

Dry Reforming-Fischer-Tropsch Synthesis-Catalytic Dehydrogenation: A method to No flaring-No CO₂ emission in the Gas Refinery

Majid Sarkari[✉]; Aran Alaie Sheikhrobat; Masood Haghghi Asl[✉]; Hassan Haghpast Khankahdani
South Pars Gas Complex Company, Asalooyeh, I.R. Iran.

Abstract

The mitigation and utilization of greenhouse gases, such as carbon dioxide and methane, are among the most important challenges in the area of energy research. In the gas refinery, tail gas in sulfur recovery unit is a main source of CO₂ emission and the natural gas to flare is also a source of methane and CO₂. In this paper, Dry Reforming-Fischer-Tropsch Synthesis-Catalytic Dehydrogenation (DRM-FTS-CDH) process is proposed to recover flare gas and tail gas in the gas refinery and calculation and simulation was done. Dry reforming of CH₄ (DRM), which uses both CO₂ and CH₄ as reactants, is a potential method to utilize the greenhouse gases in the atmosphere. DRM offers several advantages: a) mitigation of CO₂ and natural gas; b) transformation of natural gas and CO₂ into valuable syngas; c) effective utilization of low-grade natural gas resources consisting of natural gas and CO₂. Hydrogen in the product could be applied as a fuel in fuel cells and the syngas can be converted efficiently to ultraclean fuels, such as gasoline, gasoil with no sulfur and less aromatic byproducts, by Fischer-Tropsch synthesis (FTS). But with respect to nature of DRM process which results in a H₂/CO ratio of less than unity while FTS of liquid fuels requires syngas with H₂/CO≥2.0. By producing the required H₂ by catalytic dehydrogenation (CDH) of the gaseous (C₁-C₄) products of FTS, instead of WGS reaction, it could be retrieved shortage of H₂/CO ratio. In this research basic supports such as alumina, Fe-Mn-K catalyst and carbon nanotubes selected for DRM-FTS-CDH, respectively.

This new process is a suitable alternative to conventional gas flaring which prevents harmful environmental effects through emission of significant amounts of carbon dioxide in the atmosphere.

Keywords: Greenhouse gases, Reforming, Fischer-Tropsch Synthesis, CO₂ emission

Introduction:

During the past decade, there has been increasing global concern over the rise in carbon dioxide emissions from different sources into the atmosphere. The major greenhouse gases are water vapor, which contributes 36–70% of the greenhouse effect (not including clouds), CO₂, which contributes 9–26%, CH₄, which contributes 4–9%, and ozone, which contributes 3–7% [1]. Consequently, there is much interest in the utilization of CH₄ and CO₂.

A suggested method for controlling the level of greenhouse gases in the atmosphere is prevention of flaring gas. Recently, there have been many attempts to reduce the concentration of CO₂ and CH₄ in the atmosphere through their utilization. The main sources of CH₄ are from natural gas, which is made up of 98% CH₄, and biogas from biomass decomposition. Currently, the main uses of CH₄ are in combustion processes, power generation, and the production of chemicals from synthesis gas (syngas), a mixture of hydrogen and carbon monoxide, using reforming processes.

[✉] Corresponding Author: Majid Sarkari, Email: majidsarkari@gmail.com; Tel; +989368512260

[✉] Presenter

In this paper, DRM-FTS-CDH process is proposed to recover flare gas and tail gas in the gas refinery and conceptual calculation and simulation was done. A schematic diagram of such an improved DRM-FTS-CDH system is shown in Fig. 1.

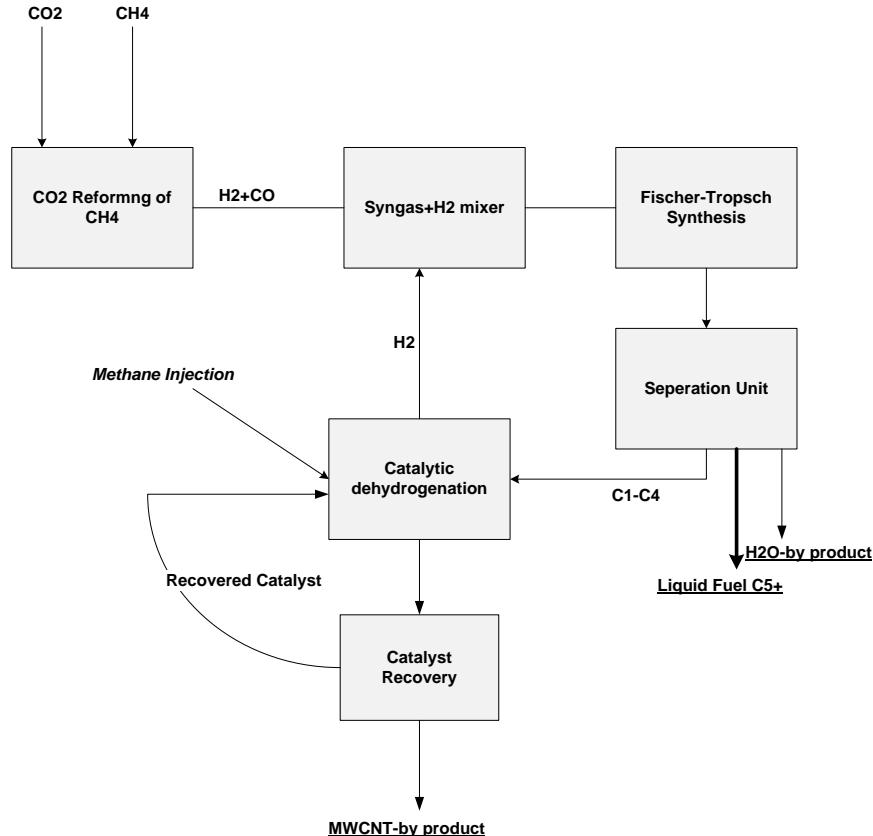


Fig 1. Schematic diagram of a CDM-FTS-CDH-MI system

Process outline

Dry Reforming of Methane

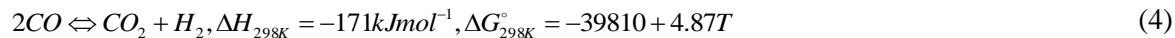
The reactions (1), (2), (3) are known as steam reforming, partial oxidation reforming and CO₂ reforming, respectively. Different combinations of these three basic reforming reactions are also possible for achieving various objectives.

Till now, steam reforming is the most mature and widely used technology for methane-based syngas production. But this process has some unavoidable drawbacks. As shown in reaction (1), the H₂/CO ratio in the syngas is theoretically 3. It is normally too high compared with what is required by many downstream synthesis processes. To avoid carbon deposition on the catalyst, excess steam more than the stoichiometry reaction required must be employed. This causes higher operation cost. In addition, the reactor of high temperature tubular heat exchanger is inefficient and very expensive for its material and manufacture. In this process, CO₂ is produced along with syngas. The removal and disposal of CO₂ is another major issue. The CH₄ partial oxidation reforming (POM), as shown in reaction (2), can theoretically yield syngas with an H₂/CO ratio of 2, which is suitable for many downstream synthesis. The POM process to produce syngas is

reported as a mildly exothermic process and provides advantages over the conventional SRM process, as the latter is highly endothermic [1,2]. There are 2 ways to reforming CH₄ to syngas, namely non-catalytic and catalytic process. The non-catalytic process has been commercialized. It is operated under the conditions of 30-100 atm and around 1573K. So high temperature means higher operation cost also can result in hot-spot formation, especially at high space velocity, which makes the control of the process very difficult and poses greater risks from the point of view of safety [1,2].

On the contrary, the catalytic process can be operated under lower temperature. Because of efficiency and economics, it has been considered to be the most promise CH₄ reforming process in the future. However, truly catalytic partial oxidation process now is limited in laboratory stage. One reason is lacking of long duration tests of catalysts [2].

In recent years, a lot of attention has been paid on CO₂ reforming because it has the potential advantages of lower theoretical H₂/CO ratio and reuse of CO₂, as show in the reaction (3). But the most difficult problem of this process is the greater potential of carbon deposition though methane decomposition and the Boudouard reaction (reaction 4), which rapidly deactivates the catalyst. Thus, catalyst development, alongside the reaction system, becomes a major aspect of research in this area [1,2].



Mechanism for the Reforming of Methane Using Carbon Dioxide

Understanding of the mechanism for the DRM process is highly important. The mechanism depends on the choice of catalysts as well as the reactants involved in the reaction. The predominant reactive steps involving CH₄ and the catalyst surface, adsorption and dissociation [3] can be either direct or precursor-mediated [4]. However, CH₄ dissociation is gradually shifted from a precursor-mediated mechanism at low temperature to a direct dissociative mechanism at high temperature. It is, however, generally accepted that CO₂ chemisorption and dissociation on transition metal surfaces is dominated by electron transfer and requires the formation of an anionic CO₂⁻ precursor [5].

Role of catalyst:

For the successful industrial application of the DRM reaction, it is important to develop cheap and economical catalysts, which are resistant to carbon deposition and exhibit high activity for the reaction. Although catalysts based on noble metals are reported to be more active and less sensitive to coking, noble metals are costly and have limited availability. Common single active site catalysts, for example, nickel-based catalysts, have been widely used for the DRM reaction, but are subject to the major drawback of high coke deposition. Thus, investigation into supports and the addition of promoters has been conducted, with the aim of improving the coke resistance of Ni-based catalysts. Fig 2 shows gas flow through a typical catalyst [6].

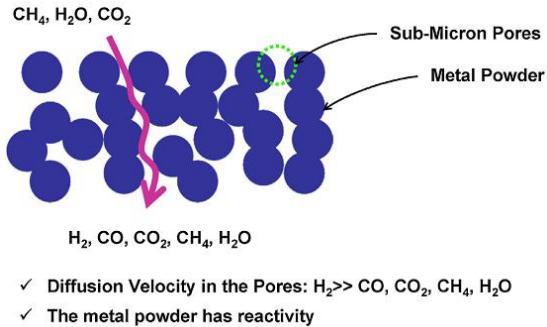


Fig 2. Gas flow passage and membrane effect in a typical catalyst.

Dry Reforming Process Technologies:

Fluidized Bed and Fixed Bed Reactors

Many studies of methane reforming with steam (SRM), carbon dioxide (DRM), or oxygen (POM) have used fluidized or fixed bed reactors. The recent trend in reforming research is towards autothermal reforming (DRM and POM) using fluidized and fixed bed reactors. Operating stability and high rates of heat transfer were obtained by using the fluidized bed reactor, whereby combustion proceeded at the entry point of the catalyst bed whereas reforming occurred near the exit point of the reactor.

Plasma Technology

Methane is the major component of natural gas and a very stable compound that is difficult to activate for reactions such as steam reforming, oxidative coupling of methane, and partial oxidation of methane. These reactions require extreme reaction conditions with high temperatures and pressures, and usually suffer from significant carbon deposition.

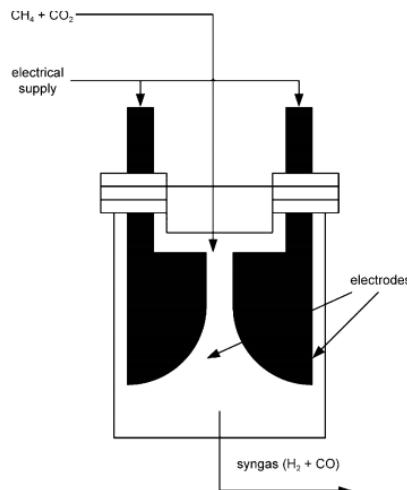


Fig 3. Schematic of a typical Plasma reactor

Thus, it is necessary to develop a new method for methane conversion, especially for Fischer-Tropsch synthesis. Methane conversion using nonthermal plasma has been widely studied as a potential solution to these problems [7]. Therefore, such reactors are an excellent source of energetic electrons, low excited-state atomic and molecular species, and free radicals at high density with energy of several electron volts

(Fig 3). The energy efficiency of the pulsed plasma can be improved by using a higher pulse frequency and a higher reaction temperature.

Membrane Technology

The reversible nature of DRM imposes a limit, determined by thermodynamic equilibrium. According to Le Chatelier's principle, CH₄ and CO₂ conversions and product yields in the DRM process will increase if both products of the reaction or, preferentially, only H₂ could be selectively removed from the reaction system. Thus, the equilibrium limitations of a conventional reactor can be circumvented. Moreover, continuous removal of H₂ from the reaction would result in suppression of the RWGS side reaction, leading to a further increase in the H₂ selectivity. Consequently, the conversion and yields of CO and H₂ are well below the commercially acceptable level, unless the reaction temperature is very high (T>1000 K). The higher required reaction temperature and higher energy consumption are the main disadvantages of using this process for industrial applications. To overcome these limitations, membrane reactors have been used in the DRM reaction (Fig 4), [8] in which a selectively permeable membrane is used to remove the product from the reaction as it is formed.

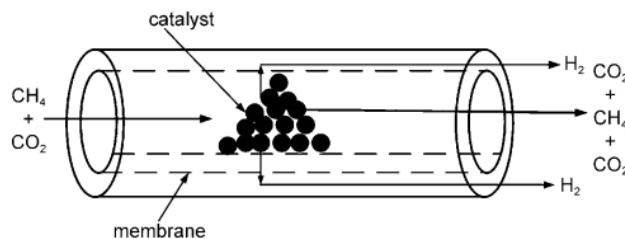


Fig 4. Typical membrane reactor configuration for DRM.

Fischer-Tropsch Synthesis-Catalyst dehydrogenation

Recently, the world energy crisis, high oil prices, and environmental pollution have received remarkable attention in the development of alternative technology i.e. GTL for the manufacture of transportation fuels. In the GTL process, Fischer-Tropsch synthesis (FTS) plays an important role for converting synthesis gas in the production of ultra-clean transportation fuels, chemicals, and other hydrocarbon products [9-11]. Research and development of a high-performance catalyst is one of the key technologies for FTS. Although the metals Ni, Fe, Co, Ru and Rh have the required FTS activity for commercial uses, under the practical operation, only Co- and Fe-based catalysts have been developed for industrial uses. These two metals have been successfully promoted by numerous additives (alkalis, rare earth and metallic oxides which can be reducible or not) and used as bulk materials or loaded on different supports such as SiO₂, Al₂O₃ and TiO₂. Iron-based catalysts due to their activity for water gas shift (WGS) reaction can be aided to make up the defective H₂ in the syngas produced from coal or biomass gasification. But cobalt-based catalysts attract most of the current attention for the direct conversion of synthesis gas in FTS due to their high activity; high selectivity for long chain paraffin, their low oxygenates selectivity and very low WGS activity, under conditions favoring the FT reactions.

The FTS is operated in two modes. The high-temperature (300 -350°C) process with iron-based catalysts is used for the production of gasoline and linear low molecular mass olefins. The low-temperature (200-240 °C) process with either iron or cobalt catalysts is used for the production of high molecular mass linear waxes. Efficient and rapid removal of heat from the highly exothermic FT reaction from the

catalyst particles is an important factor for the design of an FT reactor. Three main types of reactor are used for FT reaction:

- i) Fixed bed reactors which produce high value linear waxes at low temperatures (225°C).
- ii) Fluidized bed reactors with either a fixed or a circulating bed.
- iii) Slurry bed reactors in which gas is bubbled through a suspension of finely divided catalyst in a liquid which has a low vapour pressure at the temperature of operation.
- iv) Recently novel hydrogen-permselective membrane reactor in FTS of GTL technology proposed to enhance of production.

Catalyst dehydrogenation

By DRM normally has relatively low hydrogen content, resulting in H₂/CO ratios of approximately 0.7–1.1, and FTS of liquid fuels requires syngas with H₂/CO ratios of 2.0 or higher. Current FTS technology relies on the water–gas shift (WGS) reaction to raise the hydrogen content of the syngas to the required levels. However, the WGS reaction produces one CO₂ molecule for each H₂ molecule it adds. So it is proposed that the H₂ required to increase the H₂/CO molar ratio to values >2.0 be produced by catalytic dehydrogenation (CDH) of the (C₁–C₄) products of the Fischer–Tropsch synthesis (FTS). If the increase in the H₂/CO ratio produced by CDH of the (C₂–C₄) products of FTS is relatively small to increase the H₂/CO ratio to 2.0 or higher, which is usually the case, this can be overcome by injecting the correct amount of methane (MI) derived from NG into the CDH reactor, as illustrated in Fig. 1. Nano-scale, binary, Fe–M (M = Pd, Mo or Ni) catalysts supported on alumina have been shown to be very effective for the decomposition of lower alkanes to produce hydrogen and carbon nanofibers or nanotubes. The carbon nanotubes exhibited two distinct forms depending on the reaction temperature. Above 600 °C, they were predominantly in form of multi-walled nanotubes with parallel walls in the form of concentric graphene sheets. At or below 500 °C, carbon nanofibers with capped and truncated stacked-cone structure were produced. At 625 °C, decomposition of cyclohexane produced a mixture of the two types of carbon nanostructures [12–14].

CO₂ emissions avoided, water saved and products produced

Tail gas is a main source of CO₂ emission and flare gas is such another source of CO₂. The WGS reaction (CO + H₂O→H₂ +CO₂) in FTS produces one molecule of CO₂ and uses one molecule of H₂O for each molecule of H₂ it produces. At temperatures >450 C, the catalytic dehydrogenation (CDH) reaction converts methane and the (C₂–C₄) products of FTS into H₂ and multi-walled carbon nanotubes (MWCNT) [15,16]. To estimate the amounts of CO₂ emissions avoided, water saved, and products produced (H₂ and MWCNT), it is useful to consider a 50,000 barrel/day [17] DRM-FTS-CDH-MI plant (Fig 5).

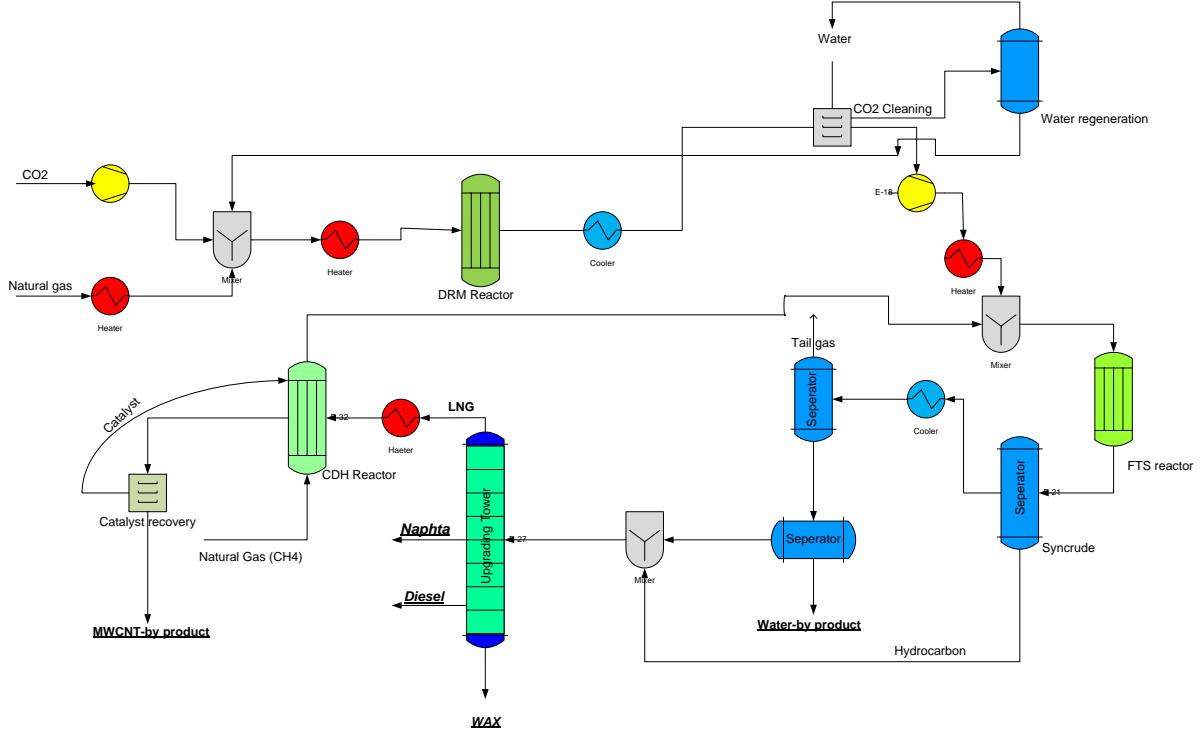


Fig 5. Schematic of proposed DRM-FTS-CDH-MI plant

Since amount of methane (ΔC_1) is injected into the CDH reactor to raise the H_2/CO ratios, the total percentage of gaseous products for a FTS-CDH-MI plant is effectively $\Delta C_1 + (C_1-C_4)$. Therefore the percentage of the total reactants yielding oil products is $C_{5+} = 100\% - (\Delta C_1 + (C_1-C_4))$. Using an oil density of 825 kg/m³, typical of high quality crude oils, and a US standard barrel of petroleum size of 42 gallons (0.159 m³), the weight per barrel is 131 kg. For a 50,000 bbl/day plant, the total weight of oil produced per day is 7229 tons. The C_{5+} weight percentage then yields a weight for the total output of all products of the plant. This allows the amounts of H_2 and MWCNT to be calculated from the percentages ΔH_2 and ΔC_{MNT} produced by the CDH reaction, which are given by Eqs. (5), (6). The square brackets [] in the equations denote wt.% and the par and ol subscripts denote paraffins and olefins.

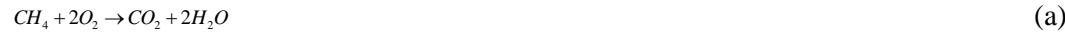
$$\Delta H_2(\text{wt.\%}) = x_1\% \times [C_1] + x_2\% \times [C_2 - C_4]_{\text{par}} + x_3\% \times [C_2 - C_4]_{\text{ol}} \quad (5)$$

$$\Delta C_{MNT}(\text{wt.\%}) = (100 - x_1)\% \times [C_1] + (100 - x_2)\% \times [C_2 - C_4]_{\text{par}} + (100 - x_3)\% \times [C_2 - C_4]_{\text{ol}} \quad (6)$$

In addition, replacing the WGS reaction with CDH saves a huge amount of water and prevents the emission of very large amounts of CO_2 . The weight of water saved = $18/2 \times$ the weight of H_2 produced by CDH, while the weight of CO_2 emissions avoided = $44/2 \times$ the weight of H_2 produced. Also the weight of CO_2 emission in DRM is calculated by Eq 7.

$$CO_2^{\text{emission}} = y_{CO_2} \times [CO_2] \quad (7)$$

With assumption that complete combustion occurred in flare the amount of CO₂ emission calculated as follow (Eq. 8):



$$CO_2^{emission} = y_1\% \times [C_1] + 2 \times y_2\% \times [C_2] + 3 \times y_3\% \times [C_3] + 4 \times (1 - y_1 - y_2 - y_3)\% \times [C_4] \quad (8)$$

where y_i denote wt.% of component in the stream toward flaring.

Summary and Conclusions

In this paper to avoid CO₂ emission and flare gas recovery it is proposed DRM-FTS-CDH/MI process. Catalytic dry reforming of methane (carbon dioxide reforming) is a promising reaction for syngas production in future fuel industries. Various types of reactors can be used for the DRM reaction, including plasma reactors, fixed and fluidized bed reactors, and membrane reactors. Membrane reactors have drawn significant attention, due to their potential for continuous product removal, which enhances the reactor performance. Also for FTS the hydrogen-permselective membrane reactor could be a good selection to enhance the products. In the other hand for CDH reaction used of fluidized bed because of countinuse catalyst and MWCNT-by product recovery could be a suitable reactor. In FTS Products and environmental savings benefits of the DRM-FTS-CDH-MI process relative to conventional FTS could be noted as follow:

- a) The mitigation and utilization of greenhouse gases, such as carbon dioxide and methane.
- b) high quality oil (C₅₊) production
- c) specific values of the H₂/CO ratio could be produced for specific products.
- d) Hydrogen in the product could be applied as a fuel in fuel cells and
- e) multi-walled carbon nanotubes (MWCNT) production, perhaps the most promising application for the large quantities of MWCNT is the production of high-strength lightweight plastic-MWCNT composites.
- f) The water saved by avoiding the water-gas shift

Acknowledgments

The authors gratefully acknowledge South Pars Gas Complex Company for their kindness and support in this research.

References

1. Mun-Sing Fan, Ahmad Zuhairi Abdullah, and Subhash Bhatia, Catalytic Technology for Carbon Dioxide Reforming of Methane to Synthesis Gas, *Chem Cat Chem*, 2009, 1, 192–208.
2. Littlewood, K., Gasification: Theory and Application. *Prog. Energy Combust. Sci.*, 1977, 3, 35-71.

3. A. C. Luntz, J. Harris, CH₄ dissociation on metals: a quantum dynamics model, *Surf. Sci.* 1991, 258, 397–426.
 4. D. C. Seets, M. C. Wheeler, C. B. Mullins, Mechanism of the dissociative chemisorption of methane over Ir(110): trapping-mediated or direct?, *Chem. Phys. Lett.* 1997, 266, 431–436.
 - 5.13. F. Solymosi, The bonding, structure and reactions of CO₂ adsorbed on clean and promoted metal *J. Mol. Catal.* 1991, 65, 337–358.
6. Emma Lovell, Yijiao Jiang, Jason Scott, Fenglong Wang, Yoel Suhardja, Mengmeng Chen, Jun Huang, Rose Ama, CO₂ reforming of methane over MCM-41-supported nickel catalysts: altering support acidity by one-pot synthesis at room temperature, *Applied Catalysis A: General*, 2014, 473, 51– 58.
 7. D. G. Cheng, X. L. Zhu, Y. H. Ben, F. He, L. Cui, C. J. Liu, Carbon dioxide reforming of methane over Ni/Al₂O₃ treated with glow discharge plasma, *Catal. Today*. 2006, 115, 205–210.
 8. H. Stphane, B. Michel, E. Barbara, Beneficial effects of the use of a nickel membrane reactor for the dry reforming of methane: Comparison with thermodynamic predictions, *J. Catal.* 2007, 252, 190–204.
 9. M. Sarkari, F. Fazlollahi, H. Atashi, A. A. Mirzaei, V.Hosseinpour, Fischer-Tropsch synthesis: Development of kinetic expression for a sol–gel Fe–Ni/Al₂O₃ catalyst, *Fuel Processing Technology*, 2012, 97, 130–139.
 10. M. Sarkari, F. Fazlollahi, H. Atashi, A. A. Mirzaei, and W. C. Hecker, Using Different Preparation Methods to Enhance Fischer-Tropsch Products over Iron-based Catalyst, *Chem. Biochem. Eng. Q.*, 2013, 27 (3) 259–266.
 11. M. Sarkari, F. Fazlollahi, H. Atashi, Fischer Tropsch Synthesis: The Promoter Effects, Operating Conditions, and Reactor Synthesis, *INTERNATIONAL JOURNAL OF CHEMICAL REACTOR ENGINEERING*, 2012, Volume 10, Article A6.
 12. Y. W, N. Shah, G. P. Huffman, Simultaneous production of hydrogen and carbon nanostructures by decomposition of propane and cyclohexane over alumina supported binary catalysts, *Catalysis Today*, 2005, 99 359–364.
 13. N. Shah, D. Panjala, G.P. Huffman, Hydrogen Production by Catalytic Decomposition of Methane, *Energy & Fuels*, 2001, 15, 1528 1534.
 14. N. Shah, Y. Wang, D. Panjala, G. P. Huffman, Production of Hydrogen and Carbon Nanostructures by Non-oxidative Catalytic Dehydrogenation of Ethane and Propane, *Energy & Fuels*, 2004, 18, 727 735.
 15. G. P. Huffman , Zero emissions of CO₂ during the production of liquid fuel from coal and natural gas by combining Fischer–Tropsch synthesis with catalytic dehydrogenation, *Fuel* 109 (2013) 206–210.
 16. Gerald P. Huffman, Incorporation of catalytic dehydrogenation into Fischer–Tropsch synthesis of liquid fuels from coal to minimize carbon dioxide emissions, *Fuel* 90, 2011, 2671–2676.
 17. M.R. Rahimpour, Z. Jamshidnejad, S.M. Jokar, G. Karimi, A. Ghorbani, A.H. Mohammadi, A comparative study of three different methods for flare gas recovery of Asalooye Gas Refinery, *Journal of Natural Gas Science and Engineering*, 2012, 4, 17-28.