanol production. The two basic chemical reactions taking part in Carnol process are described below:

Methane decomposition: $3CH_4 \rightarrow 3C+6H_2$

Methanol synthesis: $2CO_2 + 6H_2 \rightarrow 2CH_3OH + 2H_2O$

Overall Carnol process: $3CH_4 + 2CO_2 \rightarrow 2CH_3OH + 2H_2O + 3C$

Moreover, the attractiveness of the Carnol process is the carbon neutrality that all the carbon content in methane will end up as solid carbon, which can be easily handled, stored and also enhances the economics of the process. The industrial application of this process requires higher temperature 800 ^oC and not only regarded as a process to

produced hydrogen only but the produced carbon black can be used as a commodity material in the tire industry and as a pigments for inks and paints. Even though the process accomplishes a major decrease of net CO_2 emission compared to SRM process, the disadvantage of this process is lower number of moles of H_2 (2 mol) produced per 1 mol of methane decomposed; however, SRM produces 3 mol of H_2 per 1 mol of CH_4 utilized. Moreover, this process results in high operational costs for lower amount of H2 generated compared to SRM. Therefore, a combination of methane decomposition and DRM is performed to overcome this issue; however, the environmental benefits of this process are not as high as with "Carnol Process".[3]

$$CH_4 + CO_2 \leftrightarrow 2CO+2H_2$$

$$\underline{CH_4 \leftrightarrow C+2H_2}$$

$$2CH_4 + CO_2 \leftrightarrow 2CO+4H_2 + C$$

The production of suitable syn-gas ratio leads to the methanol synthesis as described in the following reaction

$$2CO + 4H_2 \leftrightarrow 2CH_3OH$$

However, the basic reaction (DRM) considered in this combination produces lower syn-gas ratio ($H_2/CO = 1$), which is only suitable for the production of Fisher-Tropsch synthesis of alkanes, and not suitable for methanol synthesis. Therefore, another combination of DRM and SRM was considered to produce syn-gas with suitable ratio ($H_2/CO = 2$) to produce methanol and this particular syn-gas was termed as met-

gas. This combination of DRM and SRM is termed as bi-reforming in which a specific ratio of methane, steam and carbon dioxide (3:2:1) is adjusted to produce met-gas.[3,19]

$$2CH_4 + 2H_2O \leftrightarrow 2CO + 6H_2O$$

$$\underline{CH_4 + CO_2 \leftrightarrow 2CO + 2H_2}$$

$$3CH_4 + 2H_2O + CO_2 \leftrightarrow 4CO + 8H_2 \leftrightarrow 4CH_3OH$$

A recent study on bi-reforming was reported by Olah et al.[19] in which NiO/MgO catalyst was investigated for this process at high pressure (5-30 atm) and temperature (800-950 ^oC). The significance of this study was the application of high pressure employed near to practical conditions, as previous studies for DRM[99,100] and SRM[101-103] were done at atmospheric pressure. In this study, NiO/MgO catalyst showed higher catalytic activity (70-75% based on single pass conversion) and stability up to 160 h and high H_2/CO ratio (1.9). However, the syn-gas ratio can be increased to suitable syn-gas ratio by adjusting H_2O to CO_2 ratio in the feed gas. Moreover, this study investigated the influence of catalysts and reactants in a single pass conversion, the overall conversions can be increased by considering the recycle of unreacted gas from outlet.[19] However, there were no more studies reported on bi-reforming process, which investigated on different aspects of process such as: different types of catalysts and the impact of recycling (untreated streams) to enhance syn-gas ratio.

3.3. Combination of DRM and POX

The combination of dry reforming and partial oxidation has several advantages such as: effective heat supply due to combination of endothermic and exothermic reactions and also the reduction of hot spots produced in POX alone.[104,105] Biogas reforming is considered as an endothermic process, therefore, to enhance acceptability and overall efficiency of the reforming process heat recovery techniques are introduced i.e., utilization of the exhaust gas heat from the engine to produce syn-gas. Lau et al.[106] investigated the possibility of utilizing biogas mixed with exhaust gas (i.e. source of O_2, H_2O, CO_2) to study the combination of DRM and POX (equation 12) and also studied the influence of O_2/CH_4 molar ratio (0.16, 0.25 and 0.57), temperature (300-900 ^oC) and GHSV (16500 and 27500 h^{-1}) on the process performance. Simultaneous DRM and POX reaction is depicted in the equation 12:

$$0.6CH_4 + 0.4CO_2 + 0.15O_2 \rightarrow 0.9CO + 1.2H_2 + 0.1CO_2 \quad (12)$$

The study indicated that addition of O_2 has higher influence on H_2 production at low temperature (500 ^oC) at any O_2/CH_4 ratio and GHSV. However, with the increase of temperature at low O_2/CH_4 ratio (0.16), there was seen a negative trend for H_2 production and this can be dedicated to the higher O_2 utilization by the complete combustion (equation 13) of methane forming H_2O and CO_2.

Complete combustion: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ (13)

Moreover, the investigation on the influence of the temperature indicates that at high temperatures the addition of O_2 had little effect on H_2 production because of the dominance of dry reforming of biogas due to its endothermic nature of reaction. Therefore, it can be concluded that the increase in temperature leads to the decrease in exothermicity of the combined POX and DRM of biogas.[107] It was reported that the effect of GHSV was more prominent at low temperature ranges, where POX is dominant. In Fig 3a, the influence of GHSV is described with the inlet temperature of 500 ^oC at the catalyst bed. The increase of peak temperature is linked with the increase of GHSV which enhanced the transfer rate of reactants on the activity sites of the catalyst surface resulting in higher rates of oxidation. The larger amounts of heat release by the exothermic reaction (POX) at high GHSV forms hot layer at the top catalyst bed which assisted in the occurrence of dry reforming process (Fig. 3a).[108] Temperature profile of the combined DRM and POX describes the change in peak temperature over the catalyst surface at inlet temperature of 400 ^oC (Fig. 3b). There can be seen a steep increase in temperature peak from 400 ^oC to 700 ^oC with the increase of O_2/CH_4 ratio (0.16 to 0.57) and can be related with the higher amount of O_2 present in the POX reaction. This high peak can be dedicated to the exothermic POX or to complete combustion of methane in biogas and the decline of the temperature is related with the dominance of DRM.

Fig. 3. (a) Influcne of GHSV on reactor temperature profile at inlet temperautre 500 ^{o}C and (b) Reactor temperature profile at GHSV 27500 h^{-1} at inlet temperature of 400 ^{o}C.[106]

Özkara-Aydinoğlu et al.[109] investigated the addition of Pt (0.2% and 0.3%) to Ni/Al_2O_3 catalyst and O_2 to dry reforming reaction mixture (CH_4:CO_2=2:1 and 1:1). Among all the catalysts prepared (0.3Pt-10Ni, 0.3Pt-15Ni, 0.2Pt-10Ni and 0.2Pt-15Ni), $0.3Pt\text{-}10Ni/Al_2O_3$ with lowest Ni/Pt ratio (110) exhibited the highest catalytic activity and stability for combined DRM and POX reaction compared to DRM alone (Table 1). X-ray diffraction (XRD) analysis for the bimetallic catalysts (0.3Pt-10Ni and 0.2Pt-15Ni) indicated that 0.3Pt-10Ni catalyst with lower Ni/Pt ratio (110) exhibited smaller Ni particle size (12.6 nm) compared to 0.2Pt-15Ni catalyst with higher Ni/Pt ratio (250), which exhibited higher particle size (19.8 nm). Moreover, lower Ni/Pt ratio assisted in the easy reduction of NiO particles and smaller Ni particles size produced having higher dispersion over the catalyst surface, which is dedicated to the intimate contact between Pt and Ni active sites.

Another study investigated the application of noble metal catalysts (Pt/ZrO_2 (PtZr), Pt/Al_2O_3 (PtAl)) for the combination of DRM and POX, moreover, the influence of 10% ZrO_2 addition on Pt/Al_2O_3 (PtZrAl) was also reported.[110] The highest catalytic activity, stability and lower deactivation rate (0.9%/h) was observed for PtZrAl compared to PtAl (0.9%/h) and PtZr (1.1%/h). Thermogravimetric analysis (TGA) depicted the higher coke deposition resistance as little weight loss (2%) was observed for PtZrAl catalyst. Furthermore, PtAl and PtZr catalysts exhibited around 10% of weight loss and coke deposition was around 6.7 mgcoke/g_{cat} h. The influence of O_2

addition was prominent at low temperatures, moreover, the increase of O_2 concentrations in the feed lead to the decrease in H_2 selectivity and this observation matched with other studies.[111,112]

Carbon deposition is a major problem during DRM reaction, which leads to severe catalyst deactivation and lower catalyst performance. Noble metal (Rh, Ru, Pt, Pd, Ir) catalysts have drawn attention for their superior coking resistance, higher stability and activity especially for higher temperature applications (> 750 ^{o}C).[113] Therefore, their application in the DRM has exhibited higher catalytic activity and superior coke deposition resistance, even though their cost is a major issue in their industrial application.[114,115] Nematollahi et al.[116] investigated the application of noble metal (Rh, Ru, Pt, Pd, Ir) catalysts supported on alumina-stabilized-magnesia (Mg/Al) for combined DRM and POX. The catalytic activity of noble metals for combined reforming reaction exhibits the following trend; Rh ~ Ru > Ir > Pt >Pd. It was observed that at low and medium temperatures, exothermic reactions (combustion and POX) were dominant; however, with the increase of temperature endothermic reaction (DRM) was dominant and exhibited higher methane conversion. Moreover, the influence of O_2 addition was significant at low temperatures (< 550 ^{o}C) in which negative CO_2 conversion were observed. This can be justified on the basis of higher dominance of methane combustion reaction at low temperatures. The activity trend exhibited in this study (Rh and Ru most active) matched with the other studies for DRM in which Rh and Ru exhibited higher catalytic activity compared to Pt, Pd and Ir catalysts.[114, 115] This was attributed to their smaller particle size, higher dispersion and ability to eliminate carbon deposition completely.

Several studies investigated the combination of DRM and POX in a fixed bed reactor (FBR)[117-119], however, there are few studies reporting the influence of fluidized bed reactor (FIBR).[120,121] The application of FIBR has the ability to exhibit effective heat transfer, stability of operation and also fluidization of particles lead to lower carbon deposition. A number of studies[105,122] reported higher methane conversion and high H_2/CO ratio for FIBR compared to FBR as depicted in Table 1. FIBR produces an opportunity for the combination of combustion and reforming process, moreover, there are two types of zones formed during the fluidization of catalysts; one is regarded as oxygen free zone and the other as oxygen rich zone (Fig. 4). In the reforming zone (oxygen free), carbon deposits on the catalyst surface and later on moves to the oxygen rich zone in which deposited carbon is gasified and regenerates the active sites of the catalyst.[123,124]

Fig. 4. Conceptual model of FIBR in methane reforming with CO_2 and O_2.[105]

The ability of supports to provide oxygen to metals, such as ZrO_2 was suggested to be more beneficial compared to irreducible oxide (Al_2O_3 or SiO_2) [125, 126]. In recent years, solid solutions based on ZrO_2 (e.g. MgO-ZrO_2, TiO_2-ZrO_2, Nb_2O_5-ZrO_2) have shown promising results for DRM.[127,128] Asencios et al.[16] reported the application of NiO-MgO-ZrO_2 (NMZ) catalyst with different Ni content (0, 10, 20 and 40 wt%) for combined DRM and POX reaction. The higher catalytic activity (62.0% CH_4 and 75.0 % CO_2 conversion) and stability (7 h) was observed for 20Ni20MZ (20 wt% Ni and 20 mol% MgO). XRD profile indicates that catalysts with higher Ni content (20Ni20MZ

and 40Ni20MZ) exhibited the formation of zirconium nickel oxide (Zr_3NiO), indicating the presence of strong interaction between NiO and ZrO_2. Various studies also confirmed the formation of NiO-ZrO_2 solid solution at higher Ni contents (20 and 40 wt%).[129-131] The lower catalytic activities for the catalysts with lower Ni content (10 wt%) can be ascribed to the presence of fewer active sites available for methane decomposition, while the lower catalytic activity at higher Ni content (40 wt%) can be related to the presence of larger crystalline size of Ni^o (60 nm), which gave rise to the sintering of Ni^o particles due to high nickel load. The carbon deposition formation rates (mmol h^{-1}) were such as: 10Ni20MZ (18) < 20Ni20MZ (20) < 40Ni20MZ (120). Sun et al.[132] studied the application of Y_2O_3 (5%, 8%, 10%) as a promoter for Ni/ γ-Al_2O_3 catalyst and reported that the increase of Y_2O_3 content (5 to 10%) in Ni/γ-Al_2O_3 leads to the production of smaller Ni particle size, higher Ni dispersion, strong basicity and higher NiO reducibility compared to unpromoted Ni/γ-Al_2O_3 catalyst. Therefore, Ni/10YAl exhibited higher catalytic activity, which can be dedicated to the higher Ni dispersion (15.7%), NiO reducibility (89.8%), CO_2 desorbed (22.3 μmol g^{-1}cat) and smaller Ni size (6.50 nm) compared to Ni/γ-Al_2O_3 exhibiting poor characteristics (10.3% Ni dispersion, 77.9% NiO reducibility, 5.70 CO_2 desorbed and larger particles size (12.1 nm)). Moreover, the addition of Y_2O_3 enhanced resistance to the metal sintering as depicted by particle size analysis before and after reforming process, as there was little change in particle size for Ni/10YAl (6.50 to 5.20 nm) compared to Ni/Al (12.1 to 14.3 nm). Ruckenstein et al.[104] investigated the combined reforming of methane (DRM and POX) over Co/SiO_2, Co/CaO and Co/MgO. The author reported higher catalytic activity, stability, lower carbon deposition and high syn-gas ratio for

Co/MgO compared to other catalysts (Co/SiO_2, Co/CaO). The superior catalytic activity was ascribed to the higher reducibility of the Co/MgO arising due to the strong interaction between metal (Co) and support (MgO). Moreover, smaller metallic crystallites site were formed on MgO-supported catalyst and were partially embedded in the MgO lattice. XRD profiles indicated the formation of different solid solutions arising due to the metal-support interactions and exhibited the presence of smaller crystalline size for Co/MgO compared to Co/CaO and Co/SiO_2. The formation of such smaller crystalline sites suppressed the occurrence of carbon deposition as encountered in the methane decomposition. Moreover, TPR profiles indicated the reduction trend in the following manner: $(Co,MgO)O << Ca_3Co_4O_9 < Co_3O_4$. The lower reducibility (5%) of the Co/MgO catalysts can be dedicated to the strong metal support interaction between CoO and MgO.

3.4. Combination of DRM and SRM

The combination of DRM and SRM has more attractiveness in its application compared to DRM alone, as the addition of steam reduces the risk of carbon deposition and gives better control over the syn-gas ratio[107,133,134]; as SRM alone produces high syn-gas ratio ($H_2/CO = 3$)[101]; which is comparatively higher for methanol synthesis.[19,20] Mostly, Ni-catalysts are applied for combined reforming due to their low cost and quite significant activity; however, the major problem with their application is their lower resistance to carbon deposition. There are various ways to diminish/ eliminate carbon deposition completely or reduce to a minimal which include application of basic

supports (MgO,CaO)[135-137], addition of various promoter[138-142] or optimization of synthesis methods[143] and in some studies addition of little amount of noble metals were also done to enhance catalytic activity of Ni-catalysts.[144-147] Therefore, to reduce carbon deposition and enhance catalytic activity Ni catalysts, Son et al.[148] investigated the combination of DRM and SRM on steam treated Ni/γ-Al_2O_3 catalyst (WNiAl) and with conventional H_2 treated Ni/γ-Al_2O_3 (NiAl). The WNiAl catalyst exhibited higher reactants conversion (97.1% CH_4 and 81.2% CO_2) compared to NiAl (90.8% CH_4 and 73.3% CO_2) and this can be related to the influence of steam treatment on structure and morphology of WNiAl catalyst. TGA analysis exhibited lower weight loss (3.6%) and carbon deposition (0.18 mg C/gcat.h) compared to NiAl (15.4% weight lost and 0.77 mg C/gcat.h carbon deposition) after 200 h of the reforming reaction (Fig. 5b). Moreover, TPR-H_2 profile indicated the shift of reduction peak to higher temperature (700-1000 ^oC) for WNiAl and exhibits the presence of strong metal support interaction; however, lower reduction peak (100-400 ^oC) was exhibited for NiAl (Fig. 5a). Furthermore, a higher decrease in pore volume (0.34 cm^3/g to 0.15 cm^3/g) was noticed for NiAl compared to WNiAl (0.45 cm^3/g to 0.39 cm^3/g) and this can be ascribed to the higher carbon deposition blocking the pore volume. This conclusion matched with the TGA results, which exhibited higher coke deposition for NiAl compared to WNiAl.

Fig. 5. (a) TPR-H_2 profiles of fresh catalysts and (b) TGA and DTG profiles of different catalysts after reforming reaction for 200 h.[148]

Huang et al.[149] investigated the promotional influence of MgO (1 wt% to 7 wt%) on Ni/SBA-15 (5 wt% to 15 wt% Ni) with the aim of enhancing catalytic activity, moreover, the influence of different feed ratios were also reported. It was reported that 10%Ni/3wt%MgO/SBA-15 exhibited the higher catalytic activity (98.7% CH_4 and 92.0% CO_2 conversion) at the suitable feed ratio of CH_4:CO_2:H_2O (2:1:1.5), respectively. Moreover, it was also noticed during the study that addition of MgO has strong influence over CO_2 conversion compared to CH_4 and this can be related to the basicity of MgO as CO_2 is acidic in nature and it leads to enhance adsorption of CO_2. However, with the increase in MgO content (> 3%), an inverse effect over CO_2 conversion was observed, as the number of active site decreased greatly due to the deep penetration of Ni^{2+} ions into the MgO lattice, which were difficult to reduce and lead to the decrease in reactants conversion.[150,151]

The catalysts applied for combined reforming of methane should have higher thermal stability as it requires higher inputs of energy due to endothermic reactions (DRM and SRM). Therefore, MgO proves to be a promising support as it has high thermal stability, reduces carbon deposition due to its basic nature and compatibility of MgO with NiO leads to the formation of NiO-MgO solid solution, which assisted in the achievement of higher catalytic activity and stability.[20,26,152] Danilova et al.[153] reported the application of Ni (1-5 wt%) catalyst supported on MgO (7-10 wt%) for combined reforming reaction (DRM and SRM) with feed composition such as: CH_4:CO_2:H_2O:N_2=35:23:39:3 vol%. The study indicated that 4%Ni/10%MgO exhibited higher methane conversion (60% stable up to 18 h) with the syn-gas ratio of 2.1-2.8, however, lower CO_2 conversions were observed. This can be attributed to the high H_2O

content in the feed compared to CO_2 as the higher steam concentration would lead to the dominance of SRM compared to DRM and in turn higher syn-gas ratios.

The influence of CeO_2 promoter over Ni/Al_2O_3 and $Ni/MgAl_2O_4$ (MgO/Al_2O_3 ratios = 3 to 7) catalysts was investigated for combined DRM and SRM. In this study, $Ni\text{-}Ce/MgAl_2O_4$ (Mg/Al = 3) exhibited higher catalytic activity compared to Ni/Al_2O_3 and $Ni/MgAl_2O_4$ (Mg/Al = 3) with suitable syn-gas ratio (>2).[154] The higher catalyst performance can be dedicated to the higher coke resistance of promoted catalyst and TGA exhibited lower weight for $Ni\text{-}Ce/MgAl_2O_4$ (Mg/Al = 3). Moreover, promoted catalysts exhibited higher resistance to agglomeration, better interactions of CeO_2 and $MgAl_2O_4$ lead to higher dispersion of Ni particles. Similar results were reported by Koo et al.[155] in which $Ni\text{-}Ce/MgAl_2O_4$ catalyst with different Ce/Ni ratio (0.0-1.0) was investigated for the combined reforming reaction. It was observed that Ce/Ni ratio of 0.25 was suitable choice and can be justified on the basis of higher metal dispersion (4.91%), smaller crystalline NiO peaks (8.3nm) and lower coke deposition (8.0%) compared to $Ni/MgAl_2O_4$ catalyst with Ce/Ni = 0 exhibiting lower metal dispersion (3.49%), higher crystalline NiO size (11.0 nm) and higher coke deposition (25.5 %). The higher catalytic activity of $Ni\text{-}Ce/MgAl_2O_4$ can be dedicated the enhanced basic sites as depicted by TPD-CO_2 results in Fig. 6A. The high intensity of strong basic sites for $Ni\text{-}Ce/MgAl_2O_4$ can be described by the shift of TPD peaks from lower temperatures to higher temperature. Moreover, TGA analysis of $Ni\text{-}Ce/MgAl_2O_4$ with different Ce/Ni ratios (0.0, 2.5, 5.0, 10.0) indicated lower weight loss for Ce/Ni = 2.5 (Fig. 6B). Therefore, it can be deduced that the addition of Ce to $Ni/MgAl_2O_4$ catalyst enhanced stability, activity and enhanced coke deposition resistance.

Fig. 6. (A)TPD-CO_2 profiles for Ni-Ce/$MgAl_2O_4$ catalyst promoted with Ce/Ni ratios (a) 0.00 (b) 0.25 (c) 0.50 (d) 1.00 and (B) TGA profiles for Ni-Ce/$MgAl_2O_4$ catalyst.[155]

Moreover, Ryi et al.[156] investigated the influence of CO_2/H_2O molar ratio (0-1.0) at different temperatures (627 ^oC to 767 ^oC) on reactants conversion and H_2/CO ratio. The influence of CO_2/H_2O ratio was not much prominent at temperature above $\geq$ 700 ^oC and this can be related to the endothermic nature of both reactions indicating that the activation energies of both reforming process (DRM and SRM) were sufficient at 700 ^oC (Fig. 7a). However, the activation energy for DRM was not sufficient at lower temperatures (650 ^oC), which matched with another thermodynamic study on DRM reporting that spontaneous reaction cannot be achieved below 640 ^oC [157]. In the combined reforming process, it was encountered that there are many side reactions occurring during the completion of reforming process, such as: SRM (equation 2), DRM (equation 8), methane decomposition (equation 5), carbon gasification ($C+2H_2O \rightarrow CO_2 + 2H_2$) Boudouard reaction (equation 6), WGS reaction (equation 3) and RWGS reaction (equation 10). In the above reactions, CO_2 is a reactant in DRM, reverse Boudouard reaction, and RWGS, and appears as a product in WGS and carbon gasification reaction. In Fig. 7b, negative CO_2 conversion indicates the dominance of WGS reaction over DRM reaction, however, with the increase of CO_2/H_2O there was an increase in CO_2 conversion and indicates the dominance of DRM reaction. In Fig 7c indicates the influence of CO_2/H_2O ratio over syn-gas ratio (H_2/CO) and it was observed that the increase in reactants molar ratio leads to the decrease in H_2/CO ratio indicating

the dominance of DRM reaction at higher CO_2/H_2O ratios and vice versa at lower CO_2/H_2O ratios.

Fig. 7. Influence of CO_2/H_2O ratio over (a) CH_4 conversion (b) CO_2 conversion and (c) H_2/CO ratio.[156]

On industrial scale gas to liquid (GTL) processes, high pressures are applied for the conversion of syn-gas to dimethyl ether (DME) and methanol; therefore, it was practical to perform combined DRM and SRM reaction at higher pressures from economical point of view. Özkara-Aydinoğlu et al.[158] investigated the influence of high pressures (1 bar and 20 bar) on combined DRM and SRM reaction at two temperatures (800 and 1000 ^oC) with different feed ratios (CH_4:CO_2:H_2O= 1/1/1/, 1/1/2, 1/1/3). The study revealed that combined reforming reaction exhibited higher methane conversion (almost 100%) at 1 bar and 800 ^oC for all feed ratios, however, the increase of pressure (1 bar to 20 bar) leads to the decrease in methane conversion. The increase in steam concentration ($CH_4/CO_2/H_2O$ = 1/1/1 to 1/13) in the feed composition leads to the increase in methane conversion (56% to 75%) at high pressure (20 bar). The author reported no significant influence of pressure (1 bar and 20 bar) on methane conversion or syn-gas ratio at high temperature (1000 ^oC) with similar feed ratios. This study indicated that the influence of pressure (1 bar and 20 bar) on methane conversion or H_2/CO ratio is more significant at low temperature (800 ^oC); however, the influence of pressure shift was minimal at high temperature (1000 ^oC).

Nakoua et al.[159] studied the addition of promoter (Ba, Cr, and La_2O_3) on Ni/Al_2O_3, effect of pressure (1-20 bar) and different flow rates of methane (0.4 to 1.0 mol/h), H_2O (1.0 to 2.25 mol/h) and CO_2 (0.2 to 0.53 mol/h) on the combined reforming process. In this study, two types of catalysts were prepared $Ni(49\%)/Al_2O_3(51\%)$ (Catalyst A) and $Ni(33\%)$-$Cr(56\%)$-$Ba(11\%)/La_2O_3(19\%)$-$Al_2O_3(31.4\%)$ (Catalyst B). It was reported that with the increase of H_2O/CH_4 ratio from 1.67 to 2.5 resulted in the increase of methane conversion (85% to 93%). It was reported that both DRM and SRM reaction are favored at low pressure, meaning any pressure above the atmospheric pressure would lead to the decrease in maximum possible reactants conversion due to molar expansion. The applied pressure near the equilibrium position will shift the equilibrium to the left leading to the decrease in reactants conversion. The partial pressure of H_2O and CO_2 in the reforming system should be adjusted such that both reactions (DRM and SRM) proceed at the same rate and reaction expression for such system can be expressed by the following equation 14

$$CH_4 + 1/3CO_2 + 2/3H_2O \rightarrow 4/3CO + 8/3H_2 \quad (14)$$

The study indicated the decrease of methane conversion with the increase of pressure (1-20 bar) as depicted in Fig. 8a. However, a favorable syn-gas ratio (2.20) for the Fischer-Tropsch synthesis was observed at 700 ^oC and 3 bar. The addition of steam leads to the decrease in CO_2 conversion due to the competition of the H_2O and CO_2 molecules for active sites, however, there was seen an increase in stability of catalyst (140 h) and minimization of carbon deposition for catalyst B. Moreover, Fig. 8b

describes the change of pressure from 0 to 42 psig after 25 h time on stream and indicated the decrease of reactants conversion with the increase of pressure.

Fig. 8. (a) Influence of reaction temperature with corresponding pressure on methane conversion (b) Reaction pressure vs time on Ni-Cr-Ba/La_2O_3-Al_2O_3 at reaction temperature 670-850 ^oC.[159]

3.5. Combination of SRM and POX

In this section, combination of SRM and POX regarded as auto-thermal reforming (ATR) will be investigated with the aim of reducing heat requirements, minimize carbon deposition, better control over syn-gas and reducing the risk of hot spots formation.[160] The previous studies revealed that such combination of exothermic and endothermic reactions will not require any external heat source[161], as the energy produced by exothermic reaction will be utilized in endothermic reactions and the equilibrium production composition and temperature will be dependent on the feed ratios (H_2O:CH_4 and O_2:CH_4). The industrial gas industry has in the last decade has shown increasing interest in ATR for commercial production of H_2 and CO or CO-rich mixtures. The desired syn-gas ratio composition for Fisher Tropsch synthesis or methanol synthesis is often characterized by an H_2/CO ratio of 2. This ratio cannot be obtained by the ATR process alone except at very low S/C ratio and by adjusting the preheat temperature. Moreover, the other possible route is by recycling a small amount

of CO_2. Large attention has been drawn on industrial scale to optimize S/C ratio in ATR process, which in turn leads to the production of suitable syn-gas ratio and improved efficiency for GTL plants. For several years, industrial operation for ATR process was conducted at S/C = 1.4. However, further studies reported the optimized ratio of S/C (0.6) and have been demonstrated in an industrial reactor. Today ATR appears to be the cheapest solution fulfilling the optimum requirements of the MeOH and FT-syntheses.[12] Moreover, such a plant based on S/C ratio of 0.6 has been commercialized by Haldor Topsøe A/S (Topsøe) and a plant in Europe has been in commercial operation. Moreover, ATR process will be favored for large capacity plants of about 6000 MTPD.[162]

Furthermore, the key controlling elements of the performance and efficiency of the ATR process depends strongly on the catalyst type, structure and composition. The catalysts function in the process is to equilibrate syn-gas and destroy soot formation. Moreover, the catalyst should be able to withstand high temperature and steam partial pressure. The more important feature of catalyst is its small particle size to avoid pressure drop, minimize the influence of sintering and have high catalytic activity.[163] Therefore, various studies were conducted to synthesize suitable catalysts by the application of suitable supports, combination of different active metals and promoters. Takeguchi et al.[164] investigated the application of several catalysts for combined reforming process and reported their catalytic activity such as: $Ni/(CaO)_{0.09}(ZrO_2)_{0.91}$ > Ni/ZrO_2 > Ni/Al_2O_3. Moreover, addition of CeO_2 over $Ni/CaO\text{-}ZrO_2$ enhanced catalyst performance and $Ni/(CaO)_{0.09}(CeO_2)_{0.05}(ZrO_2)_{0.86}$ catalyst exhibited higher methane conversion amongst all the other catalyst combinations Ni/ZrO_2, Ni/Al_2O_3, $Ni/(CaO)_{0.09}$

$(ZrO_2)_{0.91}$, $Ni/(CaO)_{0.09}(CeO_2)_{0.01}(ZrO_2)_{0.90}$ and $Ni/(CaO)_{0.09}(CeO_2)_{0.13}(ZrO_2)_{0.78}$. XRD profiles indicated the presence of small NiO crystalline size for $Ni/(CaO)_{0.09}(CeO_2)_{0.05}(ZrO_2)_{0.86}$ compared to $Ni/(CaO)_{0.09}(ZrO_2)_{0.91}$ and $Ni/(CaO)_{0.09}(CeO_2)_{0.01}(ZrO_2)_{0.90}$, which exhibited higher crystalline peaks for NiO facilitating the sintering of Ni particles. TPR-H_2 profiles for $Ni/(CaO)_{0.09}(CeO_2)_{0.05}(ZrO_2)_{0.86}$ exhibited the shift of reduction peak to high temperature (NiO > 320 ^oC) leading to the conclusion that there was strong metal-support interaction. The application of Ni/ZrO_2 catalyst in DRM reaction has exhibited significant results and this can be dedicated to the zirconia support having higher thermal stability and it acidic basic characteristics[165-167]. Therefore, based on the promising results from previous studies, Roh et al. [168] studied the application of Ni/ZrO_2 catalyst for combined SRM and POX reaction and also reported the addition of CeO_2 promoter. In this study, $Ni/Ce\text{-}ZrO_2$ catalyst exhibited higher catalytic activity (99.1% methane conversion stable up to 100 h) compared to SRM and POX alone. Moreover, the catalytic activity of $Ni/Ce\text{-}ZrO_2$ was higher compared to Ni/ZrO_2, Ni/CeO_2 and $Ni/MgAl_2O_4$ catalysts. The higher catalyst performance of $Ni/Ce\text{-}ZrO_2$ can be ascribed to the addition of ceria, which enhanced the concentration of highly mobile oxygen species and also form a highly thermal stable solid solution with ZrO_2. TPR-H_2 profile indicated the easier reducibility of $Ni/Ce\text{-}ZrO_2$, which leads to more highly oxygen species via a redox cycle and also enhanced decoking activity of the catalyst through the participation of lattice oxygen. $Ni/Ce\text{-}ZrO_2$ (254.7 μmol/g-sample) has higher oxygen species compared to MgO (3.36), ZrO_2 (5.25) and CeO_2 (251.5), however, $MgAl_2O_4$ did not exhibit any mobile oxygen species. It was suggested that $Ni/Ce\text{-}ZrO_2$ catalyst structure composed of different layers in which the upper layer consist of Ni particle and

there exists a special structure Ni-Ce-Zr-O_x, between the upper layer and support (Ce-ZrO_2), due to the strong metal and support interactions (Fig. 9).

The application of oxygen ion conducting materials such as CeO_2, ZrO_2 and TiO_2, which own oxygen vacancies, has strong influence over the metal-support interaction. This can be dedicated to the interaction of the surface oxygen vacancies of the support with the supported Ni.[169] It was suggested that H_2O dissociates over the oxygen conducting support

$$H_2O + * \rightarrow \quad H_2 + O^*$$

Whereas * denotes an active site over Ni or oxygen vacancy over ceria and O* denotes the adsorbed oxygen species over Ni or an occupied oxygen vacancy. It was reported that produced oxygen species promotes the autocatalytic H_2O dissociation

$$H_2O + * + O^* \rightarrow H_2 + 2O^*$$

Moreover, the surface O species produced by H_2O dissociation lead to the lower rate of carbon formation due to the interfacial reaction of carbon species with surface O species such as

$$CH_x + O \rightarrow \quad CO + xH$$

Huang et al.[169] reported that the catalysts without oxygen conducting materials CeO_2 has a much higher carbon formation such as Ni/γ-Al_2O_3 and it was dedicated to the absence of surface oxygen species.

Fig. 9. Conceptual trilateral catalyst structure of Ni/Ce-ZrO_2.[168]

In this study, Dantas et al.[170] investigated the influence of various promoters (Ag, Fe, Pt, Pd) over Ni/$CeZrO_2$ catalyst applied for combined reforming process (SRM + POX). Among all the series of catalysts prepared, Ag promoted catalyst exhibited higher catalytic activity (55% methane conversion) and stable up to 25 h. This can be related with the ability of silver to modify catalyst structure and this is evident from TRP-H_2 and TPD profiles, which indicates higher reducibility and redox properties of Ag promoted catalyst. In previous DRM studies, it was concluded that the addition of noble metals (Pt, Pd, Ru, Rh) on monometallic Ni catalysts exhibited higher catalytic activity and stabilities compared to monometallic catalysts.[109,145,171,172] Therefore, Li et al.[173] investigated the addition of noble metal (Pt) on monometallic Ni catalysts and also adopted two different methods for the addition of Pt such as: sequential impregnation (Pt/Ni) and co-impregnation method (Pt-Ni). The study indicated that addition of Pt by sequential method (Pt/Ni) is more effective to locate Pt on the surface to form Pt-Ni alloy compared to co-impregnation method (Pt-Ni). Moreover, it was reported that addition of Pt to Ni/Al_2O_3 leads to enhanced catalyst activity due to the decreased Ni oxidation rates near the bed inlet and this keeps Pt-Ni in metallic sites, which enhances the catalyst performance compared to monometallic Ni/Al_2O_3.

All the previous studies on combined reforming were done at atmospheric pressure; however, there was lack of studies regarding the influence of high pressure on the combined reforming performance. In this framework, Chen et al. [160] investigated the influence of high pressure (15 bar) and feed ratios (H_2O/CH_4 and O_2/CH_4) on combined reforming. The study of different H_2O/CH_4 ratios at 1 bar and 15 bar indicated that with the increase of H_2O/CH_4 ratio there was an increase in methane conversion, and H_2/CO

ratio, however, a decrease in CO selectivity was observed and this can be dedicated to the dominance of SRM. Moreover, the decrease of CO selectivity can be related to the occurrence of WGS reaction, which utilizes some part of the produced CO to enhance H_2 yield. However, the shift of reforming process to higher pressure (from 1 bar to 15 bar) indicates that it requires higher H_2O/CH_4 ratio (2.0) to achieve thermodynamic methane conversion (90% methane conversion) compared to lower pressure reforming, where it requires lower H_2O/CH_4 ratio (0.75) to achieve thermodynamic equilibrium methane conversion (98%) and produces high H_2 yield (2.2 mol) compared to high pressure reforming (1.3 mol of H_2 at 15 bar) as depicted in Fig. 10. The study on the influence of O_2/CH_4 indicates that methane conversion was increased with the increase of O_2/CH_4 ratio, while H_2 yield; CO selectivity and syn-gas ratio was decreased. This can related with the dominance of POX compared to SRM. The investigation on thermal efficiency indicated that combined reforming was more thermally efficient process (55.6%) compared to POX, which gives only 35.8% thermal efficiency. The investigation on the various aspects of reforming process indicates that combined reforming of methane is more suitable in terms of methane conversion, thermal efficiency and moreover, assisted in the minimization of carbon formation dramatically at elevated pressures. The addition of steam has strong influence in the minimization of carbon deposition only 2.7 wt% was observed for combined reforming process, while POX depicted 6.7 wt% of carbon deposition. Moreover, the catalysts employed for combination of reforming process alone with their reaction conditions, feed ratios, reactants conversion and syn-gas ratio are listed in Table 1.

Fig. 10. Effect of steam to CH_4 ratio on (a) Methane conversion at reaction conditions (750 ^oC, 1 bar, 8000 ml g_{cat}^{-1} h^{-1}, CH_4:O_2:N_2 = 1:0.5:1.887) and (b) Methane conversion at reaction conditions (850 ^oC, 15 bar, 8000 ml g_{cat}^{-1} h^{-1}, CH_4:O_2:N_2 = 1:0.5:1.887).[160]

Different types of catalyst were applied for the combined reforming process with the aim of achieving higher catalyst performance, however, the application of basic metal oxides (MgO, ZrO_2) both as a support material and promoter leads to the better catalyst performance. Moreover, the addition of cerium oxide (CeO_2) as a promoter for different catalysts leads to superior catalyst properties, particularly for Ni/Ce-ZrO_2 catalyst, which was studied extensively for the combined reforming processes. The attractiveness of this catalyst can be related to the higher oxygen storage capacity (OSC), highly thermal stable (ZrO_2 support), enhanced metal support interaction and formation of large number of mobile oxygen. From the studies on the combined reforming processes (DRM+POX, DRM+SRM, SRM+POX), it can be concluded safely that combined reforming processes are more economical, environmental friendly and with adjustable syn-gas ratio and minimized risk of carbon formation. The choice of reforming process will affect the thermal efficiency of the plant, plant size and location, plant capital cost, the need for oxygen plant or oxygen enriched facilities, the physical size of downstream gas handling equipment, syngas composition and the downstream conversion process. Moreover, the investigations on the ATR process reveal higher performance and feasibility for large scale plants. Moreover, the combination of exothermic and endothermic reactions (SRM+POX) will lead to thermo-neutral process. However, this process still faces the challenges of the availability of low cost oxygen as

discussed earlier in the POX section. The availability of low cost oxygen will have a direct impact on the production cost of syn-gas and will enhance the attractiveness of the ATR process.

Table 1 List of different catalysts and reactions conditions applied for reforming processes

3.6. Methanol synthesis via tri-reforming

Technologies for CO_2 conversion and utilization are an essential part of chemical research to attain the goal of sustainable environment, moreover, CO_2 being an important source of carbon for fuels and as a chemical feedstock in the future.[98,174,175] Flue gases from electricity power plants are considered to be a major source of CO_2 and flue gases from NG fired power plants contain 8-10% CO_2, 18-20% H_2O, 2-3% O_2 and 67-72%N_2. However, coal fired boilers may have little different proportions 12-14% CO_2, 8-10% H_2O and 3-5% O_2 and 72-77% N_2 [176]. Extensive research is focused on the separation of pure CO_2 from its sources, by absorption, adsorption or membrane process[177], however, these processes require substantial amount of energy and are quite expensive[178-182]. It was estimated that 90% CO_2 capture in the flue gas by amine absorption system leads to the loss of total power plant electricity output by 30% and the CO_2 capture cost per ton was around $40-100. The high energy demand by CO_2 capture

system leads to the increase of electricity cost in the range of 50-90% based on the 90% CO_2 capture.[181]

The different reforming combinations discussed in the above section lacks the direct application of these processes to existing facilities such as flue gases from fuel fired power plants, because it will require pre-separation steps. Therefore, tri-reforming process which is a combination of SRM, POX and DRM utilizing the feed sources (e.g., flue gases) without CO_2 pre-separation to produce suitable syn-gas ratio for methanol synthesis.[176] In the proposed tri-reforming process, CO_2 conversion is executed by mixing flue gas with NG and the advantage is the utilization of waste heat in the power plant and in situ heat generation by O_2 oxidation.[176] The proposed concept of tri-reforming of NG for the production of syn-gas using flue gases is depicted in Fig.11.

Fig. 11. Conceptual block diagram of tri-reforming of natural gas.[176]

The combination of SRM and POX with DRM generates heat in situ as POX is exothermic in nature, which will reduce the energy requirements and in turn enhance energy efficiency.[176, 183] Moreover, addition of O_2 will assist in the reduction or elimination of carbon formation on the reforming catalysts. Overall, tri-reforming process leads to the increased catalyst life, process efficiency [176] and has low energy requirements and lesser amounts of CO_2 emissions to produce syn-gas (1.5-2.0) compared to DRM and SRM.[175] Song and Pan[176] investigated the series of catalysts for tri-reforming with feed composition CH_4:CO_2:H_2O:O_2 = 1:0.48:0.54: 0.1 at 700-850 ^oC and reported their catalytic activity in terms of CO_2 conversion the following trend:

Ni/MgO > Ni/MgO/CeZrO > Ni/CeO_2 ≈ Ni/ZrO_2 ≈ Ni/Al_2O_3 > Ni/CeZrO. The higher catalytic activity of Ni/MgO catalyst can be ascribed to the influence of strong metal–support interaction and basicity of support, which leads to the better CO_2 adsorption. However, as syn-gas ratio (H_2/CO) depends strongly on the H_2O and CO_2 conversion, the higher H_2O conversion leads to the higher syn-gas ratio. Therefore, the trend for syn-gas ratios was different compared to CO_2 trend and it was reported that higher syn-gas ratio were obtained for Ni/CeZrO, while Ni/CeO_2, Ni/ZrO_2 and Ni/Al_2O_3 exhibited the similar syn-gas ratio. However, Ni/MgO depicted the lower syn-gas ratio due to its basicity. It was reported that higher catalytic activity (97% CH_4 and 80% CO_2 conversion) and syn-gas ratios of 1.5-2.0 can be achieved at higher temperature 800-850 ^oC for Ni supported catalysts. Minutillo and Perna[184] described a novel approach to capture and utilize CO_2 from flue gases emitted by fossil fired power plant. This strategy is based on the concept of utilizing flue gases as a co-reactant in a catalytic process regarded as tri-reforming process to produce syn-gas with a suitable ratio for the methanol and DME synthesis. They proposed an integrated system referred as integrated tri-reforming power plant (ITRPP) composed of a power island and a methane tri-reforming island. In tri-reforming system, the exhaust from the power plant is reacted with methane to produce suitable syn-gas ratio for methanol synthesis. However, power island consists of two types of turbines: steam turbine power plant utilizes coal as fuel (ITRPP-SC) and a gas turbine combined cycle fuelled with NG (ITRPP-CC) (Fig. 12). In this study, different thermochemical and thermodynamic models were applied to calculate the syn-gas composition, energy and mass balances and CO_2 emission from each integrated system.

Fig. 12. Block diagram for the (a) ITRPP-SC and (b) ITRPP-CC.[184]

In both configurations of power plants, flue gases were sent to the reforming reactor, where it was reacted with methane and the syn-gas from reactor leaves at high temperatures. A heat recover system (HRS) was installed to bring the temperature in the suitable range for methanol synthesis. The recovered heat can be utilized to produce high pressure steam, which was recycled to the steam turbine to produce additional electrical power and makes the process economical and more attractive. However, the analysis showed that the suitable syn-gas ratio ($H_2/CO = 2$) is impossible to achieve from ITRPP-SC and to overcome this problem, water was added (Fig. 12a). The main feature of this ITRPP is the reduction in CO_2 emission, which was estimated to be 83% (15.4 vs. 93.4 $kg/GJ_{Fuelinput}$) for ITRPP-SC and 84% (8.9 vs. 56.2 $kg/GJ_{Fuelinput}$) for ITRPP-CC. This integrated system showed convincing results in terms of reduction of CO_2 emission, energy requirements and energy recovery compared to conventional CO_2 capture techniques in power plants, where ammines are applied for chemical adsorption of CO_2. The drawbacks of the CO_2 capture process are the higher energy demand to regenerate the solvent, consequently, the energy will be supplied by power plant indicating the fact that CO_2 effectively avoided is less that of captured. However, in the integrated system, there are no such surplus energy requirements.

Halmann and Steinfeld[185] reported on the utilization of flue gases from coal and NG fired power plants by tri-reforming process to produce syn-gas with the aim of production of useful products such as methanol, hydrogen and ammonia or urea. This

study emphasized on the advantages of this process in terms of CO_2 emission reduction, fuel saving, economic viability and exergy efficiency. The analysis of flue gas from coal fired plant indicated that it consists of CO_2, H_2O, O_2 and N_2 in the ratio of 13:9:4:74, respectively[186], however, to adjust suitable molar ratio of constituents it requires addition of CH_4, H_2O and air (20, 11 and 24 parts, respectively). The final composition of flue gases will be treated at 727 ^oC (1000 K) and 1 atm.

$$13\ CO_2 + 20\ H_2O + 9\ O_2 + 20\ CH_4 + 93\ N_2 = 12.79\ CO_2 + 18.30\ H_2O + 20.12\ CO + 41.49\ H_2 + 0.09\ CH_4 + 93\ N_2 \quad (15)$$

The syn-gas ratio was around 2.06, which is deemed suitable for the production of methanol and Fischer-Tropsch syntheses. CO_2 emissions based on a conventional 45% efficient 500MW coal fired power plant were reported to be 0.75 ton CO_2/MWh, which are around 3.29 $x10^6$ ton CO_2 per annum. According to the equation 15 describing tri-reforming, 98.4% of the flue gas CO_2 (~3.24 $x10^6$ ton per annum) would be released. Assuming 90% overall yield in the conversion of CO in the syn-gas to methanol, would produce 3.33 x 10^6 tons of methanol per annum, which makes around 8.5% of the current worldwide capacity for methanol. However, to achieve similar production of methanol (3.33 x 10^6 tons) from conventional SRM, would lead to 2.79 $x10^6$ ton of CO_2, and the addition of untreated CO_2 (3.29 $x10^6$) from flue gas around would lead to total emission of CO_2 around 6.08 $x10^6$ ton CO_2/year. Therefore, the overall CO_2 emission avoidance by the application of tri-reforming and production of methanol synthesis would be around 46.7% compared to conventional SRM route.

Further studies on the flue gases composition (CO_2: H_2O: O_2: N_2 =9:19:2.5:69.5) from NG fired power plant[186] and addition of NG and air (15 and 19 parts) leads to the final composition such as:

$$9\ CO_2 + 19\ H_2O + 6.8\ O_2 + 15\ CH_4 + 85.6\ N_2 = 8.71\ CO_2 + 17.89\ H_2O + 15.29\ CO + 31.1\ H_2 + 0.003\ CH_4 + 85.6\ N_2 \quad (16)$$

The syn-gas ratio (H_2/CO) was 2.03, moreover, calculations based on conventional 49% efficient 400 MW NG fired power plant indicates that around 1.47 x 10^6 ton of CO_2 will be emitted per year (0.42 ton CO_2/MWh) [187]. According to equation 16, 96.8% of CO_2 would be emitted by tri-reforming, which is around 1.42 x 10^6. Similar assumption for methanol production (90% yield), indicates that it would produce around 1.635 x 10^6 ton methanol per annum. The production of similar amounts of methanol with conventional SRM would lead to higher CO_2 emissions 2.84 x 10^6 ton CO_2/year compared to tri-reforming process (1.42x10^6 ton CO_2/year). This indicates that tri-reforming of the flue gas followed by the methanol synthesis has CO_2 emission avoidance of around 50.0% compared to conventional SRM route. The comparison of both processes based on different process parameters are listed in Table 2.

Table 2 Analysis of different parameters for tri-reforming relative to SRM

However, there was a lack of study focusing on the economics analysis of tri-reforming to describe the attractiveness of this process. Therefore, a recent study was

conducted to predict the minimization of utility and capital costs with the application of heat integration on tri-reforming process.[188] The heat exchange network (HEN) proposed for minimization utility and capital costs, leads to 34.3% and 32.2% energy saving for methanol production system. After heat integration, the specific energy requirement for CO_2 capture was reduced from 29.0 kWh/kgCO_2 (before integration) to 19.0 kWh/kgCO_2 (after integration). The comparison of tri-reforming with steam CO_2 reforming process (SCM) indicates that the later requires lesser specific energy (11.5 kWh/kg CO_2) compared to tri-reforming (19.0 kWh). However, this drawback was compensated by higher methanol production (2.75 Kg/kg CO_2) for tri-reforming process compared to SCM. Tri-reforming process coupled with methanol production can be considered as an attractive option for the long term global management of carbon. The comparison of utility costs and annual profits before and after heat integration shown in (million dollar US) is depicted in Fig.13.

Fig. 13. Comparison of utility cost (a) and annual profits (b) before and after integration.[188]

Moreover, Zhang et al.[189] investigated the operating cost, utility usage, energy savings for combined process (SRM, DRM and POX) and compared it with conventional SRM. In this study, syn-gas production was coupled with CO_2 separation system; here amine based CO_2 absorption was applied to separated CO_2 from water. The overall mass balance of the SRM and combined process to achieve production rate of 300 kmol h^{-1} of syn-gas accompanied with suitable ratio, is exhibited in Fig.14.

Fig.14. The overall mass balance of (a) SRM and (b) combined process.[189]

The hydrogen production in combined process was small (98 kmol h^{-1}) compared to SRM (588.9 kmol h^{-1}). However, it can be seen that CO_2 produced by combined process was less (34.6 kmol h^{-1}) compared to SRM (122.1 kmol h^{-1}). These results suggested that combined reforming process was more efficient in the regard that at similar syn-gas production rate, CO_2 emissions were less due to recycling of CO_2 in the combined process. Moreover, the detailed analysis of the utility usage by each component in the process indicates that there are 31.2% energy savings with the combined process compared to reference SRM. These energy savings for the combined process can be related to the lower raw materials requirements compared to SRM, which requires large raw materials. Another benefit of combined process is the lower utility costs compared to reference SRM and leads to 24.3% utility cost savings. This high utility cost for SRM can be related to its high heating and cooling requirement compared to combine process. Moreover, total operating cost (TOC) highlighted the better performance of combined process compared to SRM in Fig 15. This indicates that cost of raw materials is high for SRM compared to combined process and can be related to the CO_2 recycled in the process. However, SRM has higher H_2 credit compared with combined process, but the high cost of raw materials and utilities has a bigger impact on TOC and leads to the increase in TOC for SRM process. Therefore, this study leads to the conclusion that combined process is more economically attractive, more feasible,

environmental friendly and lower operating costs. This suggests that tri-reforming process is a suitable option to treat CO_2 effectively and minimize its emissions.

Fig. 15. Total operating costs (TOC) of reference SRM and combined process.[189]

The discussions in the above studies were focused on the economic analysis, energy efficiency, and feasibility of the tri-reforming process. However, an important section of the system, suitable catalysts for tri-reforming was not discussed yet. Therefore, the following section will discuss in detail the influence of different types of active metal, support materials, promoters and the effect of feed gas ratios (H_2O/CH_4, O_2/CH_4) on the syn-gas ratio. It has been suggested that the catalyst employed for tri-reforming must have certain feature such as: high surface area, high OSC, good redox properties, resistance to carbon deposition and metal sintering.[190]

Gracia-Vargas et al.[191] investigated the effect of different active metal precursors with different supports and their influence on catalyst activity, stability, and carbon deposition was reported. Different Ni metal precursors such as: acetate (A), nitrate (N), chloride (C) and citrate (Ci) and two types of support (CeO_2 (C) and SiC (S) were employed and the catalyst combinations were denoted as Ni-AC, Ni-NC, Ni-CC, Ni-CiC and Ni-AS, Ni-NS, Ni-CS, Ni-CiS. In this study, a mixture of reactants $CH_4:CO_2:H_2O:O_2$ = 1/0.5/0.5/0.1 at 800 ^oC was employed for the different catalysts. The higher catalytic activity, stability, lower carbon deposition and high syn-gas ratio (H_2/CO) was obtained for Ni-AS and Ni-NS due to higher metal dispersion and smaller Ni particles, which are considered an important factor for achieving higher activity and

reducing carbon deposition. However, Ni-AC, Ni-NC, produced large metal particles. Moreover, the lower carbon deposition of Ni-AS and Ni-NS was linked with the strong metal-support interactions revealed by TPR results. The lower syn-gas ratio in case of CeO_2 supported catalyst were dedicated to high basicity of CeO_2, which leads to enhance CO_2 adsorption and in turn leads to lower H_2/CO ratio compared to SiC. Therefore, it was concluded that Ni/β-SiC catalyst coupled with acetate and nitrate precursor can be considered as promising catalyst for tri-reforming.

Sun et al.[192] investigated the effect of O_2 and H_2O addition on biogas (60-65% methane and 40-35% carbon dioxide) to produce syn-gas in the presence of Ni/SBA-15 catalyst and mixture of feed gas (CH_4, CO_2, H_2O and O_2) in different molar ratios. The search for the suitable O_2 molar ratio (CH_4:CO_2:O_2=2:1:X, where X=0-1) in feed gas leads to the conclusion that O_2 addition has different effects on CH_4 and CO_2 conversion. Methane conversion was increased from 65.1% to 86.3% for X=0.4, and reached to 99.1% for X=1.0. This suggests that addition of O_2 could promote the conversion of CH_4 but had a contrary effect on the conversion of CO_2, when X > 0.6 the CO_2 conversion decrease rapidly and for X=1.0, CO_2 conversion decrease from 87.1% to 66.0%. Similar profile was reported for the addition of steam (CH_4:CO_2:O_2:H_2O = 2:1:0.6:Y, where Y=0-1) in the feed gas as discussed above for O_2 addition (Fig. 16). Therefore, feed gas CH_4:CO_2:O_2:H_2O = 2:1:0.6:0.6 exhibited higher catalytic activity (92.8% CH_4 and 76.3% CO_2 conversion), syn-gas ratio (1.35) and stable up to 100 h at 800 ^oC.

Fig. 16. The effect of the added oxygen (a) and steam (b) on the catalytic performance.[192]

In the above studies, lower syn-gas ratios were obtained[192,193], however another study reported the application of Ni-MgO-(Ce,Zr)O_2 catalyst for tri-reforming and produced higher syn-gas ratio (>2).[190] The higher catalytic activity and syn-gas ratio can be ascribed to the high OSC produced by the presence of CeO_2[164,194], moreover, the addition of ZrO_2 to CeO_2 eventually enhanced OSC, thermal stability, high metal dispersion and redox properties.[168,195-199] Moreover, basic oxides (MgO and ZrO_2) assisted in the enhancement of carbon deposition resistance due to enhanced basic sites of the catalyst. These basic sites will have higher CO_2 and H_2O adsorption capacity and will result in higher CO_2 conversion and H_2 production.[176, 200] It was reported that each reactant has a different influence on the tri-reforming reaction. While, O_2 has high affinity for active sites and in turn leads to higher O_2 conversion, however, H_2O and CO_2 compete with each other for active sites, increase in H_2O molar ratio produced high H_2/CO ratio. This can be attributed to the high H_2O adsorption on active sites attenuating CO_2 adsorption to produce high H_2/CO ratio. However, there lies a certain limit after which higher H_2O molar ratio leads to a decrease in CO_2 reforming. The major goal of tri-reforming is to achieve high CO_2 conversion, which make process environmental friendly and improved efficient for the Fischer-Tropsch synthesis for liquid hydrocarbons. Therefore, it is required to perform tri-reforming process at certain H_2O concentrations, which does not affect CO_2 conversions and maintaining the high syn-gas ratio (~2).

Sun et al.[183] studied Ni-MgO-ZrO_2 catalyst for tri-reforming with feed gas composition as, CH_4:CO_2:H_2O:O_2:N_2 = 1/0.45/0.45/0.1/0.4 and produced syn-gas ratio (H_2/CO) of 1.5. The influence of H_2O/CO_2 and O_2/CO_2 ratios on reactants conversion matched with the above explained phenomenon[190], indicating that increase of H_2O led to the decrease in CO_2 conversion and high H_2/CO ratio and similar trend was observed for O_2/CO_2 ratios. The increase in O_2/CO_2 ratio, increased H_2/CO from 1.1 to 1.4 and this can be attributed to the higher occurrence of POX compared to DRM. However, in this study (Ni-MgO-ZrO_2) lower syn-gas ratio was achieved compared to NiMg-$Ce_{0.6}Zr_{0.4}O_2$ (> 2)[190], which probably can be attributed to the absence of CeO_2, because all the other process parameters are same for both studies (preparation methods (co-precipitation) and reaction temperatures (800 ^oC)).

Jiang et al.[201] investigated Ni/$Mg_xT_{1-x}O$ (x = 0-1), Ni/TiO_2 and Ni/MgO catalysts for tri-reforming with feed gas of composition as, CH_4:CO_2:H_2O:O_2 = 1:0.48:0.54:0.1 at 850 ^oC. The catalytic activity and stability for the catalysts were such as: Ni/$Mg_{0.25}T_{0.75}O$ ≈ Ni/TiO_2 < Ni/MgO < Ni/$Mg_{0.75}T_{0.25}O$ ≈ Ni/$Mg_{0.5}T_{0.5}O$. The lower stability of Ni/$Mg_{0.25}T_{0.75}O$ and Ni/TiO_2 was dedicated to the formation of stable graphitic carbon (γ-C) deposits, which is difficult to be oxidized by the oxidants (H_2O and O_2) in the feed compared to α-C and β-C, which are easily oxidized. However, Ni/MgO catalyst showed higher resistance towards carbon deposition and no γ-C was formed due to strong metal-support interaction between Ni^o and MgO. Therefore, re-oxidation of Ni^o (formation of NiO) leads to the difficulty in reducing Ni/MgO solid solution and in turn Ni^o active sites gradually decreased leading to lower CH_4 and CO_2 conversion. However, Ni/$Mg_{0.5}T_{0.5}O$ and Ni/$Mg_{0.75}T_{0.25}O$ exhibited no graphitic carbon

peaks and no carbon fibers were found, however, a re-oxidation phenomenon occurs but different compared to Ni/MgO. In this re-oxidation phenomenon, the formation of Ni^{2+} (re-oxidation of Ni^{o}) was exhibited for $Ni/Mg_{0.5}T_{0.5}O$ and $Ni/Mg_{0.75}T_{0.25}O$ catalysts, which can be easily reduced by produced H_2 and CO compared to Ni/MgO (as confirmed by TPR profile Fig.17), leaving the number of active sites constant. This leads to the higher stability and catalytic activity for this pair of catalysts. TPR profiles indicate the shift of reduction peaks to higher temperature with the increase of x value (0 - 1) for $Ni/Mg_xT_{1-x}O$ and the reduction peak for Ni/MgO become broader and smaller compared to Ni/TiO_2.

Fig. 17. TPR profiles of calcined catalysts (a) Ni/TiO_2 (b) $Ni/Mg_{0.25}Ti_{0.75}O$ (c) $Ni/Mg_{0.5}Ti_{0.5}O$ (d) $Ni/Mg_{0.75}Ti_{0.25}O$ (e) Ni/MgO.[201]

Pino et al.[200] investigated the effect of dopant lanthana (La) over $Ni\text{-}CeO_2$ catalyst and reported that modified catalyst have higher activity and stability (96% CH_4 and 86.5% CO_2 conversion) compared to unmodified catalyst $Ni\text{-}CeO_2$ (93% CH_4 and 83% CO_2 conversion). It was attributed to the formation of Ce^{3+} ions arising from the strong interaction between nickel-lanthana-surface oxygen vacancies of ceria, which leads to higher metal dispersion and promotes catalytic activity. Moreover, the production of intermediate and strong basic sites leads to enhanced CO_2 chemisorption due to its acidic nature and in turn produced higher catalytic activities. Similar results were reported for tri-reforming over Ni/La-Ce-O with the feed gas (CH_4:CO_2:H_2O:O_2 = 1:0.66:0.66:0.10) at 800 ^{o}C by Pino et al.[193]. The study reported higher reactants

conversion rates for CH_4 and CO_2 (1.56 and 0.56 mmol/s g_{Ni}, respectively) stable up to 150 h and syn-gas ratio of 1.57 was obtained for Ni/La-Ce-O.

There are various studies focusing over the synthesis of novel catalysts for tri-reforming to achieve higher catalytic activity and stability, however, their comparison with commercial catalysts is essential to justify their enhanced benefits. It was reported in previous studies that NiO-YSZ-CeO_2[202,203] exhibited higher catalytic activity for DRM compared to NiO-YSZ-MgO. Kang et al.[204] investigated the combination of YSZ-CeO_2 supported over Ni for tri-reforming and compared their catalytic activity with commercial HT (Holder Topsoe) catalyst. It was reported that synthesized catalyst exhibited higher CO_2 conversion compared to commercial HT catalyst, moreover, the analysis of outgases indicates the traces of CH_4 and CO_2 (< 1%) for NiO-YSZ-CeO_2 compared to HT catalysts exhibiting 0.5-1.5% CH_4 and 9-11% CO_2. The higher catalytic activity and stability of NiO-YSZ-CeO_2 was attributed to the higher carbon resistance (absence of NiC) confirmed by XRD (Fig.18A). Moreover, TEM image (Fig. 18B) indicated the presence of Ni metal particles in dark spots (< 10nm) and gray parts depicts the presence of YSZ support, however, there was no significant amount of carbon deposition.

Fig. 18. (A) XRD profiles of the NiO-YSZ-CeO_2 catalyst (a) before reduction, (b) after reduction, (c) after tri-reforming for 120h and (d) dry reforming methane. (B) TEM image of NiO-YSZ-CeO_2 catalyst after tri-reforming.[204]

Solov'ev et al.[205] investigated tri-reforming and reported that addition of O_2 favored the occurrence of endothermic reactions (SRM and DRM) due to the formation

of hot zones on the surface of catalyst. In this study, modification effect of rare earth metals (La, Ce) was investigated for Ni/Al catalyst. The unmodified catalyst Ni/Al showed higher methane conversion (100%) for combined SRM and DRM reaction, however, the addition of O_2 lead to the drastic decrease in the methane conversion. This can be attributed to the oxidized Ni present under these conditions and exhaustive oxidation of methane occurring on its surface. However, modified catalyst (NiLaAl) exhibited higher catalytic activity (98% to 100% methane conversion) for tri-reforming process. As depicted in Table 3, higher concentrations of O_2 leads to the increase in methane conversion and syn-gas ratio accompanied a decrease in CO_2 conversion. Similar effects were observed for NiCeAl, however, on the whole, NiLaAl exhibited a better catalytic activity and higher syn-gas ratio (H_2/CO =2.5) compared to NiCeAl (H_2/CO= 2.02). The role of rare earth metals in the enhancement of catalytic activity can be attributed to their high OSC, which assists in the possible accumulation of O_2 and control oxygen concentration in the catalysis zone.[190, 206, 207] Another important factor for the better catalytic activity lies in the ability of rare earth metals to decrease in the strength of Ni and Al_2O_3 in spinel $NiAl_2O_4$.[207] This facilitates the reduction process of NiO and assisted in the release of Ni from spinel $NiAl_2O_4$ structure leading to the higher activity and stability for tri-reforming.

Majewski et al.[208] investigated the application of novel core-shell catalyst (Ni@SiO_2) in which SiO_2 core was protected by Ni shell, which will limit the access to silica surface as previous studies reported that application of silica support for SRM exhibited serious issues. Tri-reforming reaction was investigated over core-shell catalyst by varying feed ratio (CH_4:H_2O = 1:0-3.0 and CH_4:O_2 = 1:0-0.5) and temperature (550-

750 ^{o}C). The influence of temperature was significant in the enhancement of catalytic activity as increase of temperature from 550 to 750 ^{o}C leads to increase of methane (24% to 70%) and carbon dioxide (4% to 52%) conversion; however, syn-gas ratio was seen to be decreased from 3.7 to 2.6. The higher temperature favors the endothermic reforming reactions (SRM and DRM), however, the decrease of syn-gas ratio can be dedicated to the higher occurrence of RWGS reaction, which will utilize some of the H_2 produced and produced more CO. Moreover, the rise of temperature has strong impact on the morphology of the catalyst as described in the Fig 19 by the scanning electron microscopy (SEM). The spent catalyst for tri-reforming at 550 ^{o}C indicated the presence of whisker carbon or carbon nanotubes (Fig.19a), however, there was no such significant amount of carbon nanotubes on the spent catalyst at 750 ^{o}C (Fig.19b). This phenomenon also matches with the TPO results, which indicates the presence of higher coke deposition on spent catalyst at 550 ^{o}C (99 mg/g_{cat}) compared to spent catalyst at 750 ^{o}C (5 mg/g_{cat}). Moreover, the study indicates the influence of molar feed ratios; as the suitable molar ratio (CH_4:CO_2:H_2O:O_2: He = 1:0.5:0.5:0.1:0.4) not only produced higher methane (73%) and CO_2 (55.6) conversion but also exhibited lower coke deposition (5 mg/g_{cat}). The higher CO_2 conversion (91.1%) for the case without H_2O addition can be dedicated to the enhanced CO_2 adsorption on the active sites, as there will be no competition between H_2O and CO_2. However, the addition of H_2O in the system leads to the decrease in CO_2 conversion due to the competition for active sites.

Fig. 19. SEM micrographs of Ni@SiO_2 catalyst after 4 h reaction at (a) 550 ^{o}C and (b) 750 ^{o}C, with feedstock composition CH_4:CO_2:H_2O:O_2:He = 1:0.5:0.5:0.1:0.4.[208]

In the above section, the detailed study of economic aspects, feasibility and influence of different types of catalysts and feeds gas ratios has been reported. However, the influence of reactor type which is an important aspect of any process was not discussed. A recent study investigated the tri-reforming process in a comparison study for FBR and FIBR.[209] FIBR are considered to have good heat management ability, proper mixing of catalyst particles, lower pressure drop and diffusion limitation removal. The study leads to conclusion that the application of FIBR has strong influence over the enhancement of methane conversion and CO_2 consumption by 1.2% and 6%, respectively compared to FBR. This enhancement in reaction efficiency was dedicated to the better temperature management, lower pressure drop and as well as decline in hot spot temperature in the catalytic bed.[209] Moreover, a recent study reported the thermodynamic analysis of tri-reforming process at various reaction conditions such as temperature (200-1000 ^oC), pressure (1-20 atm) and inlet feed gas O_2/CH_4 (0-1.0), H_2O/CH_4 (0-3.0) and CO_2/CH_4 (0-3.0) mole ratios.[210] The study revealed that this reaction is thermodynamically favorable at high temperature and low pressure to produce higher H_2 yield and CO_2 conversion. Furthermore, the study on the inlet gas mole ratios lead to conclusion that the high concentration of H_2O, O_2, CO_2 produced lower H_2 yield and CO_2 conversion, whereas, low concentration of H_2O,O_2,CO_2 resulted in the severe carbon formation. Therefore, to achieve higher H_2 yield and CO_2 conversion and to avoid carbon formation; the optimized feed ratio proposed in the tri-reforming process was such as: $CH_4/CO_2/H_2O/O_2 = 1:0.291:0.576:0.088$.[210] The detailed reaction conditions and reactants conversion are listed in Table 3.

Tri-reforming reaction study indicates that this process is favored at high temperature and low pressure ranges. Moreover, various parameters such as: proper choice of modifier, support and active metal played an important role in enhancing catalytic activity. The interesting feature of tri-reforming process is the combination of endothermic and exothermic reactions and also the direct utilization of CO_2 from industrial sources. This process has been studied extensively at the laboratory scale for the production of methanol and DME; and in the recent years the production of DME at pilot plant scale has been demonstrated in Korea.[211] However, in the best of our knowledge there is no industrial scale operation on tri-reforming process for methanol synthesis. The detailed investigation on the process economics, feasibility, feed gas ratios and catalyst types indicated that tri-reforming is an interesting option for long term global carbon management and for the synthesis of methanol.

Table 3 List of different catalysts and reactions conditions applied for tri-reforming.

4. Future outlook and conclusion

The utilization of the greenhouse gas sources for methanol synthesis will be a tremendously important step for slowing down climate change and to decrease our reliance on fossil fuels. The utilization of COG for the syn-gas generation appears to be a suitable option; however, there was lack of studies on the application of novel catalysts to investigate the influence on catalytic activity and syn-gas ratio. The application of

basic metal oxides (CaO, MgO) and the addition of metal oxides such as: ZrO_2 and CeO_2 as a promoter and support materials for Ni-based catalysts will be suited for this application due to higher OSC, thermal stability and higher carbon deposition resistance. The combination of two endothermic reactions (DRM+SRM) in the bi-reforming process reduced its attractiveness for industrial applications. The required methanol synthesis plant capacity plays a major role in the selection of reforming processes. For small-to-medium scale operations, SRM has been regarded as a suitable option in the past years for industrial operation; however the higher energy requirements in this era of awareness regarding the efficient utilization of resources urge us to search for alternative processes. Therefore, detailed investigation on the different reforming processes (DRM+SRM, ATR, DRM+POX, Bi-reforming, Tri-reforming) with suitable feed sources (biogas, COG, flue gas) and their economic analysis leads to the conclusion that ATR and tri-reforming process seemed to be the promising processes. ATR process has been in operation on the industrial scale and is considered suitable for large scale syn-gas plant capacities; however, tri-reforming process besides its advantages of utilizing flue gases without CO_2 separation is still in its infancy and till now not pursued on industrial scale probably due to the presence of comparably more mature technologies (ATR and SRM) with plenty of industrial experience. Therefore, further investigations on tri-reforming process needs to be focused on its suitability for the large scale plant capacities and also it demands a detailed economic analysis in the future by including the estimation of capital costs and equipment depreciation in the economic analysis to fully reveal the economic feasibility of tri- reforming of methane to produce methanol.[188] It can be anticipated that further studies on tri-reforming process will

highlight its economic benefits and the implementation of tri-reforming process on industrial scale will support our commitment towards the achievement of cleaner and sustainable environment. In the recent years, CO_2 hydrogenation has been extensively studied for methanol synthesis utilizing renewable and non-renewable energy sources and searching for efficient and economical CO_2 capture technologies. In future, it will be interesting to perform a comparison study for methanol synthesis via CO_2 hydrogenation and tri-reforming process from the economical point of view and reduction in net CO_2 emissions because the basic difference between these processes is the CO_2 capture from flue gases in hydrogenation process or utilizing directly into the tri-reforming process. Moreover, the uncertain and continuous depleting resources of fossil fuels require aggressive efforts to pursue for alternative solutions to fulfill our energy demands as there is no single solution available to the facing global challenges. It can be anticipated that the further advancement in different aspects such as: reactor type, catalysts type, and utilization of renewable energy sources will bring significant progress in the abatement of major greenhouse gases (CH_4 and CO_2) and to produce clean liquid fuel (methanol) with minimal environmental damage.

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LIST OF FIGURES

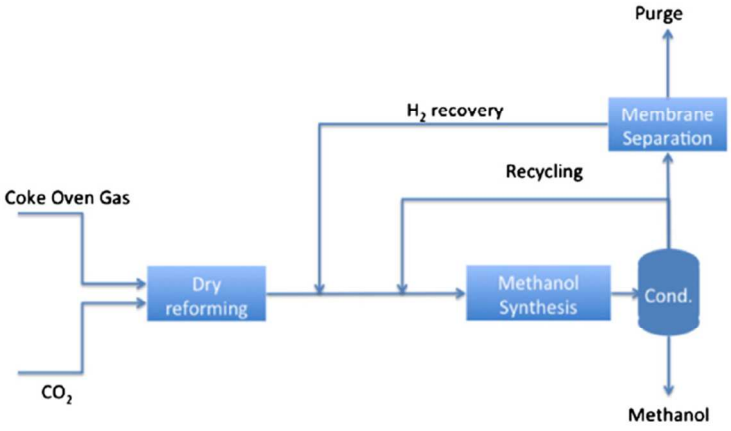

Fig.1. Block diagram of DR-COG process.[94]

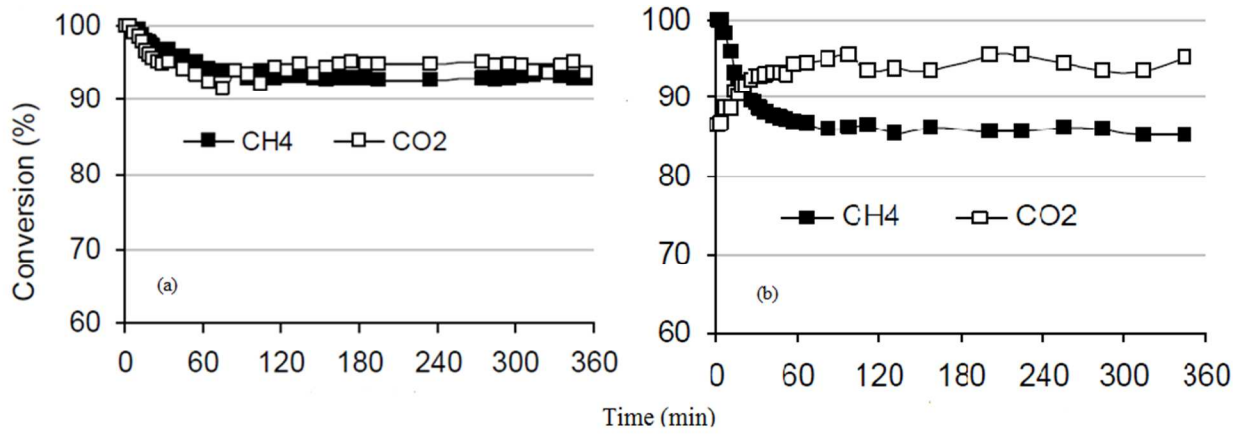

Fig. 2 The comparison of (a) CO_2 reforming of methane and (b) CO_2 reforming of GTM.[92]

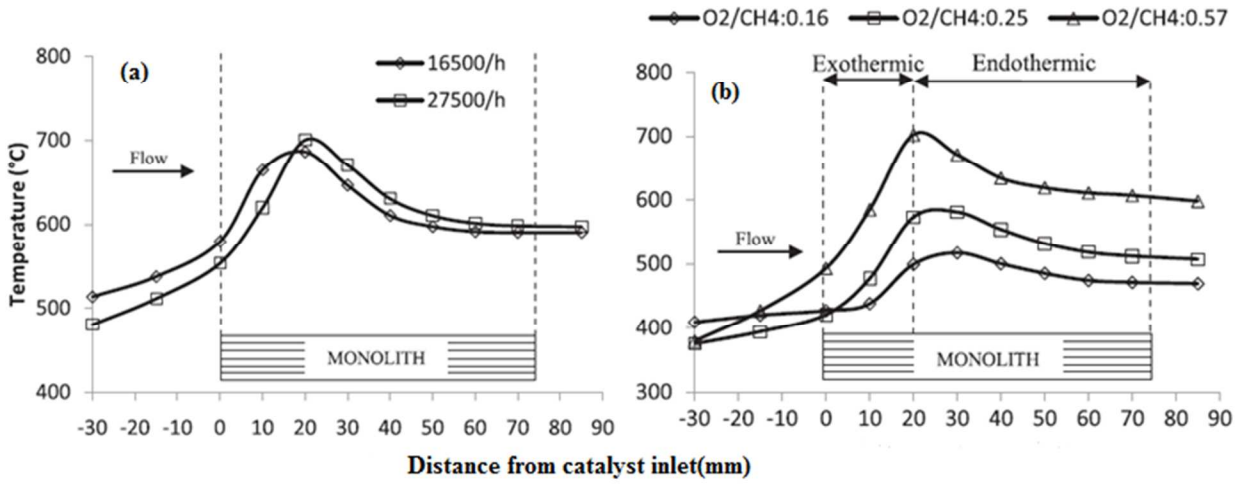

Fig. 3 (a) Influcne of GHSV on reactor temperature profile at inlet temperautre 500 ^{o}C and (b) Reactor temperature profile at GHSV 27500 h^{-1} at inlet temperature of 400 ^{o}C.[106]

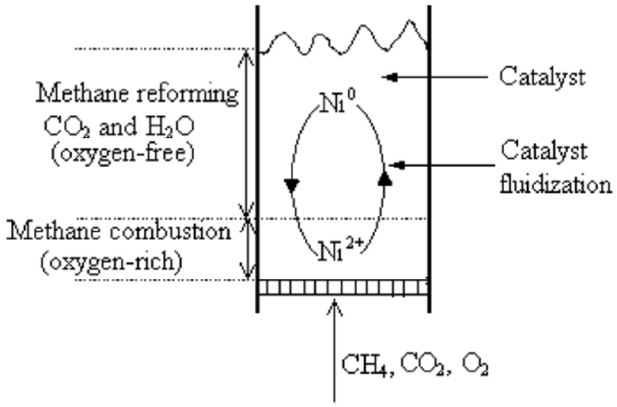

Fig. 4 Conceptual model of FIBR in methane reforming with CO_2 and O_2.[105]

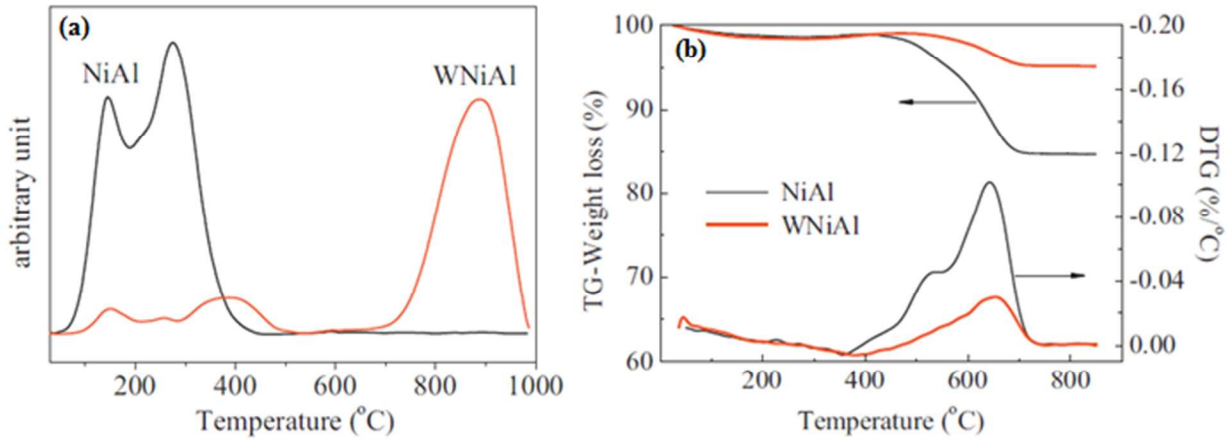

Fig. 5 (a) TPR-H_2 profiles of fresh catalysts and (b) TGA and DTG profiles of different catalysts after reforming reaction for 200h.[148]

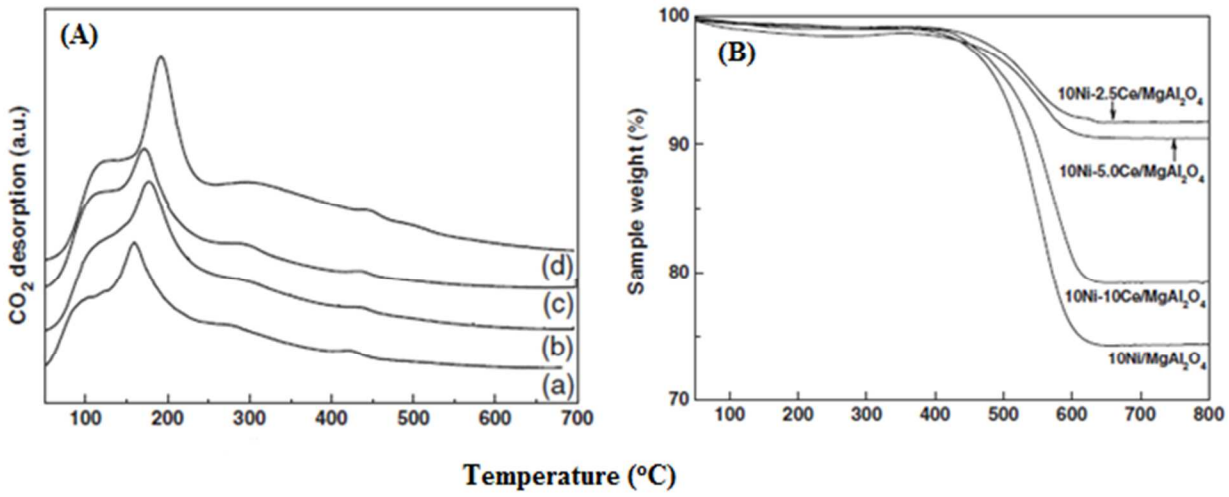

Fig. 6 (A)TPD-CO_2 profiles for Ni-Ce/$MgAl_2O_4$ catalyst promoted with Ce/Ni ratios (a) 0.00 (b) 0.25 (c) 0.50 (d) 1.00 and (B) TGA profiles for Ni-Ce/$MgAl_2O_4$ catalyst.[155]

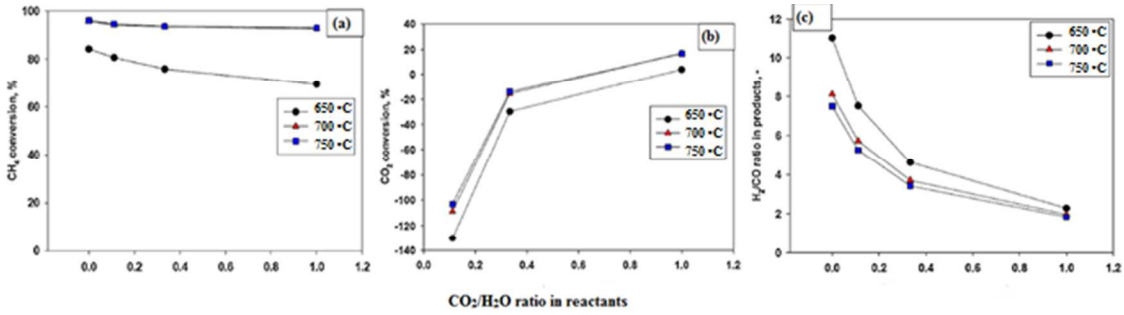

Fig. 7 Influence of CO_2/H_2O ratio over (a) CH_4 conversion (b) CO_2 conversion and (c) H_2/CO ratio.[156]

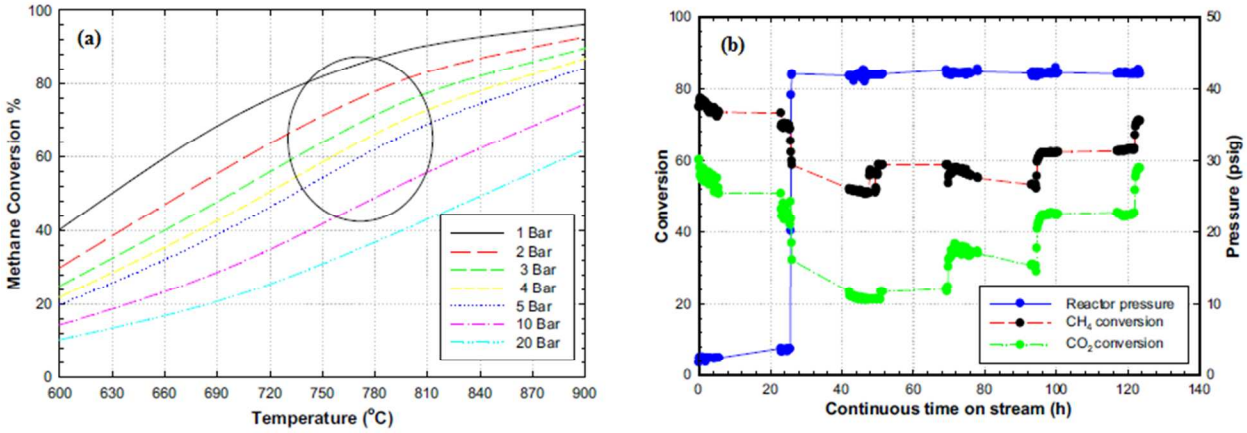

Fig. 8 (a) Influence of reaction temperature with corresponding pressure on methane conversion (b) Reaction pressure vs time on Ni-Cr-Ba/La_2O_3-Al_2O_3 at reaction temperature 670-850 ^oC.[159]

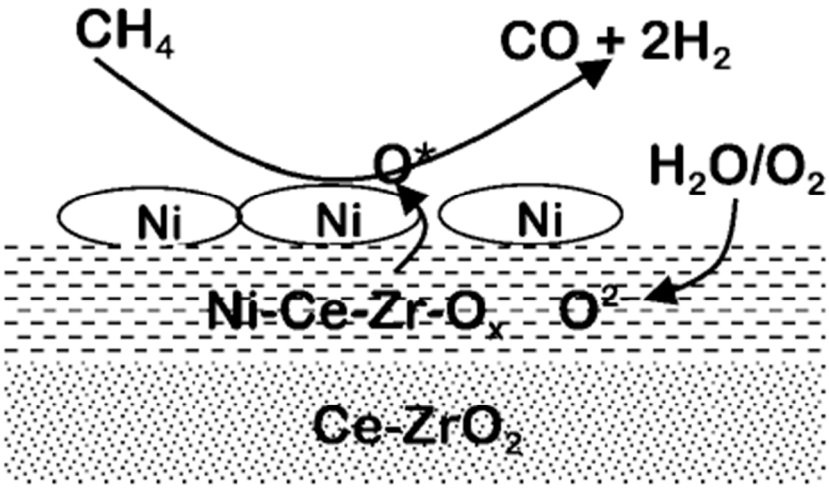

Fig. 9 Conceptual trilateral catalyst structure of Ni/Ce-ZrO_2.[168]

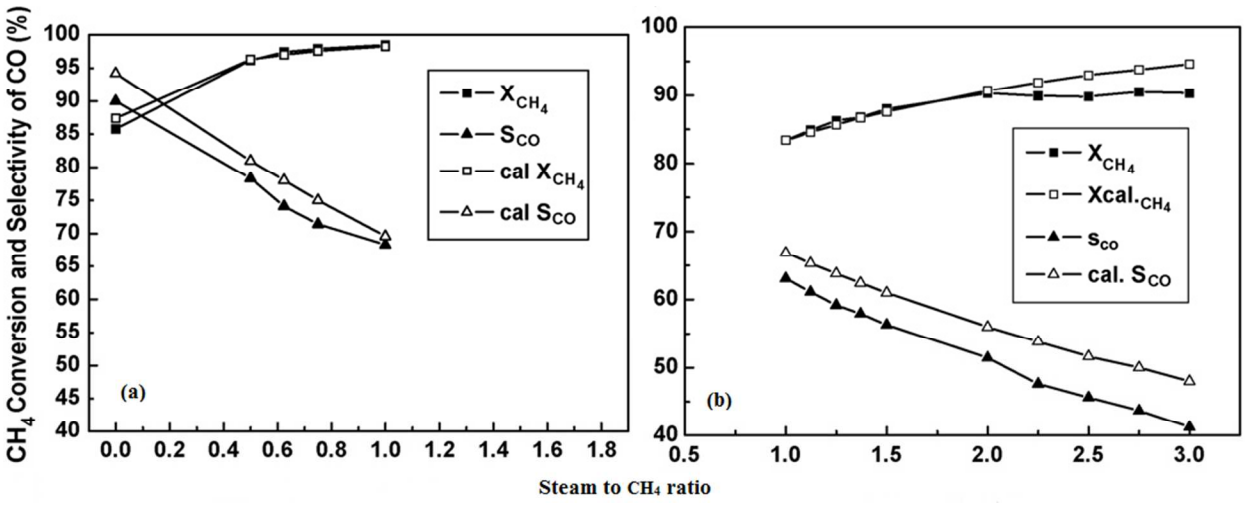

Fig. 10 Effect of steam to CH_4 ratio on (a) Methane conversion at reaction conditions (750 ^oC, 1 bar, 8000 ml g_{cat}^{-1} h^{-1}, CH_4:O_2:N_2 = 1:0.5:1.887) and (b) Methane conversion at reaction conditions (850 ^oC, 15 bar, 8000 ml g_{cat}^{-1} h^{-1}, CH_4:O_2:N_2 = 1:0.5:1.887).[160]

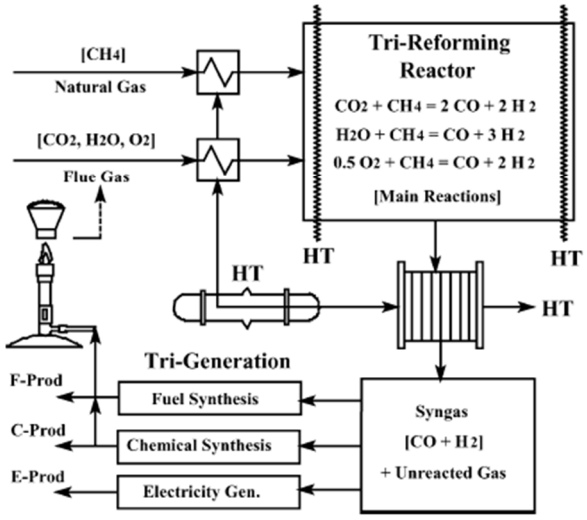

Fig. 11 Conceptual block diagram of tri-reforming of natural gas.[176]

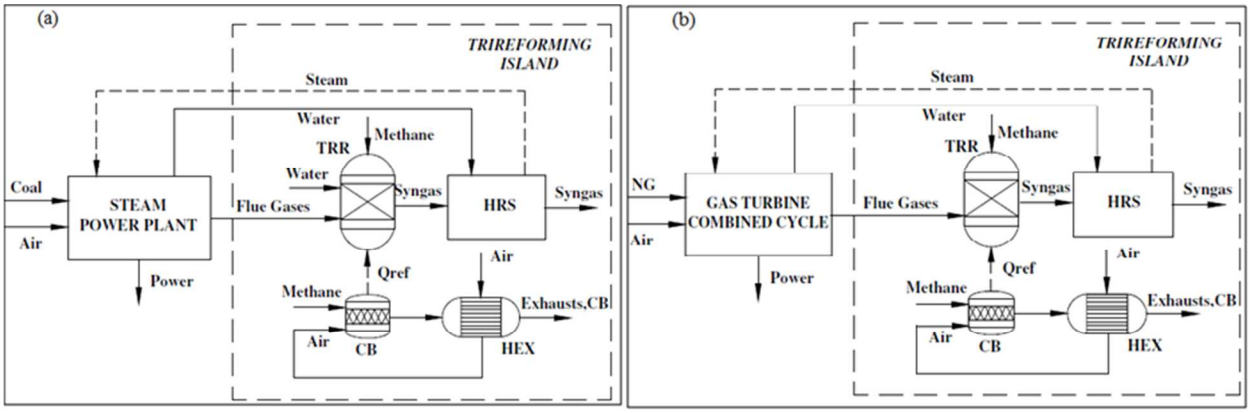

Fig. 12 Block diagram for the (a) ITRPP-SC and (b) ITRPP-CC.[184]

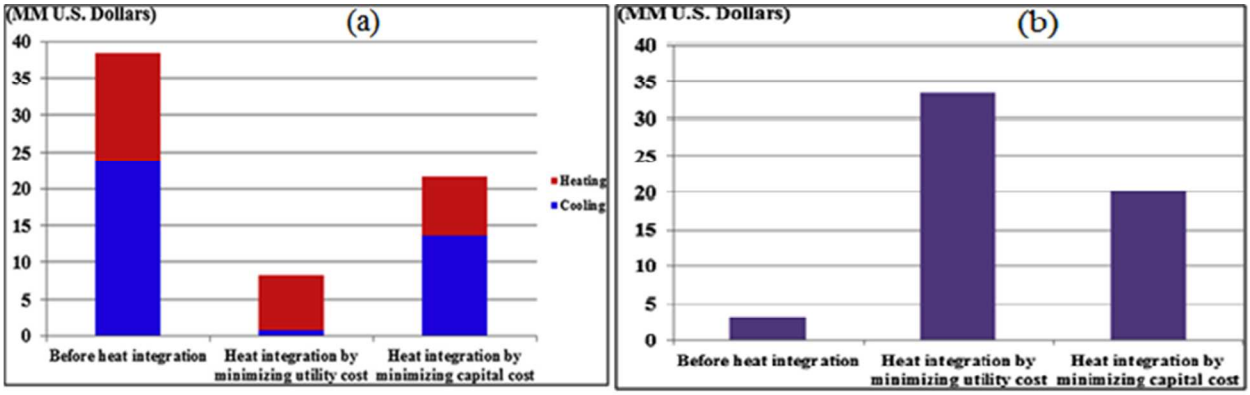

Fig. 13 Comparison of utility cost (a) and annual profits (b) before and after integration.[188]

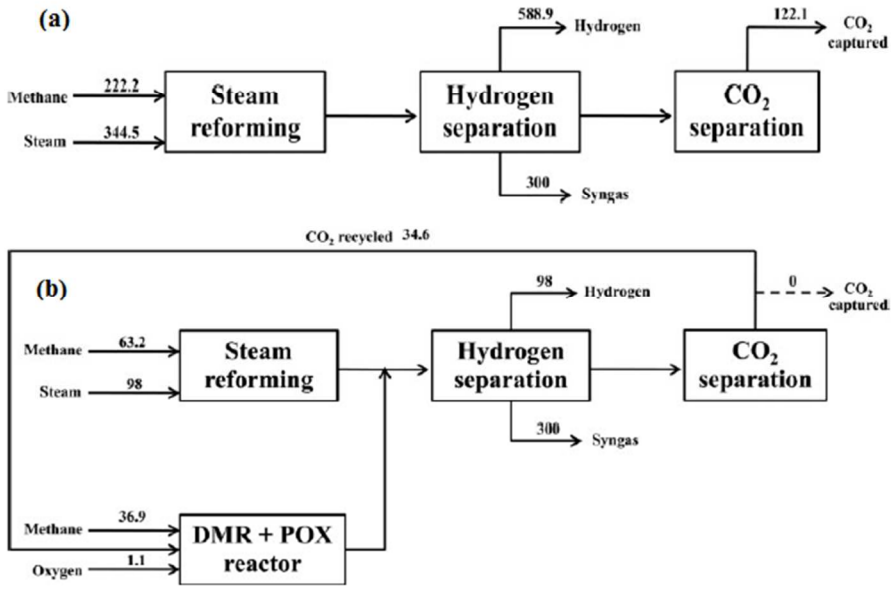

Fig.14 The overall mass balance of (a) SRM and (b) combined process.[189]

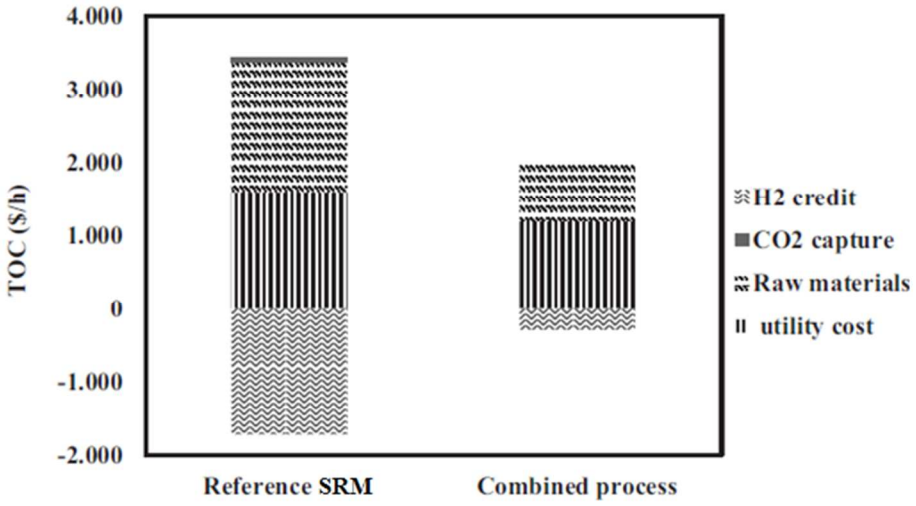

Fig. 15 Total operating costs (TOC) of reference SRM and combined process.[189]

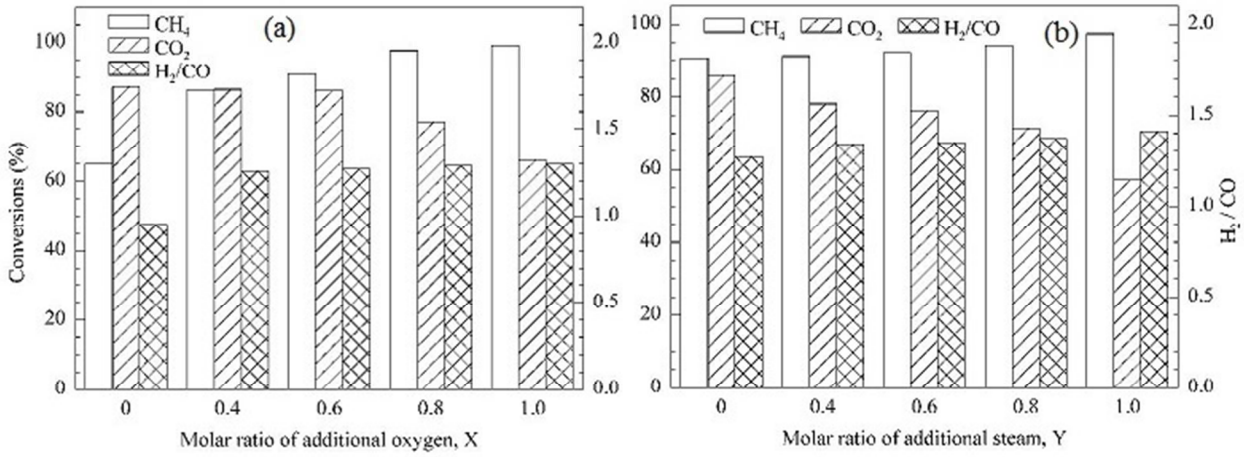

Fig. 16 The effect of the added oxygen (a) and steam (b) on the catalytic performance.[192]

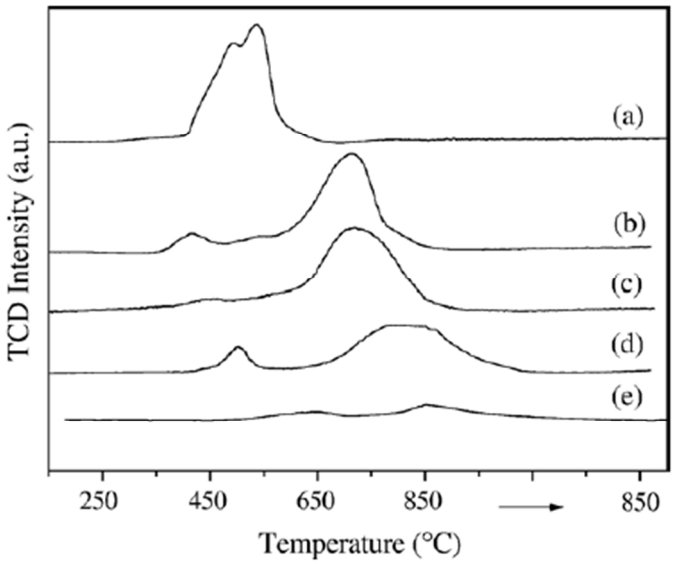

Fig. 17 TPR profiles of calcined catalysts (a) Ni/TiO_2 (b) $Ni/Mg_{0.25}Ti_{0.75}O$ (c) $Ni/Mg_{0.5}Ti_{0.5}O$ (d) $Ni/Mg_{0.75}Ti_{0.25}O$ (e) Ni/MgO.[201]

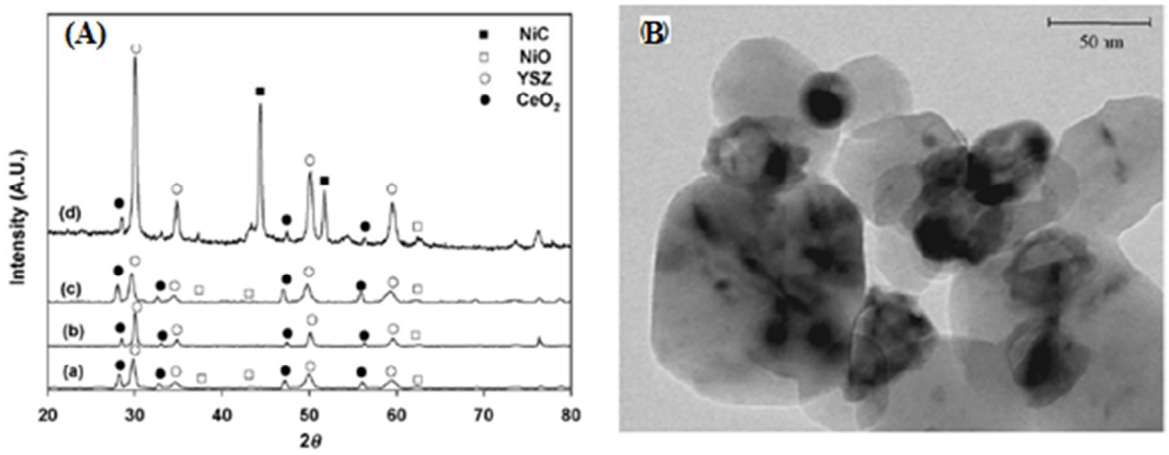

Fig. 18 (A) XRD profiles of the NiO-YSZ-CeO_2 catalyst (a) before reduction, (b) after reduction, (c) after tri-reforming for 120h and (d) dry reforming methane. (B) TEM image of NiO-YSZ-CeO_2 catalyst after tri-reforming.[204]

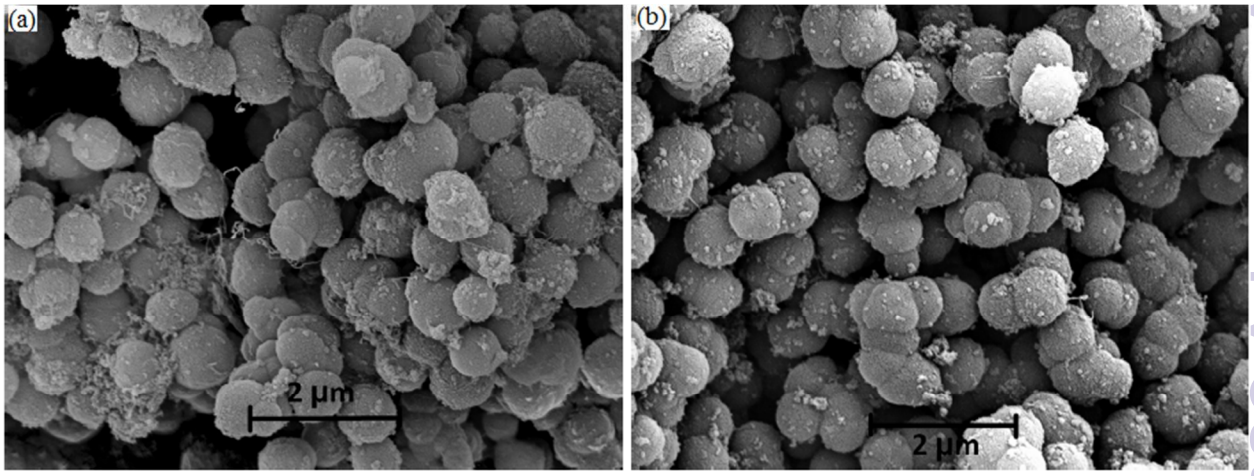

Fig. 19 SEM micrographs of Ni@SiO_2 catalyst after 4 h reaction at (a) 550 ^oC and (b) 750 ^oC, with feedstock composition CH_4:CO_2:H_2O:O_2:He = 1:0.5:0.5:0.1:0.4.[208]

LIST OF TABLES

Table 1 List of different catalysts and reactions conditions applied for reforming processes

Technology	Catalyst	T/t/GHSV	Feed gas composition $CH_4/CO_2/H_2O/O_2/N_2$	Reactor	Conversion		H_2/CO	Ref
					CH_4	CO_2		
DRM+POX	Ni/SiO_2	700/-/9000[a]	176/71/-/53[g]/-	FBR	55.0	-	1.21	105
				FIBR	75.0	-	1.53	
	$Ni/MgO-SiO_2$			FBR	58.3	-	1.2	
				FIBR	79.6	-	1.62	
	$Pt-Ni/MgO-SiO_2$			FBR	80.7	-	1.5	
				FIBR	81.5	-	1.67	
	$Ni_{0.15}Mg_{0.85}$	800/-/75000[b]	50/20/-/30[h]/-	FBR	66.0	-	1.4	122
				FIBR	78.0	-	1.4	
	3mol%Ni/MgO			FBR	65.0	-	1.3	
				FIBR	64.0	-	1.4	
	3mol%Pt/MgO			FBR	53.0	-	1.2	
				FIBR	56.0	-	1.3	
	$Ni/MgO-ZrO_2$	750/7/-	1.5/1/-/0.25/-	FBR	62.0	75.0	1.2	16
	Ni/Y_2O_3- γ-Al_2O_3	700/-/30000[c]	1/0.8/-/0.1/0.4	QR	91.8	73.9	0.84	132
	Co/MgO	900/110/105000[c]	4/2/-/1/-	FBR	97.0	96.0	1.40	104
	0.3Pt-10Ni	650/4/-	2/1/-/0.25/-	FBR	58.6	49.0	1.35	109
		650/4/-	1/1/-/0.5/-		87.0	49.0	1.20	
		650/4/-	1/1/-/-/-		75.3	75.0	0.88	
	0.2Pt-15Ni	650/4/-	2/1/-/0.25/-		78.0	71.3	1.30	
		650/4/-	1/1/-/0.5/-		86.1	45.0	1.20	
		650/0.5/-	1/1/-/-/-		33.0	38.0	1.1	
	PtAl	800/35/-	20/10/-/5[i]/-	FBR	61.0	-	-	110
	PtZr	800/35/-			60.5	-	-	
	PtZrAl	800/55/-			80.0	-	-	

	Rh/Mg-Al	700/-/16000[c]	1/1/-/0.5/-	FBR	91.2	26.7	1.09	116
	Ru/Mg-Al		1/1/-/0.5/-		91.9	28.3	1.02	
	Ir/Mg-Al		1/1/-/0.5/-		87.5	29.2	0.98	
	Pt/Mg-Al		1/1/-/0.5/-		73.1	18.9	0.87	
	Pd/Mg-Al		1/1/-/0.5/-		56.3	-	0.81	
	NiAl	850/200/50666[c]	1/0.4/0.8/-/1.6	FBR	90.8	73.3	2.16	148
	WNiAl				97.1	81.2	2.03	
	Ni/MgO/SBA-15	850/-/27000[c]	2/2/0.5/-/-	FBR	97.7	94.1	1.61	149
			2/1.5/1/-/-		98.3	92.5	1.66	
			2/1/1.5/-/-		98.7	92.0	1.74	
			2/0.5/2/-/-		98.9	84.0	1.85	
DRM+SRM	4%Ni/10.4%MgO	750/18/62.5[d]	35/23/39/-/3[g]	QR	60.0	-	2.7	153
	Ni-Ce/Al_2O_3	850/20/5000[c]	3/1.2/3/-/3	FBR	79.7	47.4	2.23	154
	Ni/$MgAl_2O_4$				81.1	44.4	2.28	
	Ni-Ce/$MgAl_2O_4$				83.4	51.8	2.20	
	Ni-Ce/$MgAl_2O_4$	700/5/530000[c]	1/0.4/0.8/-/1	QR	81.3	65.9	2.1	155
	Thermodynamic analysis	800/-/-/P = 1 bar	1/1/1	-	99.0	58.0	1.52	158
	based on ASPEN-HYSYS	800/-/-/P= 20 bar			56.6	37.6	1.40	
		800/-/-/P = 1 bar	1/1/2		99.6	30.8	2.05	
		800/-/-/P= 20 bar			67.2	20.2	2.07	
		800/-/-/P = 1 bar	1/1/3		99.8	11.5	2.60	
		800/-/-/P= 20 bar			75.4	6.7	2.67	
	Ni/Al_2O_3	750/-/180000[e]	10/-/30/2/58[g]	FBR	68.0	-	-	164
	Ni/ZrO_2				81.0	-	-	
	Ni/$(CaO)_{0.09}(ZrO2)_{0.91}$				87.0	-	-	
	Ni/$(CaO)_{0.09}(CeO_2)_{0.01}(ZrO_2)_{0.90}$				88.0	-	-	
	Ni/$(CaO)_{0.09}(CeO_2)_{0.05}(ZrO_2)_{0.86}$				92.0	-	-	
	Ni/$(CaO)_{0.09}(CeO_2)_{0.13}(ZrO_2)_{0.78}$				83.0	-	-	
	Ni/Ce-ZrO_2	750/-/-	30/-/30/15[i]/-	FBR	99.1	-	3.4	168
ATR	Ni/$CeZrO_2$	800/24/-	2/-/1/0.5/-	-	53.0	-	-	170
	0.1%Ag-Ni/$CeZrO_2$				55.0	-	-	
	0.1%Fe-Ni/$CeZrO_2$				35	-	-	
	0.1%Pd-Ni/$CeZrO_2$				49	-	-	

0.1%Pt-Ni/$CeZrO_2$				47	-	-	
Ni/Al_2O_3	850/-/0.16[f]	40/-/30/20[h]/-	FBR	97	79	2.9	173
Pt/Al_2O_3				90	75	2.8	
$Pt/Ni/Al_2O_3$				>99	82	2.7	
1wt%NiB/Ca-Al_2O_3	850/70/3000[c]/15bar	1/-/1/0.5/1.887	QR	78	-	2.78	160
	850/70/8000[c]/15bar			85	-	3.50	

T: ^oC; t: h; GHSV: Gas hour space velocity; a: h^{-1}; b: $cm^3g^{-1}h^{-1}$; c: ml $h^{-1}g^{-1}cat^{-1}$; d: L g^{-1} h^{-1} e: L $kg^{-1}h^{-1}$; f: g h mol^{-1}; g: vol% ; h: partial pressure ratio; i: Flow rate (cm^3/min) FBR: Fixed bed reactor; FIBR: Fluidized bed reactor; QR: Quartz tubular reactor.

Table 2 Analysis of different parameters for tri-reforming relative to SRM

Flue gas treatment	Product	% CO_2 emission avoidance	Fuel saving	% Exergy efficiency	% World capacity
Tri-reforming[a]	Methanol	46.7	30.9	71.7	8.5[c]
Tri-reforming[b]	Methanol	50.0	31.8	72.7	4.2[d]

[a] Flue gas treatment of coal fired power plant relative to syn-gas production by SRM. [b] Flue gas treatment of NG fired power plant relative to syn-gas production by SRM. World capacity (%) of the products from flue gas of: [c] 500 MW coal based power plant and [d] 400 MW NG fired power plant.

Table 3 List of different catalysts and reactions conditions applied for tri-reforming

Catalyst	T/t/GHSV	Feed gas composition $CH_4/CO_2/H_2O/O_2/N_2$	Reactor	Conversion		H_2/CO	Ref
				CH_4	CO_2		
Ni-NC	800/4/60000[a]	1/0.5/0.5/0.1/-	QR	11.5[d]	-	1.65	191
Ni-AC				4.5[d]	-	1.5	
Ni-CC				4.4[d]	-	2.3	
Ni-CiC				9.2[d]	-	2.3	
Ni-NS				12.1[d]	-	2.0	
Ni-AS				12.2[d]	-	2.0	
Ni-CS				10.3[d]	-	1.5	
Ni-CiS				10.0[d]	-	2.1	
Ni/SBA-15	800/100/24000[a]	2/1/0.6/0.6/-	FBR	92.8	76.3	1.35	192
Ni/La-Ce-O	800/150/31000[b]	1/0.66/0.66/0.10/-	FBR	1.56	0.56	1.57	193
8Ni8Mg/	800/30/61000[b]	1/0.7/0.085/0.2/-	FBR	98.9	86.9	2.1	190
$Ce_{0.6}Zr_{0.4}O_2$	800/4/61000[b]			98.9	87.8	2.0	
	800/30/61000[b]	1/0.7/0.23/0.2/-		98.8	76.3	2.2	
	800/4/61000[b]			97.3	77.6	2.1	
	800/30/61000[b]	1/0.7/0.3/0.2/-		99.5	69.0	2.3	
	800/4/61000[b]			99.4	70.2	2.1	
	800/30/61000[b]	1/0.7/0.5/0.2/-		99.6	66.3	2.3	
	800/4/61000[b]			99.6	65.6	2.2	
Ni-Mg-ZrO_2	800/58/30000[a]	1/0.45/0.45/0.1/0.4	QR	99	65	1.5	183
$Ni/Mg_{0.5}Ti_{0.5}O$	850/50/1.78[c]	1/0.48/0.54/0.1/-	FBR	90	60	-	201
$Ni/Mg_{0.75}Ti_{0.25}O$				98	80	1.5	
Ni-CeO_2	800/-/30000[b]	1/0.46/0.46/0.1/-	FBR	93	83	1.65	200
Ni-La-CeO_2				96	86.5	1.62-1.65	
NiO-YSZ-CeO_2	800/120/10000[b]	1/1/1/0.1/-	FBR	-	100	1-1.1	204
Commercial HT	800/60/10000[b]			-	75	1.7	
NiAl	710/-/12000[b]	1/0.9/0.65/0/-	QR	99.8	68	1.59	205
		1/0.9/0.65/0.25/-		19	-	-	

NiLaAl	605/-/12000[b]	1/0.95/0.7/0/-		88	65	1.46	
	725/-/12000[b]	1/0.9/0.7/0.3/-		100	28	2.50	
	725/-/12000[b]	1/0.55/1.0/0.2/-		100	46	2.06	
NiCeAl	705/-/12000[b]	1/0.7/0.65/0/-		98	74	1.71	
	560/-/12000[b]	1/0.7/0.7/0/-		69	40	1.71	
	705/-/12000[b]	1/0.7/0.65/0.2/-		99	43	1.83	
	560/-/12000[b]	1/0.7/0.7/0.4/-		85	9	2.02	
	560/-/12000[b]	1/0.6/0.9/0.2/-		80	16	1.96	
	560/-/12000[b]	1/0.6/0.5/0.2/-		78	13	2.02	
Ni2CeAl	615/-/12000[b]	1/0.55/0.45/0.2/-		91	16	1.73	
	615/-/12000[b]	1/1.0/0.55/0.2/-		94	34	1.42	
Ni@SiO_2	750/4/-	1/0.5/0.0/0.1/0.4	FBR	31.8	91.1	2.0	208
		1/0.5/0.5/0.1/0.4		73.0	55.6	2.6	
		1/0.5/1.0/0.1/0.4		71.2	63.0	1.5	
		1/0.5/3.0/0.1/0.4		73.1	42.8	1.7	

T: ^{o}C; t: h; GHSV: Gas hour space velocity; a: ml $h^{-1}g^{-1}cat^{-1}$; b: h^{-1}; c: g h mol^{-1}; d: 10^{-4} mol s^{-1} g^{-1}_{Ni} h gcat; QR: Quartz reactor; FBR: Fixed bed reactor; HT: Holder Topsoe catalyst.

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