INDUSTRIAL SCALE EXPERIENCE ON STEAM REFORMING OF CO_2-RICH GAS

Peter Mølgaard Mortensen, Ib Dybkjær, Gabriel Antberg
Haldor Topsøe A/S, Denmark
Email: PMOR@topsøe.dk

Summary

This paper summarises experiences on industrial scale reforming of CO_2-rich natural gas. Methane can react in a direct route with CO_2 to form a synthesis gas consisting of CO and H_2, so called dry reforming (DMR). This reaction is closely related to steam methane reforming (SMR). DMR has received much attention as it in theory offers a way of using CO_2, which is considered in many industries as a waste product and environmentally as a polluting greenhouse gas. In an industrial scale with realistic feedstock, water cannot be completely omitted from the reaction, as this specifically will be needed for removal of higher hydrocarbons. Instead, high severity CO_2-reforming can be done, which have been proven in several industrial plants. Sulfur passivated reforming (SPARG) has demonstrated that CO_2-reforming can be achieved without use of expensive noble metals. In addition to thermodynamic consideration, mass balance constrains must be considered. Mass balance dictates that high severity CO_2-rich gas will result in a synthesis gas with low H_2/CO ratio. Thus, the commercial feasibility of CO_2-reforming is highly dependent on the desired product. CO_2 reforming may be an attractive solution for product requiring lower H_2/CO ratio, such as higher alcohols, reducing gas, and acetic acid, etc.

Key words: *CO_2-reforming, Dry reforming, DMR, SPARG, Methanol synthesis.*

1. Introduction

The last 40 years have seen significant developments in the petrochemical industry. In 1975, the world was facing an oil crisis when the cost of a barrel exceeded the record price of USD 13. This resulted in the search for many alternative technologies to most efficiently utilise energy and rapidly expanded searches for new energy sources. It was also the time that Petrovietnam was founded and for Haldor Topsøe a time of new technologies including further development of its reforming technology and the start of its formaldehyde technology.

Fast forward 40 years and today we think that oil is cheap at less than USD 50/barrel. We also have a wide array of new technologies available which are optimised for various applications. Today, Petrovietnam is reviewing utilisation of a CO_2-rich natural gas and the solution to such utilisation is part of the developments in reforming technology which was initiated 40 years ago.

The utilisation of CO_2-rich gas requires extra considerations compared to traditional high methane containing natural gas feed. The primary challenge in reforming CO_2-rich gas is carbon formation, as the low H/C ratio of the feed implies that a high potential for carbon formation exists.

Synthesis gas production is one of the largest industries in the world with its development stemming back from 1930 [1]. Important bulk chemicals such as hydrogen, ammonia, and methanol are produced on the basis of this. Among the reforming reactions, steam reforming of methane-rich natural gas (SMR) must be considered as the principal reaction for production of synthesis gas and hydrogen. Steam reforming of CO_2-rich gas (in the following referred to as “CO_2-reforming”) or reforming of methane-rich feedstock with carbon dioxide alone (“dry methane reforming”, in the following referred to as DMR) are receiving much attention as they in theory offer ways of using CO_2, which is considered in many industries as a waste product and environmentally as a polluting greenhouse gas.

One of the primary tasks in the development of CO_2-reforming or DMR is to find operating conditions in combination with a suitable catalyst to avoid carbon formation. Nickel (Ni), cobalt, and noble metal catalysts have been tested as catalyst for CO_2-reforming, with nickel being the most investigated system, as this is the conventional choice in SMR and a relatively cheap catalyst in comparison to noble metals [2].

Haldor Topsøe A/S has many years of experience in reforming. The first start-up of a steam reformer designed by Haldor Topsøe dates back to 1956. In the current work, our experience within the field of CO_2-reforming and DMR is summarised, starting with a short review on the science behind the CO_2-reforming process in industrial scale.

2. Thermodynamic considerations

Traditional SMR is the endothermic reaction between steam and methane at elevated temperatures to produce synthesis gas:

$$CH_4\,(g) + H_2O\,(g) \leftrightarrows CO\,(g) + 3H_2\,(g) \qquad (1)$$

DMR takes place in a similar way, but with CO_2:

$$CH_4\,(g) + CO_2\,(g) \leftrightarrows 2CO\,(g) + 2H_2\,(g) \quad (2)$$

The stoichiometric DMR reaction yields a synthesis gas with a H_2/CO ratio of 1, compared to 3 for SMR.

Besides the reforming reactions, also water gas shift (WGS) takes place during reforming; specifically reverse water gas shift (RWGS) is relevant for DMR:

$$CO_2\,(g) + H_2\,(g) \leftrightarrows CO\,(g) + H_2O\,(g) \quad (3)$$

The reforming reactions and the RWGS are all endothermic reactions, and temperatures in the order of 750°C are required for an effective conversion of methane and carbon dioxide [3 - 4].

Besides the endothermic reforming reactions, the choice of operating conditions is additionally influenced by the Boudouard reaction (also called CO disproportionation), the CO reduction reaction, and the methane decomposition reaction:

$$2CO\,(g) \leftrightarrows C\,(s) + CO_2\,(g) \quad (4)$$

$$CO\,(g)+H_2\,(g) \leftrightarrows C\,(s) + H_2O\,(g) \quad (5)$$

$$CH_4\,(g) \leftrightarrows C\,(s) + 2H_2\,(g) \quad (6)$$

As these may be responsible for carbon formation during the reaction, it should be emphasised that carbon formation is a non-linear phenomenon and prediction of the risk for carbon formation will require a thermodynamic evaluation for a given feed composition.

3. Carbon deposition

The low H/C ratio in DMR makes carbon formation a major challenge [5]. For practical application of the reforming reactions, it is a mandatory to ensure that carbon formation does not take place [6]. The methane decomposition reaction (6) and the Boudouard reaction (4) are the primary sources of carbon on the catalysts during DMR and these reactions can to some extent be predicted on the basis of thermodynamic calculations.

Noble metals are more resistant toward carbon formation than nickel, and have a low tendency for formation of whisker carbon [7]. The potential for carbon formation is significantly decreased by lowering the nickel particle size. Even lower potential for carbon formation was achieved by Rostrup Nielsen and Bak Hansen [8] by passivating the nickel catalysts with sulfur giving an equilibrium constant for methane decomposition comparable to Ru and Rh catalysts. Overall, it is apparent that the potential for carbon formation is dictated by thermodynamics, but it can be markedly influenced by the choice of active material on the catalyst and the particle size of this, as this determines the stability of the formed carbon. Besides carbon formation on catalysts, also carbon formation on/in metal surfaces (as the reactor wall and equipment downstream the primary reformer) can be a problem during reforming, a phenomenon known as metal dusting. This causes disintegration of metal alloys of Fe, Ni, and Co, observed as loss of surface material as a metal dust due to carbon formation in the metal [9]. This is usually a problem on reactor walls of plants operating with aggressive carbonaceous gases with high CO partial pressure and low water partial pressure. CO and CH_4 are usually reported as the source of metal dusting by reactions (4) and (6) [9 - 11].

4. Industrial experience with large scale reforming of CO_2-rich gas

A typical layout for an industrial scale reforming plant is illustrated in Figure 1. The feedstock, which may range from lean natural gas to heavy naphtha, is heated to around 400°C and then cleaned for sulfur species in a desulfurisation section [12]. Subsequently, any higher hydrocarbons in the feedstock are reformed to a mixture of H_2, CO_2, CH_4, and traces of CO in a pre-reformer. This is done at relatively low temperatures of 400 - 550°C to avoid carbon formation from the higher hydrocarbons [13]. The actual reforming takes place in a tubular reformer (primary reformer) for the conversion of the CH_4/H_2O/CO_2 mixture to synthesis gas. In this configuration, many tubes are placed in a row (or parallel rows) in a furnace box where heat is delivered to the endothermic reaction by combustion of fuel. Typically, the inlet temperature is adjusted to 400 - 600°C prior to the primary reformer and then heated to an exit temperature up to 950°C in the reformer tubes. The high exit temperature is required for sufficient conversion of the methane when the process gas flows through the reformer tubes in plug flow it will be close to equilibrium. Thus, carbon formation can be expected if the principle of equilibrated gas predicts carbon formation at any temperature between 400 - 1,000°C for a given feed gas composition.

It is essential to design a reforming plant to completely avoid carbon formation. If a potential for carbon formation exists, it will only be a matter of time before a shutdown will be forced due to too high pressure drop. In industrial context this will be expensive due to lost time on stream and loading of a new batch of catalyst. It is emphasised that carbon formation at reforming conditions is as whisker carbon. This is destructive in nature toward the catalyst pellet and regeneration is therefore not an option.

Thus, the possible operating range for a tubular reformer will be defined by the conditions which will not have a potential for carbon formation. When sufficient knowledge about the thermodynamics of carbon formation for a specific catalyst is known, the exact limit for carbon formation can be calculated and this can be illustrated by the carbon limit curve depicted in Figure 2 [14 - 15]. The curves are derived from the principle of equilibrated gas and show the most severe conditions (as a function of initial H_2O/CH_4 and CO_2/CH_4 ratio or O/C and H/C ratio) which can be tolerated in the entire temperature range from 400 - 1,000°C at a pressure of 25.5bar. Carbon formation will be expected on the left of the curves and "safe" operation on the right. This shows that the tendency for carbon formation increases with decreasing CO_2/CH_4 and H_2O/CH_4 ratios. The severity of operation can be defined relative to the placement compared to the carbon limit curves; operation far beyond the carbon limit curve is considered very severe.

The limit for carbon formation can be pushed by the choice of catalyst. Thus, more severe conditions can be tolerated with a Ni catalyst compared to formation of graphitic carbon (Figure 2). However, performing "traditional" DMR, without H_2O in the feed, over a Ni catalyst in a tubular reformer, will result in carbon formation as this is placed far beyond the carbon limit curve for Ni catalysts in Figure 2. Instead, CO_2-reforming is possible as long as the H_2O/CH_4 ratio is balanced accordingly.

The cases in Table 1 cover operation at full scale plants (referred to on the basis of the nations where the plants were constructed) and tests in a pilot plant placed in Houston, Texas, United States (referred to as HOU). The industrial references in Table 1 are all examples of plants which have been designed around the principle flow sheet in Figure 1, but adapted to the specific needs of the site and the downstream requirements for the synthesis gas utilisation. The sizes of these plants range from production of 2,400Nm^3/hour up to 133,000Nm^3/hour of dry synthesis gas. A differentiation is made between plants operated with a natural gas feed (natural gas in Table 1) or a naphtha feed. Natural gas is considered as a gaseous feed consisting mainly of methane, but can also contain CO_2, higher hydrocarbon (C_2 - C_6), among other gas species. Naphtha is a heavier liquid feedstock which will consist mainly of C_6 to C_{12} hydrocarbons. For naphtha based plants the prereforming section is an important and integrated part of the plant as the very reactive higher hydrocarbons should be converted prior to the primary reformer to avoid carbon formation from these. Several of the plants addition-

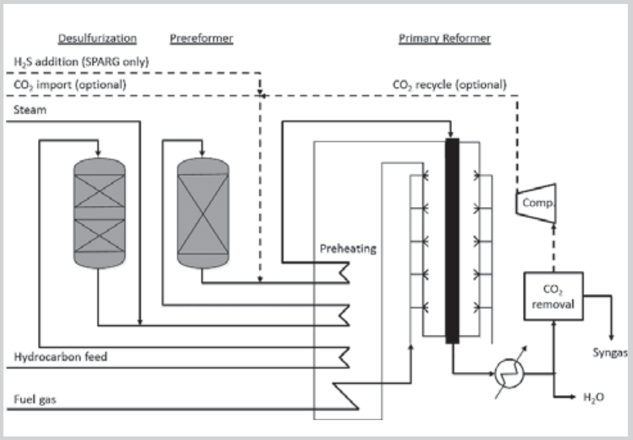

Figure 1. *General flow sheet of a reforming process. Dotted lines indicate optional configurations.* CO_2 *can be added to adjust the feed gas composition or recycle from the* CO_2 *removal unit.* H_2S *import is only used for the SPARG process*

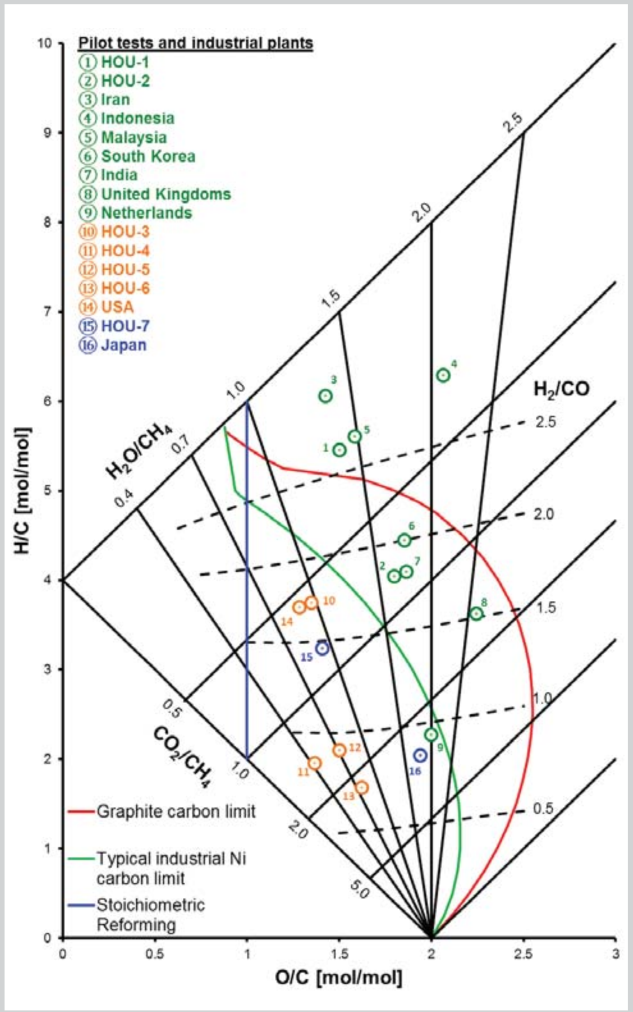

Figure 2. *Carbon limit diagram at different* H_2O/CH_4 *and* CO_2/CH_4 *feed ratios. The curves are the carbon limits at 25.5bar for graphite and a typical industrial Ni catalyst. The left-hand sides of the curves are the areas where carbon formation is expected for temperatures between 400°C and 1,000°C. The product* H_2/CO *ratio is evaluated at TExit = 950°C. The stoichiometric reforming region is shown for reference. The points refer to specific large scale tests with Ni catalysts (green), SPARG (orange), and noble metal catalysts (blue), further information on these is found in Table 1*

Table 1. *Comparison of full size monotube pilot experiments (HOU) and industrial plants (referenced with countries where they are constructed) of CO_2 rich reforming with different catalysts and under different conditions. SPARG: Sulfur-passivated reforming, NG: Natural gas, TOS: Time on stream*

		Operating conditions			
		Catalyst	Feed	P (barg)	T_{Exit} (°C)
Ni catalyst	HOU-1	$Ni/MgAl_2O_4$	Natural gas	23	945
	HOU-2	$Ni/MgAl_2O_4$	Natural gas	24	945
	Iran	$Ni/MgAl_2O_4$	Natural gas	20	960
	Indonesia	$Ni/MgAl_2O_4$	Natural gas	12	960
	Malaysia	$Ni/MgAl_2O_4$	Natural gas	25	950
	South Korea	$Ni/MgAl_2O_4$	Naphtha	25	900
	India	$Ni/MgAl_2O_4$	Naphtha	22	920
	United Kingdom	$Ni/MgAl_2O_4$	Naphtha	20	900
	Netherlands	$Ni/MgAl_2O_4$	Natural gas	15	815
Sulfur-passivated reforming (SPARG)	HOU-3	$Ni/MgAl_2O_4$	Natural gas	6	890
	HOU-4	$Ni/MgAl_2O_4$	Natural gas	6	930
	HOU-5	$Ni/MgAl_2O_4$	Natural gas	14	930
	HOU-6	$Ni/MgAl_2O_4$	Natural gas	15	945
	USA	$Ni/MgAl_2O_4$	Natural gas	7	900
Noble catalyst	HOU-7	$Ru/MgAl_2O_4$	Natural gas	23	940
	Japan	$Ru/MgAl_2O_4$	Natural gas	2	850

ally operated with a CO_2 import or recycle stream to give a high CO_2/CH_4 ratio in the feed gas to the primary reformer.

4.1. Ni catalysts for CO_2-reforming

As already discussed, Ni based catalysts are industrially preferred. Table 1 lists several examples of how Ni based catalysts have been used for CO_2-reforming. A few references were made at the full size monotube reforming reactor in Houston in the beginning of the 1990s (tests denoted HOU1-2), but several full scale plants have been designed and constructed relative to the principle of equilibrated gas and the carbon limit curve shown in Figure 2. Common for all of these references is that they were operated over long periods (several years) without problems with carbon formation. As long as the plant is operated as intended and not poisoned by external sources, lifetimes of more than a decade can be obtained for industrial reforming catalysts [16]. Large fractions of CO_2 in the feed were demonstrated in the Houston pilot plant demonstration run 2 and the plants in India, South Korea, and the United Kingdom. However, as seen from both Figure 2 and Table 1, significant amounts of water were needed in the feed to comply with the limitations of the carbon limit curve and additionally to adjust the composition so the synthesis gas is produced with the desired H_2/CO ratio. The plant in the Netherlands was operated under very severe conditions for a Ni based catalyst with 71 dry mole % of CO_2 in the feed, producing a synthesis gas with a H_2/CO ratio of 1.2. As seen from Figure 2, this plant was operated slightly beyond the conventional border for carbon formation for Ni catalysts. After two years of operation at these conditions, analysis of the spent catalyst revealed insignificant carbon formation, varying between 500 - 1,100ppm$_w$ along the length of the reactor tube. Analysis of the spent catalyst showed that operation under the quite severe conditions was only possible because the Ni particles were stabilised at a significantly lower particle size than what is usually seen during steam reforming at industrial conditions, which was helped by the relatively low exit temperature of 815°C used for the current plant. However, it should still be noted that a H_2O/CH_4 ratio of 2 was used at the given operating conditions. Operation at the same conditions with a Ni catalyst with larger Ni particles later proved to cause carbon formation, supporting the fundamentals on carbon formation. All the examples presented for Ni based CO_2-reforming show how important it is to know where the limit for carbon formation is, as this confines the freedom for designing reforming processes.

4.2. SPARG process

In the SPARG (Sulfur passivated reforming) process, sulfur is used to selectively poison the most active sites and in this way prevent formation of carbon while maintaining some activity for reforming. Rostrup-Nielsen [17] described that coke formation requires a larger ensemble of Ni atoms compared to SMR and that one sulfur atom quenches the four neighbouring Ni atoms. Thus, sulfur will more effectively inhibit carbon formation than SMR/DMR activity. Ideally, the sulfur coverage should be larger than 0.7 to prevent carbon formation [17]. On the basis of the observations of the beneficial effect of sulfur passivation, the SPARG process was developed. Here, a small co-feed of H_2S was added to prevent carbon formation on Ni-based catalysts. This should be accompanied by a small co-feed of hydrogen ($H_2S/H_2 < 0.9$) to avoid formation of bulk Ni sulfides. The SPARG approach offers a route to circumvent the carbon limit curve in Figure 2. The first large scale test of this concept was made in the full size monotube pilot plant in Houston at a CO_2/Natural gas feed ratio of 0.65 and H_2O/Natural gas ratio of 1.0, and an outlet temperature of 890°C. These conditions would result in carbon formation on a conventional Ni catalystas illustrated by point 10 (HOU-3) in Figure 2. However, with the sulfur-passivated Ni catalyst no carbon was observed after 500 hours of operation at the conditions. Building on the success of HOU-3, "dry" DMR tests were made in the pilot plant with the sulfur-passivated Ni catalyst, a CO_2/Natural gas feed ratio of 2.5, and 890°C as outlet temperature. However, at these conditions, carbon deposition was observed in the first part of the reactor tube after a short period of operation. This was concluded to be due to cracking of the larger hydrocarbons in the natural gas on the sulfur passivated catalyst, which now had insufficient activity for higher hydrocarbon reforming. To avoid the severe carbon deposition observed from higher hydrocarbons, it was realised that a pre-reformer was essential prior to the tubular reformer to remove the higher hydrocarbons in the natural gas. On the basis of this experience, a general flow-sheet for CO_2-reforming using the SPARG technology should therefore be as illustrated in Figure 1. Initially, sulfur is removed from the natural gas to enable pre-reforming of the higher hydrocarbons over a Ni based catalyst, which is intolerant to sulfur. A controlled amount of H_2S is then added to the gas mixture of $H_2O/CO_2/CH_4$ prior to the primary reformer.

The SPARG technology was demonstrated in industrial scale by revamping the reforming plant in the United States (Figure 2 and Table 1) from SMR to CO_2-reforming. Originally, the plant operated at a S/C of 1.9 and a CO_2/C of 0.4 with an exit temperature of 900°C, but to increase the production of CO the plant was modified with the SPARG technology to operate at a S/C of 0.9 and a CO_2/C of 0.5 instead. Table 2 shows a comparison between the synthesis gas composition out of the primary reformer of the plant prior to the revamp and at SPARG conditions. A significant increase in the CO concentration was achieved by implementing the SPARG conditions. The only major difference between the original operation and the SPARG operation was that a pre-reformer had to be installed to remove the higher hydrocarbons prior to the primary reformer, as also observed in the pilot experiments. The primary reformer and the surrounding equipment could all be used directly for the SPARG process.

Table 2. *Comparison of the synthesis gas composition from the plant in USA pre-SPARG and during SPARG*

	Pre-SPARG	SPARG
H_2 (dry mole%)	65	60
CO (dry mole%)	24	33
CO_2 (dry mole%)	8	5
CH_4 (dry mole%)	3	3
N_2 (dry mole%)	0.1	0.1
H_2/CO	2.7	1.8

Carbon free-operation was demonstrated throughout four years of continuous operation on one batch of catalyst on the SPARG conditions. The revamp of the plant from SMR to SPARG was calculated to give 23% savings in production costs at that time [18].

4.3. Noble metal catalysts for CO_2-reforming

As already discussed in Section 0, noble metals generally have a lower tendency for carbon formation compared to Ni catalysts. This group of catalysts therefore offers a route for operation at severe conditions without carbon formation. This was demonstrated in large scale with the HOU-7 pilot test where a ruthenium catalyst was used to operate at a H_2O/CH_4 of 0.9 and a CO_2/CH_4 of 0.8. These conditions are far beyond the carbon limit curve of the Ni catalyst, as shown in Figure 2. The experience from HOU-7 was used to demonstrate the durability of the catalyst prior to installation in a convection reformer in Japan. The plant should produce CO from a mixture of natural gas, a CO_2 import stream, and a recycle stream, which ultimately meant that high amounts of CO_2 should be processed. Use of the noble metal catalyst enabled operation at quite severe conditions while maintaining a syngas H_2/CO product ratio of 1. This plant operated for several years without any catalytic problems.

5. Mass balance constraints

DMR and SMR result in synthesis gases with different stoichiometric composition; DMR a H_2/CO ratio of 1, compared to 3 for SMR. The suitability of the synthesis gas depends on the downstream utilisation. For instance, methanol synthesis requires a gas module, $M = (H_2 - CO_2)/(CO + CO_2)$ of 2 for optimal performance in order to avoid excess H_2, CO or CO_2. Reaction (7) visualizes the stoichiometric ideal reaction for syngas production for methanol synthesis.

$$3CH_4\,(g) + CO_2 + 2H_2O\,(g) \leftrightarrows 4CO\,(g) + 8H_2\,(g) \quad (M = 2) \qquad (7)$$

Reaction (7) is a net result of reactions (1 - 3) and can closest be categorised as being SMR with addition of CO_2 to achieve an ideal syngas module, M, for methanol production. Higher concentration of CO_2 than suggested in reaction (7), hence $M < 2$, will cause a shortage of H_2 in the methanol synthesis and excess CO_2 which will cause costly operation of the methanol synthesis. This means that an ideal feed gas for methanol production contains 1 CO_2 for each 3 CH_4 available (on mole basis) in the feed gas.

CO_2 reforming may be an attractive solution for product requiring lower H_2/CO ratio, such as higher alcohols, reducing gas, and acetic acid, etc.

6. Conclusions

The DMR reaction is closely related to the SMR reaction.

Despite having origin in different reactants, the fast equilibration of the WGS results in similar reaction conditions in the two processes at an early stage in a reactor. Carbon deposition must be considered as the biggest challenge of DMR, as the stoichiometric DMR reaction implies severe conditions for carbon formation. This phenomenon is to a large extent controlled by thermodynamics and the principle of equilibrated gas is an important method to determine suitable operating conditions. Water cannot be completely omitted from the reaction, as this specifically will be needed for removal of higher hydrocarbons. Thus, "dry" DMR is difficult to realise in large scale with realistic feedstocks, but high severity CO_2-reforming can be done. Pushing the potential for carbon formation can be aided by approaches such as the SPARG process. Several CO_2-reforming plants have been designed using Ni based catalysts, SPARG or noble metals, where the latter two allow for more severe operating conditions. In addition to thermodynamic consideration, mass balance constrains must be considered. DMR produces a synthesis gas with a H_2/CO ratio of 1 and SMR a H_2/CO ratio of 3. To what extent CO_2 reforming is attractive depends on the downstream utilization of the synthesis gas. For instance, methanol requires a gas module, $M = (H_2 - CO_2)/(CO + CO_2)$ of 2. The net reaction to produce such synthesis gas can closest be categorised as being SMR with addition of CO_2. The net reaction also reveals that the ideal feed gas for synthesis production to methanol should contain 1 CO_2 for each 3 CH_4 available (on mole basis). CO_2 reforming may be an attractive solution for product requiring lower H_2/CO ratio, such as higher alcohols, reducing gas, and acetic acid, etc.

References

1. J.R.Rostrup-Nielsen. *Steam reforming of hydrocarbons: A historical perspective.* Studies in Surface Science and Catalysis. 2004; 147: p. 121 - 126.

2. J.R.Rostrup-Nielsen, L.J.Christiansen. *Routes to syngas.* Concepts in Syngas Manufacture. Imperial College Press. 2011; 10: p. 3 - 72.

3. Mun-sing Fan, Ahmad Zuhairi Abdullah, Subhash Bhatia. *Catalytic technology for carbon dioxide reforming of methane to synthesis gas*. ChemCatChem. 2009; 1(2): p. 192 - 208.

4. M.K.Nikoo, N.A.S.Amin. *Thermodynamic analysis of carbon dioxide reforming of methane in view of solid carbon formation.* Fuel Processing Technology. 2011; 92(3): p. 678 - 691.

5. C.Papadopoulou, H.Matralis, X.Verykios. *Utilization of biogas as a renewable carbon source: Dry reforming of methane*. Catalysis for Alternative Energy Generation. Springer. 2012: p. 57 - 127.

6. Jens Rostrup-Nielsen, Lars J.Christiansen. *Concepts in syngas manufacture*. Catalytic Science Series. Imperial College Press. 2011; 10: p. 233 - 294.

7. S.E.L.W.Madsen, J.H.Bak Hansen, J.R.Rostrup-Nielsen. *Industrial aspects of CO_2-reforming*. AIChE Spring Meeting. 1997.

8. J.R.Rostrup-Nielsen, J.H.B.Hansen. *CO_2-reforming of methane over transition metals*. Journal of Catalysis.1993; 144(1): p. 38 - 49.

9. A.Agüero, M.Gutiérrez, L.Korcakova, T.T.M.Nguyen, B.Hinnemann, S.Saadi. Oxidation of Metals. 2011: p. 1 - 20.

10. H.J.Grabke. *Metal dusting.* Material and Corrosion. 2003; 54(10): p. 736 - 746.

11. P.V.Daham S.Gunawardana, Thoa Thi Minh Nguyen, John C.Walmsley, Hide J.Venvik. *Initiation of metal dusting corrosion in conversion of natural gas to syngas studied under industrially relevant conditions*. Industrial and Engineering Chemistry Research. 2014; 53(5): p. 1794 - 1803.

12. K.Aasberg-Petersen, T.S.Christensen, I.Dybkjær, J.Sehested, M.Østberg, R.M.Coertzen, M.J.Keyser, A.P.Steynberg. *Synthesis gas production for FT synthesis*. Fischer-Tropsch Technology. Amsterdam: Elsevier. 2004; 4: p. 258 - 405.

13. T.S.Christensen. *Adiabatic prereforming of hydrocarbons - an important step in syngas production.* Applied Catalysis A: General. 1996; 138(2): p. 285 - 309.

14. H.C.Dibbern, P.Olesen, J.R.Rostrup-Nielsen, P.B.Tøttrup, N.R.Udengaard. *Make low H_2/CO syngas using sulfur passivated reforming*. Hydrocarbon Processing. 1986; 65(1): p. 71 - 74.

15. J.R. Rostrup-Nielsen. *40 years in catalysis*. Catalysis Today. 2006; 111(1-2): p. 4 - 11.

16. L.Storgaard, H.C.Nielsen. *Catalysts for cost effective hydrogen production*. Digital Refining. 1999: p. 1 - 8.

17. J.R.Rostrup-Nielsen. *Sulfur-passivated nickel catalysts for carbon-free steam reforming of methane.* Journal of Catalysis. 1984; 85(1): p. 31 - 43.

18. N.R.Udengaard, J.H.B.Hansen, D.C.Hanson, J.A.Stal, *Sulfur passivated reforming process lowers syngas H_2/CO ratio*. Oil and Gas Journal. 1992; 90(10): p. 62 - 67 .