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Natural Gas Dual Reforming Catalyst and Process

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1. Introduction

Natural gas consists primarily of methane, typically with 0–20% higher hydrocarbons. It is always associated with other hydrocarbon fuel, in coal beds, as methane clathrates, and is an important fuel source and a major feedstock for fertilizers. Natural gas is commercially extracted from oil fields and natural gas fields. Gas extracted from oil wells is called associated gas. The natural gas industry is extracting gas from increasingly more challenging resource types: sour gas, tight gas, shale gas, and coalbed methane. In fact, methane can also be produced from landfill site or anaerobic digestion, which is called biogas, it is in fact a kind of young age natural gas.

Components	(mol %)
CO_2	71
CH_4 + C_2+ hydrocarbons	28
H_2S	0.5
N_2	0.5

Table 1. Typical composition of Natuna gas field (Richardson and Paripatyadar 1990; Suhartanto, York et al. 2001)

In naturel gas, non-hydrocarbon gases (CO_2, N_2, H_2S) can account between 1% to 99% of overall composition. High carbon dioxide (CO_2) concentrations are encountered in diverse areas including South China Sea, Gulf of Thailand, Central European Pannonian basin, Australian Cooper-Eromanga basin, Colombian Putumayo basin, Ibleo platform, Sicily, Taranaki basin, New Zealand and North Sea South Viking Graben. The composition of CO_2 can reach as high as 80% in certain natural gas wells such as wells at the LaBarge reservoir in western Wyoming and the Natuna production field in Indonesia. Besides, purged gas from a

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gas-reinjected EOR (Enhanced Oil Recovery) well can contain as much as 90% CO_2 (Ricchiuto and Schoell 1988; Schoell 1995; Ballentine, Schoell et al. 2001; Cathles and Schoell 2007).

So far in industry, there have been several ways to bringing gas to the market. These include gas pipeline, liquid natural gas (LNG), and compressed natural gas (CNG). The costs of different fuel transportation are shown in Fig. 2. Also in gas transportation, any impurities such as CO_2 and H_2S must be fully removed, so as to protect the gas pipeline and container. This again will emit lot s of CO_2, the main green house gas into atmosphere. In terms of cost, as shown in Fig. 2, clearly the smallest gas field has highest transportation cost in both onshore and off shore. In a relatively high gas field, the transportation cost increase not as fast as the small gas field, but still much faster in transportation in cost, while the oil transport cost increases much smaller compared to the natural gas. Normally the gas and oil field are co-existed, and far away from the market, so the transportation cost must be taken into consideration. This may be another reason more and more attentions are being paid to the conversion of the gas into liquid, e.g., gas to liquid, and then the resultant liquid is mixed with the crude oil for transportation.
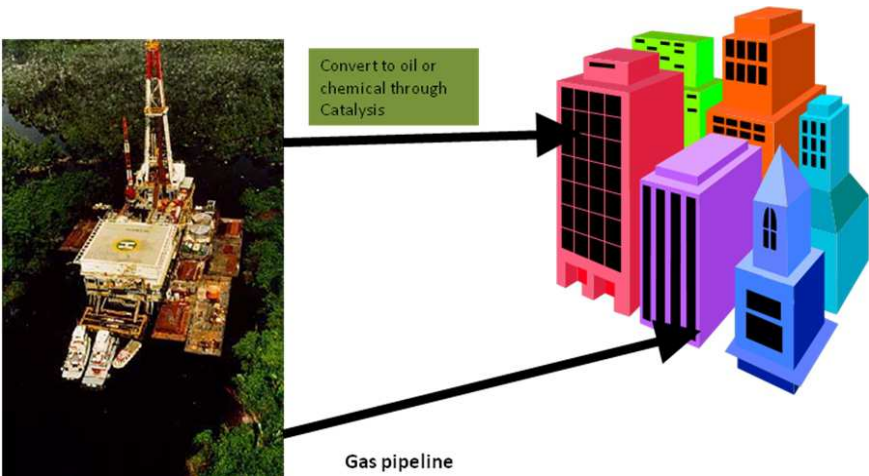

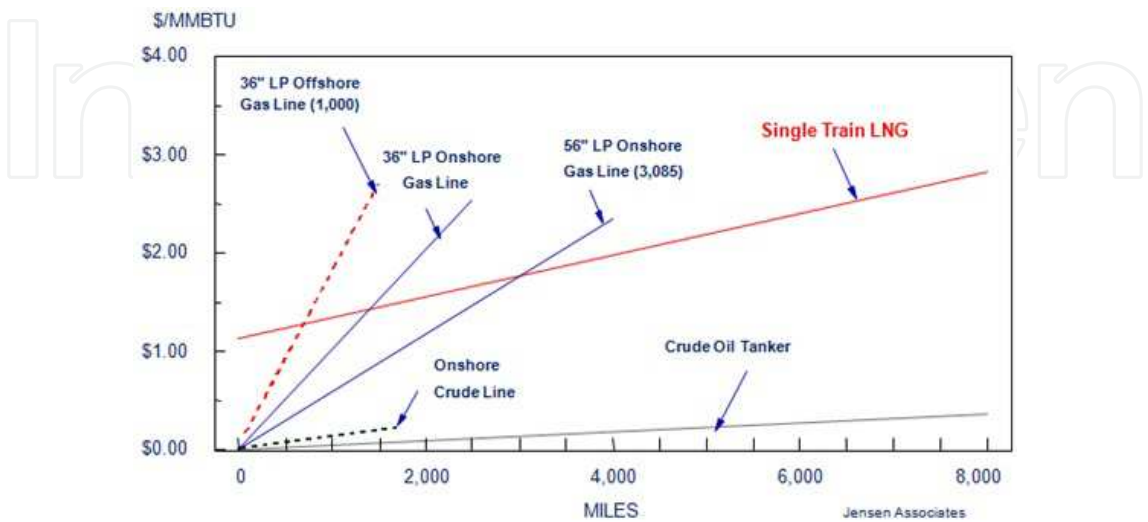Fig. 1. The ways to bring natural gas into market

Fig. 2. The dependence of transportation cost on the distance for various fuels.

Indeed, Gas-to-liquids (GTL) has been a technology operated by industry for many years, while continuing improvement. It is a developing technology that converts stranded natural gas into synthetic gasoline, diesel or jet fuel through the Fischer-Tropsch process. Such fuel can be transported to users through conventional pipelines and tankers. Proponents claim GTL burns cleaner than comparable petroleum fuels. Most major international oil companies are in an advanced stage of GTL production, with a world-scale (140,000 barrels (22,000 m^3) a day) GTL plant in Qatar already in production in 2009.

The gas to liquids (GTL) process comprises three main process steps, firstly the reforming of natural gas to syngas, a mixture of gases containing hydrogen, carbon monoxide, carbon dioxide and unreacted methane, secondly the Fischer Tropsch (FT) conversion of carbon monoxide and hydrogen to long chain hydrocarbons and thirdly the upgrading and refining of these hydrocarbons into a specific state of liquid fuels.. The syngas step converts the natural gas to hydrogen and carbon monoxide by partial oxidation, steam reforming or a combination of the two processes. The key variable is the hydrogen to carbon monoxide ratio with a 2:1 ratio recommended for F-T synthesis. Steam reforming is carried out in a fired heater with catalyst-filled tubes that produces a syngas with at least a 5:1 hydrogen to carbon monoxide ratio, as shown in Fig 3. To adjust the ratio, hydrogen can be removed by a membrane or pressure swing adsorption system. Helping economics is the surplus hydrogen is used in a petroleum refinery or for the manufacture of ammonia in an adjoining plant. Because of the steam reforming occurring under very harsh conditions and also giving much higher H$_2$/CO ratio, it accounts up to 60% of the GTL cost (Shamsi and Johnson 2001). Another way to give ideal H$_2$/CO mixture syngas is through partial oxidation, which has been well developed in lab scale and going to industrial pilot operation.
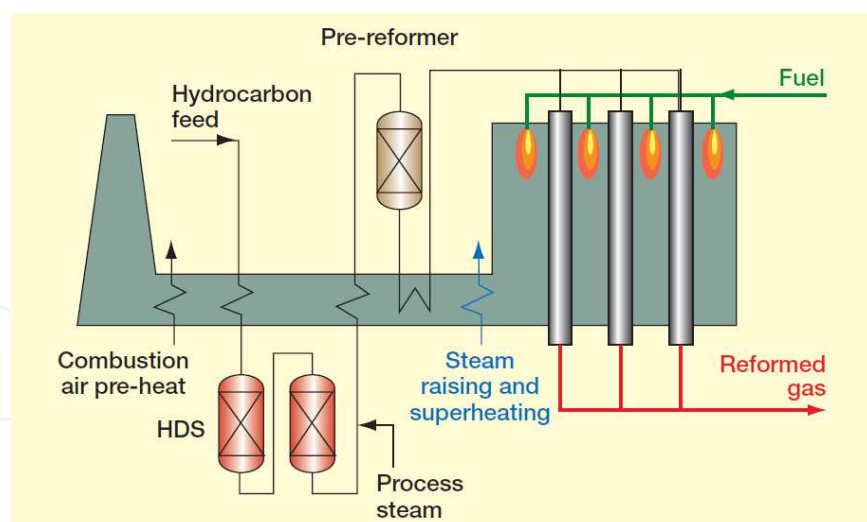

Fig. 3. Diagram of industrial steam reforming process

Another way to give approximate H$_2$/CO ratio of 2 is to combine dry and steam reforming, e.g., through the following reactions

$$CH_4 + H_2O === CO + 3H_2 \qquad (1)$$
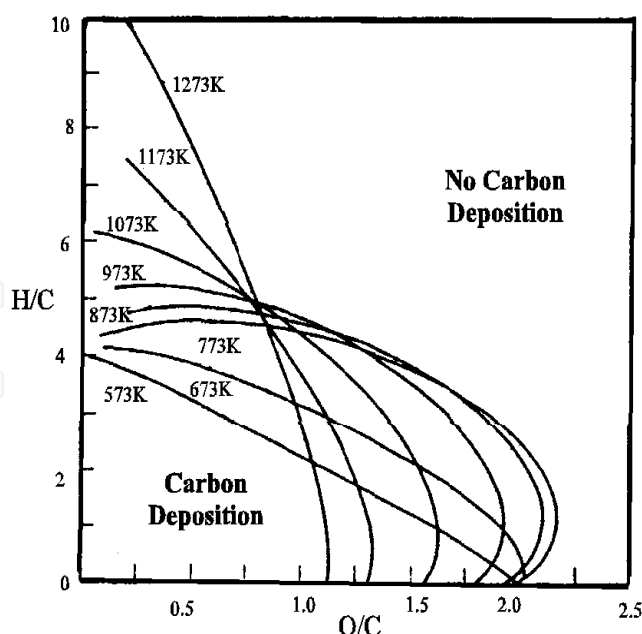
$$CH_4 + CO_2 === 2CO + 2H_2 \qquad (2)$$

Fig. 4. The dependence of carbon deposition on H/C and O/C in the reforming system (Shimura, Yagi et al. 2002; Zhang, Li et al. 2004)

This combining process here is named as dual reforming process, which can theoretically give H_2/CO in the reaction products to 2:1 ratio, which is suitable for the follow up Fischer Tropsch synthesis. Also this can make use of the CO_2 in the natural gas, especially in the gas field where high CO_2 may be contained. It is well known that transporting the gas through LNG or CNG or even pipeline transportation requires eliminating the CO_2 to avoid the corrosion. (Butts 2006; Do 2007; Bhattacharya, Newell et al. 2009) Converting the CO_2 containing gas into liquid through the dual reforming process not only converts the natural gas into liquid, which can be transported as liquid with low cost, but also can make use of the CO_2 in the gas, thus to reduce green house gas emission. The dual reforming process in principle does not require any modification of the steam reforming reactor, but may have much harsh requirements on the catalyst, because the H_2/C in the products would be much less than the steam reforming alone (Wang, Li et al. 1996; Ding, Yan et al. 2001; Shamsi and Johnson 2003), also the O/C in the products is not very high, carbon thus very easily occurs over the system from the thermodynamic view.

Recently steam/CO_2 methane reforming in the syngas reformer is one of particularities of our new catalysts development. We intend to stick to the currently in-use reforming reactor, but feeding both steam and CO_2, which already exists in the natural gas feedstock ranging from 10% to 60%. Through properly adjusting the CO_2 and H_2O ratio, we hope to utilize CO_2 contained in the natural gas and does not require any CO_2 separation. The Ni based reforming catalyst has been prepared using a special dispersion agent, and an oxygen storage material is introduced into the lattice of spinel support, so as to depress the carbon formation. The catalyst has been successfully applied in steam reforming of natural gas for ammonia industry, and the life time has been as long as 6 years. Here we report the application of the catalyst in dual reforming for syngas production. The optimal operating conditions for dual reforming have been explored.

2. Catalyst design

The preparation of steam reforming catalysts based on nickel as the active component has been extensively and intensively studied for years. Over a given nickel contained catalyst with similar nickel metal dispersion (which can be affected by the preparation, activation and operation conditions), the industrial catalyst activity would depends more in the catalyst shape. In fact, the major geometric factor affecting the activity of catalyst particles is the ratio of the particle's geometric surface area to volume, SA/V. When applying the catalyst to industrial reactor, the optimization of catalyst particles must take the three key factors, e.g., low pressure drop, high radical and high strength into consideration. These factors have direct relations with the shapes and size of the catalyst. For example, the high voidage e.g., large particles gives low pressure drop, however, smaller particles can give higher surface area, leading to more active site exposed to the reactants. Also due to the strong endothermic reaction properties, the reactor requires the catalyst to have good radial mixing so that the heat can be transferred from the reactor wall to the centre for the reaction. Also the strength of the catalyst particles are more important, due to the high pressure and high temperature conditions, the catalyst strength must be strong enough to resist the variations.

In the early stage of reforming catalyst development, ring or rasching shapes have been developed. Normally the smaller the particles the higher the catalytic activity and the better heat transfer properties but the higher the pressure drop as the gases pass through the reformer tube. Since 1990s, more and more attentions are been paid to catalyst geometric shapes to increase the geometrical surface area and hence the catalytic activity. The geometric surface area of a catalyst should be $200 m^2/m^3$ or above. In recently years, strong shaped reforming catalysts with higher surface areas and voidage has been developed, as shown in Fig 5. Given the same dispersion of the active metal in the overall catalyst, which can give the same intrinsic activity when the mass transfer factors are eliminated, in industrial application, the physical properties of the catalyst in fact exert more influence on the catalyst performance. From Table 2, it is expected that the catalyst with 10 holes would have higher activity. This has also been confirmed by our industrial operation results.

Fig. 5. The novel shapes with high strength of the reforming catalyst and support.

Catalyst Geometry	Surface Area(m²)	Void Fraction	SA/V(m⁻¹)
1-hole	0.00503	0.66	1.151*10³
1-hole -6-grooves	0.0052	0.72	1.733*10³
4-hole	0.00523	0.62	1.703*10³
10-hole	0.00642	0.7	2.013*10³

Table 2. The physical properties of various shaped reforming catalysts.

3. Dual reforming catalyst performance test

3.1 Experiments

The reactions were carried out in a 70cm stainless steel reactor tube with id and od of 1.2cm and 2cm respectively. The furnace, comprising 6 individually heated zones, was specially designed to allow a temperature profile to be set across the reactor mimicking that of an industrial reformer. Four thermocouples were positioned inside a thermowell (inside the catalyst bed) to record the temperature of the catalyst bed at the inlet, exit and two intermediate positions. A diagram of the reactor and test setup is shown in Figure 6.

The rig has a supply of CH_4, CO_2, H_2, N_2 controlled by mass-flow controllers and an HPLC pump delivers H_2O, which is fed and mixed with the gases to flow together through a vaporiser where steam is generated before flowing into the reactor. Temperature programmes can be set on the vaporiser and all reactor furnace zones. Before any reactions were started, it was necessary to set a temperature profile across the reformer tube. The profile was designed to be similar to that of an industrial reformer, ensuring a cooler temperature at the tube inlet and gradually increasing the temperature towards the exit.
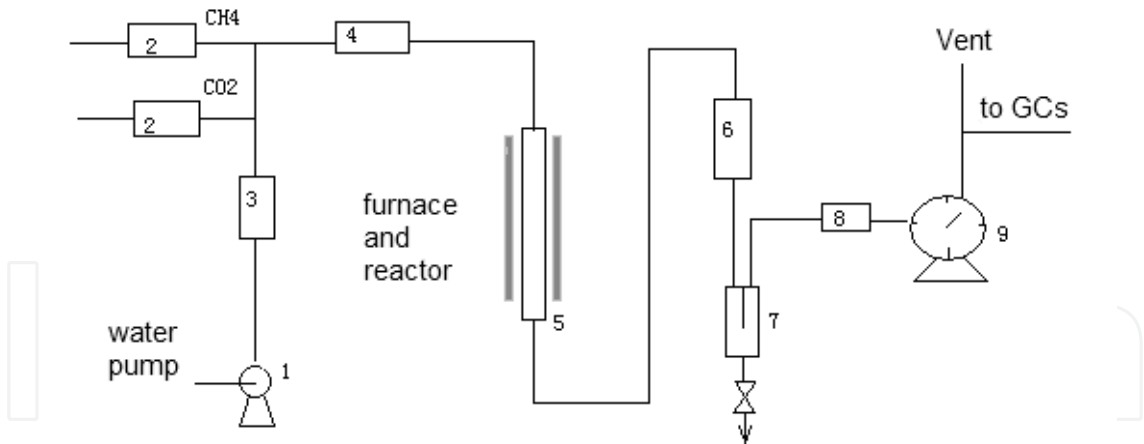

Fig. 6. Pressure Test system setup, 1–water pump, 2–gas MFC, 3–Purifier, 4–Mxier, 5–Tubular reactor, 6–condenser, 7–separator, 8–Back-Pressure regulator, 9–Wet flowing meter

In reforming reaction, carbon will most likely form via the methane cracking reaction which is promoted by high temperature:
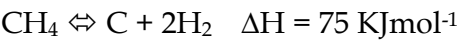
$$CH_4 \Leftrightarrow C + 2H_2 \quad \Delta H = 75 \text{ KJmol}^{-1}$$

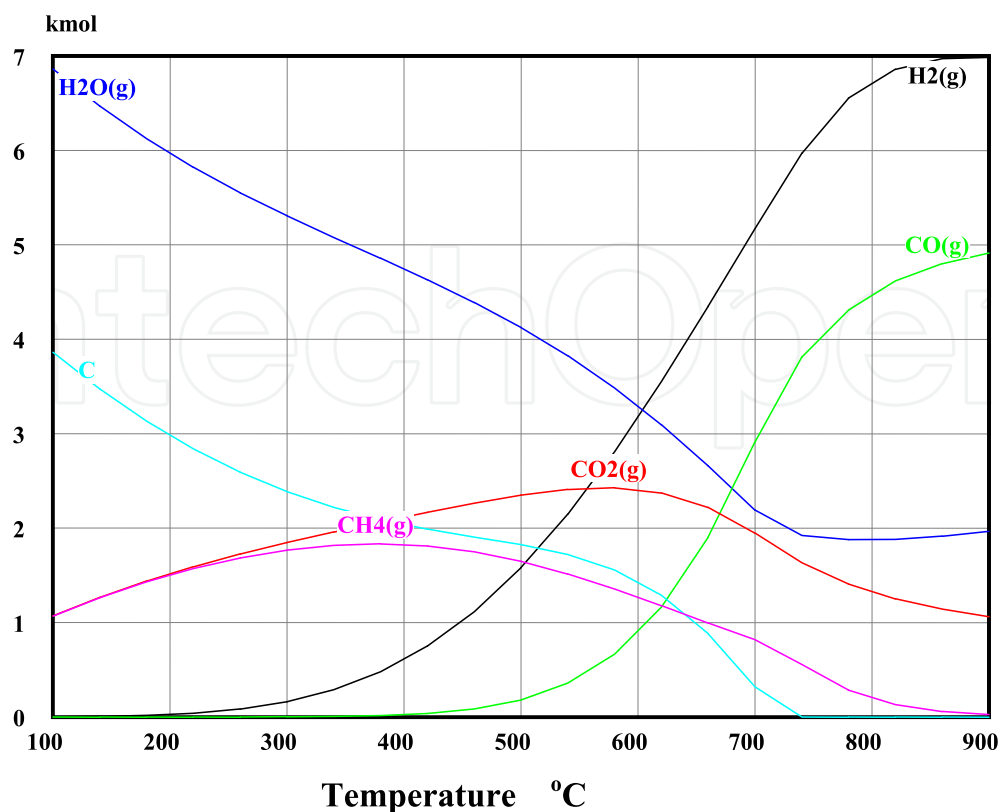Figure 7 shows equilibrium data for CH_4 cracking with a CH_4 only feed at 3 bar.

Fig. 7. CH_4 cracking reaction at equilibrium. 3bar and CH_4 only feed at various temperatures

At the catalyst bed inlet there is very little H_2 from reforming available to promote the reverse reaction and so the catalyst inlet is susceptible to coking by CH_4. It is therefore necessary to keep the temperature low enough where the thermodynamics of carbon formation via methane cracking are less favourable (Shamsi and Johnson 2001). However, it must also be sufficiently high to allow some H_2 production to prevent cracking further down the bed. Similar to an industrial reformer, the bed inlet temperature of the current study was 550°C (Valdes-Perez, Fishtik et al. 1999; Shamsi and Johnson 2003; Snoeck, Froment et al. 2003).

Another common carbon forming reaction is the Boudouard reaction (Riensche and Fedders 1991):

$$2CO \Leftrightarrow C + CO_2 \quad \Delta H = -171 \text{ KJmol}^{-1}$$

No carbon is predicted from the Boudouard reaction at the bed inlet under the conditions in the present study as there is only CO_2 and no CO.

Towards the exit of the catalyst bed, enough H_2 has been produced from reforming to prevent C from methane cracking reaction and so the temperature can be increased. The reforming reaction is endothermic and favoured by high temperatures so it is desirable to use as high a temperature as possible. Figure 8 shows equilibrium data for a dual reforming reaction at 3 bar with feed $CH_4:CO_2:H_2O$ 1:1:1.

Clearly the high temperature favors the CH_4 conversion and H_2 and CO yields (Treacy and Ross 2004; Maestri, Vlachos et al. 2009), however, it is difficult for CO_2 to be fully converted
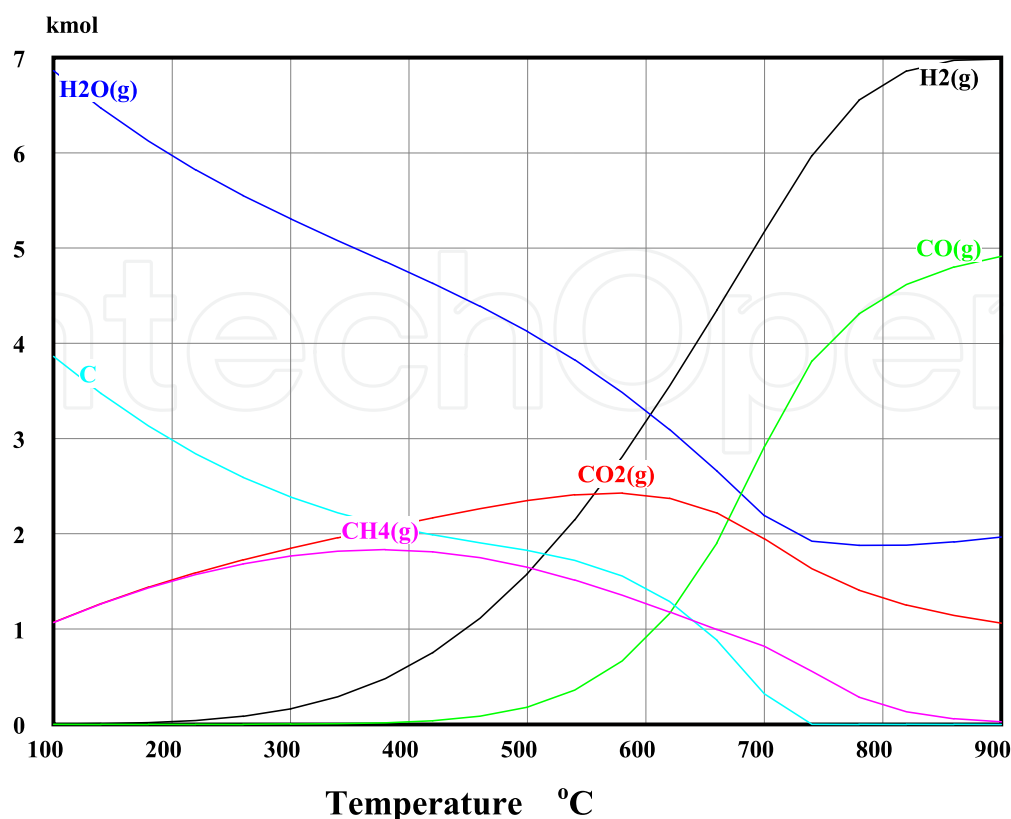
Fig. 8. Dual reforming equilibrium data at increasing temperature. 3bar, $CH_4:CO_2:H_2O$ 1:1:1 feed

into CO even at high temperature. Also at high reaction temperature, such as 750℃ or above, no carbon deposition is expected from the thermodynamic views.

3.2 Catalyst charging

The test was carried out in a 100ml pressure reactor system to simulate industrial operation conditions. Natural gas and CO_2 were controlled to feed the reactor using two gas MFCs. De-ionised water was fed using a quantitative pump, first vaporisation then mixing with the gas feedstock. The mixing system was then heated to the required inlet temperature, and further going to pass the catalytic reactor. The reactor converter was a tubular style system, which was heated at different heating zones so as to mimic the industrial reactor temperature distribution. Thermocouples were installed inside the tube to monitor the catalyst bed temperature at different points. The products from the reactor were firstly cooled down to separate liquid, so as to become dry gas. The dry gas was measured and the composition was analysed. The schematic setup can be seen in Fig. 6.

3.3 Catalyst properties

The catalyst sample is from the industrial proved catalyst system for natural gas reforming, whose physical property is shown in table 3. This catalyst combination has been used in both China and abroad in the industries of ammonia, synthetic methanol, industrial hydrogen generation, and the performance is extraordinary.

Indicator	BOXE-1	BOXE-2
Shape and color	10-hole pellet, gray	1-hole grooved pellet gray
Dimensions (od×h) (mm)	Φ10×14	Φ14×14
density (kg/l)	1.10~1.15	1.10~1.15
Radius-strength (N/pellet)	>350	>500
Main composition NiO (m/m) support	>13 Al_2O_3	>13 $CaAl_2O_4$

The catalyst was reduced before use so as to convert nickel oxide into active metal.
$NiO+H_2=Ni+H_2O$

Table 3. The dual reforming BOXE catalyst properties

The physical properties of the steam reforming supports are as follows:

For the 10-hole pellet shaped catalysts, the support consists of pure α- Al_2O_3, surface area: 3.0~3.5m^2/g; pore volume: 0.2~0.25ml/g;

For the 1-hole grooved pellet shaped catalyst, the main phase of the support is $CaAl_2O_4$ Surface area: 5~8m^2/g; Pore volume: 0.2ml/g; average pore size: 1000A;

Pore distribution:

>1500A:	75.70%,
1000~1500A:	10.7%,
500~1000A:	8.58%,
100~500A:	3.85%,
<100A:	1.23%

3.4 Feedstock

Natural gas is civil use grade, whose composition is shown in table 4. CO_2 is industrial grade, and the de-ionised water is normal purified grade. The catalyst reduction hydrogen is industrial grade H_2.

component	Volume percentage %
methane	96.0
ethane	2.35
nitrogen	0.57
CO_2	1.08

Table 4. Typical low CO_2 containing natural gas composition

3.5 Catalyst activation

After catalyst is loaded, pressure test was carried out to ensure no leak occuring. Then the reactor temperature was increased at 10 ℃/min to 500℃ at inlet, 720℃ in the middle and 800℃ at the outlet, then hydrogen reduction was started and last for 8 hours

The reduction media is H_2/H_2O at ratio of 1:5, which is the same as industry. Hydrogen GHSV is about =1000h^{-1} at ambient pressure.

4. Results and discussion

4.1 Test under pressure conditions

This series test is to mimic industrial practical process and operation. The conditions are under high pressure at $H_2O/C=2.0$ at low inlet temperature 500℃. These conditions are widely used in industry taking the techo-economical factors.

4.1.1 CO_2 fed amount effect on the product composition at $H_2O/C=2.0$

Pressure   2.6Mpa,
CH_4 GHSV   1200h^{-1},
Inlet T: 500℃
Outlet T: 900℃

The effect of CO_2 feeding (in terms of CO_2 GHSV) on the product composition is shown in Table 5. Each test was carried out for 400 hours to get steady and reproducible results. In industry, the catalyst performance in most case is measured in terms of H_2 and CO yield, and the reactants conversion. The conversion of methane is referred to the slip methane content, meaning the concentration of methane in the products (the dry gas base after steam removal and C elimination). The higher slip methane in the products suggests lower catalyst activity.

No.	NG GHSV H^{-1}	CO_2 h^{-1}	CO_2/CH_4	Inlet T	Outlet T	CH_4 %	CO %	CO_2 %	H_2 %	H_2/CO	CH_4 %
1	1200	2200	1.83	502	901	1.67	27.1	27.6	43.63	1.61	2.31
2	1200	2700	2.25	501	899	1.23	28.2	31.6	38.97	1.38	1.80
3	1200	3200	2.67	500	899	1.00	30.0	34.0	34.10	1.14	1.38
4	1200	3700	3.08	500	896	0.78	32.2	38.0	29.02	0.90	1.28
5	1200	4200	3.50	501	899	0.60	33.3	41.8	24.30	0.73	1.03

Table 5. Dependence of product composition on CO_2 feeding amount

The dependence of H_2/CO ratio on the CO_2/C ratio can be seen in Fig. 9, and the effect of CO_2/C on the slip methane content can be seen in Fig. 10.
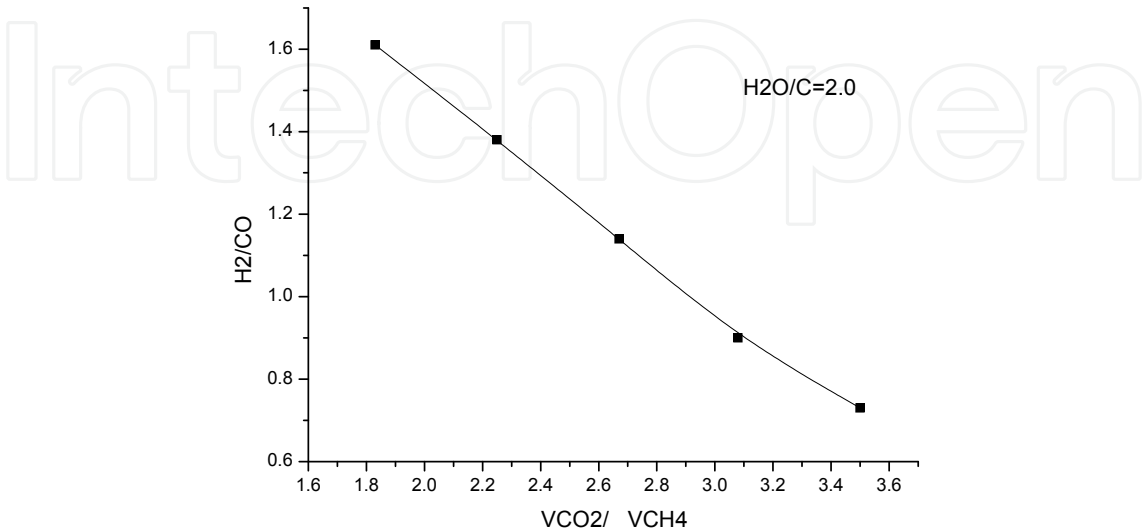

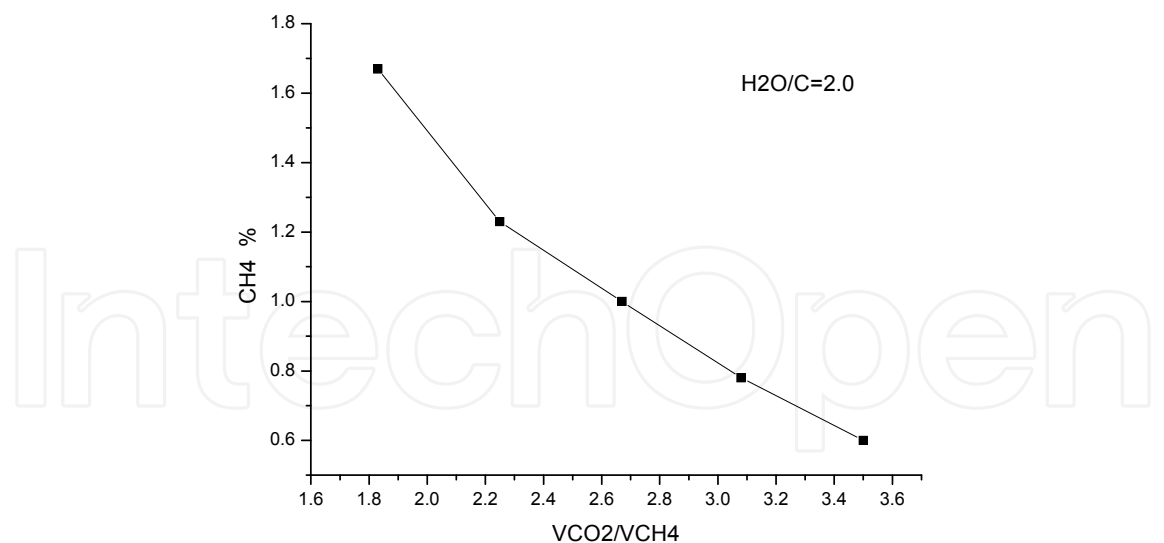Fig. 9. Dependence of H_2/CO ratio in the product on the CO_2/C ratio in feedstock

Fig. 10. Effect of CO_2/CH_4 ratio in the feedstock on slip CH_4 content

Clearly Fig 10 shows that the increase of CO_2 in the feedstock leads to the decrease of H_2/CO ratio in the products, and the slip methane content also decrease. This is helpful for the methane conversion and CO production.

4.1.2 Effect of pressure on the composition of products

The reaction conditions were set as follows;

H$_2$O/C: 2.0,
Methane GHSV: 1200h^{-1},
CO$_2$ GHSV: 4200h^{-1},
Inlet T: 500℃
Outlet T: 900℃

The effect of pressure on the gas product composition is shown in Table 6. Please note that each test was continued for 100 hours to get the steady state results, during the time on stream test, no catalyst activity drop or selectivity changes were observed, suggesting that the catalyst has high stability under the test conditions

No.	P MPa	Inlet T	Outlet T	CH$_4$ %	CO %	CO$_2$ %	H$_2$ %	H$_2$/CO	After CO$_2$ removal CH$_4$%
1	2.2	501	899	0.50	33.4	40.9	25.2	0.75	0.85
2	2.6	501	899	0.60	33.3	41.8	24.3	0.73	1.03
3	3.0	497	900	0.76	31.9	42.0	25.3	0.79	1.31

Table 6. Dependence of product composition on the pressures

With the increase of pressure, the slip methane content rises in the products, while H_2/CO ratio was little changed. The is in agreement with the thermodynamic equilibrium, because the reforming reaction gives more mole of gases than the reactants, increase the pressure leads to lower methane conversion(Friedmann, Burruss et al. 2003; Shamsi and Johnson

2003; Zhang, Li et al. 2004). However, the overall delta T to the equilibrium is about 5°C, which showed the super performance of the BOXE reforming catalysts.

4.1.3 Effect of outlet temperature on the composition of the product

Conditions:

H_2O/C: 2.0,
P: 2.6Mpa,
Carbon GHSV in terms of CH_4: $1200h^{-1}$,
CO_2 GHSV: $4200h^{-1}$,
Inlet T: 500°C

The outlet temperature effect on the product distribution is listed in table 7.

No.	Inlet T	Outlet T	CH_4 %	CO %	CO_2 %	H_2 %	H_2/CO	After CO_2 removal CH_4%
1	500	872	0.89	28.9	42.9	27.3	0.94	1.56
	499	872	0.89	29.0	42.5	27.6	0.95	1.55
2	501	899	0.60	33.3	41.8	24.3	0.73	1.03
	501	899	0.54	33.1	42.1	24.3	0.73	0.93

Table 7. The effect of outlet temperature on the gas product composition

Increasing outlet temperature favors the formation of CO, and helps to decrease the slip CH_4 content in the product. However, the outlet temperature may be restricted by the materials of the tubular reactor and energy consumption. The increase of outlet T may not be always a good solution to increase CH_4 conversion and decrease H_2/CO ratio. So far, most industrial operation for BOXE reforming catalysts uses 870°C as the outlet temperature.

4.1.4 Effect of CO_2 added in the feedstock on the gas product composition

Under of CH_4 GHSV of $1272h^{-1}$, the results were shown in Table 8. It is shown that at VCO_2/VCH_4 ratio of 1.51, H_2/CO in the gas product is about 1.5, and slip CH_4 is only 0.1%. Comparison with Table 3 suggests that at the same GHSV of carbon (hydrocarbons), decreasing H_2O/C ratio and reducing P favour the CO generation and reducing CH_4 content.

P	GHSV h^{-1}		$CO_2/$	H_2O/C	T °C		Product dry gas composition %					
Mpa	CH_4	CO_2	CH_4		Inlet	Outlet	CH_4	CO	CO_2	H_2	H_2/CO	After CO_2 removal C_{CH4}
0.3	1272	1283	1.01	1.5	600	900	0.1	27.6	16.1	56.2	2.04	0.12
0.3	1272	1492	1.17	1.5	602	900	0.1	29.5	16.5	53.9	1.83	0.12
0.3	1272	1687	1.33	1.5	601	900	0.1	30.5	17.8	51.6	1.69	0.12
0.3	1272	1916	1.51	1.5	603	900	0.09	31.5	19.8	48.6	1.54	0.11
0.3	1272	2148	1.69	1.5	605	900	0.06	32.5	21.5	45.9	1.41	0.08
0.3	1272	2336	1.84	1.5	605	900	0.05	34.9	22.7	42.4	1.21	0.06

Table 8. Effect of CO_2 added in the feedstock on the product composition at relatively low pressure range

| P Mpa | GHSV h^{-1} | | CO_2/C | H_2O/C | T ℃ | | Gas composition % | | | | | |
	CH$_4$	CO$_2$			Inlet	Outlet	CH$_4$	CO	CO$_2$	H$_2$	H$_2$/CO	After CO$_2$ removal CH$_4$ (%)
0.3	2561	1283	0.5	1.5	602	900	0.25	26.3	8.7	64.8	2.46	0.27
0.3	2561	2596	1.01	1.5	603	900	0.09	31.5	14.8	53.6	1.70	0.11
0.3	2561	2996	1.17	1.5	602	895	0.08	32.5	17.2	50.2	1.54	0.10
0.3	2561	3406	1.33	1.5	602	894	0.07	33.6	18.8	47.5	1.41	0.09
0.3	2561	3867	1.51	1.5	603	900	0.05	34.7	20.8	44.5	1.28	0.06

* Each test lasts for 400 hours to get steady and stable results

Table 9. Under relatively high methane GHSV, the dependence of gas product composition on the CO_2 feeding amount

Figs 10 and table 8 results suggest that low pressure and low H_2O/C ratio are favourable for methane conversion. Even when CH$_4$ GHSV was increased by one time (2561h^{-1}), slip methane in the gas products does not change significantly. However, the GHSV of methane has significant effect on the H_2/CO ratio. At CH$_4$ GHSV of 2561h^{-1}, and even when VCO_2/VCH_4 is only 1.17, H_2/CO is already nearly 1.5 in the product, suggesting high GHSV of methane is good for producing syngas with low H_2/CO ratio. This may be more useful for the production of syngas for carbonyl synthesis such as MEG production. It is contrary to the many industrial results.

The effect of GHSV of methane and CO_2/CH_4 ratios in the feedstock on the H_2/CO ratios are summarised in table 10. It is shown that the retention time exerts significant effect on the H_2/CO ratio in the products. High GHSV, e.g., shorter contact time of the reactants would have lower H_2/CO with the increase of VCO_2/VCH_4, which is much lower than the system with lower GHSV. The results are in agreement with the literature (Zhang, Li et al. 2004; Chen, Chiu et al. 2010). This suggests that the reaction is kinetics controlled, It may be worthwhile increasing the pressure so at the narrow the gap between the high and low GHSV for H_2/CO ratios.
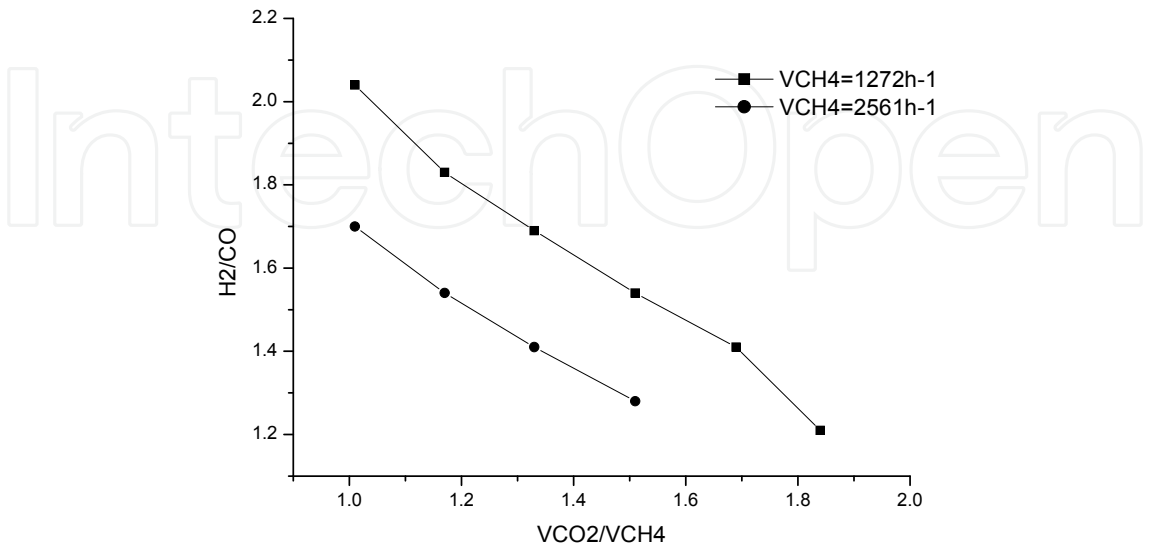

Fig. 11. Effect of GHSV of methane and CO_2/CH_4 ratios in the feedstock on the H_2/CO ratio in the products.

P Mpa	GHSV h^{-1}		CO$_2$/C	H$_2$O/C	T °C		Gas composition %					
	CH$_4$	CO$_2$			Inlet	Outlet	CH$_4$	CO	CO$_2$	H$_2$	H$_2$/CO	% CH$_4$*
0.3	2561	2592	1.01	1.3	610	900	0.13	32.4	13.7	53.8	1.66	0.15
0.3	2561	2592	1.01	1.5	601	900	0.08	31.6	14.8	53.6	1.70	0.11
0.3	2561	2592	1.01	2.0	600	899	0.06	27.6	17.3	55.0	1.99	0.07
0.3	2561	3406	1.33	1.5	602	894	0.07	33.6	18.8	47.5	1.41	0.09
0.3	2561	3406	1.33	2.0	601	900	0.04	30.5	22.9	53.4	1.75	0.05
0.3	2561	2592	1.01	1.5	601	900	0.08	31.6	14.8	53.6	1.70	0.11
0.45	2561	2592	1.01	1.5	603	895	0.35	29.5	15.4	54.8	1.86	0.41
0.6	2561	2592	1.01	1.5	608	890	0.65	29.2	15.7	54.5	1.87	0.77

* The CH$_4$ concentration refers to the one after excess CO$_2$ removal.

Table 10. Effect of CO$_2$ amount in the feedstock on the products compositions, CH$_4$ GHSV = 2561h^{-1}

4.1.5 The effect of CO$_2$ and H$_2$O added in the feedstock on the gas product composition under the constant CH$_4$ GHSV H$_2$O/C ratio, P and temperatures

The catalyst has been tested at various ratios of H$_2$O/CH$_4$ and CO$_2$/CH$_4$ at different pressures and outlet temperatures. The highest H$_2$/CO ratios with a low slip methane results were obtained under the conditions of 0.3Mpa, CO$_2$/CH$_4$ 1.01 and H$_2$O/methane 2.0 at inlet temperature of 602°C and outlet temperatures of 899°C. The gas products can be used directly for Fischer Tropsch. However, if a CO rich products are desired, the reaction conditions can be changed to 0.3Mpa, CH$_4$ GHSV 2561h^{-1}, CO$_2$ GHSV 3406h^{-1}, inlet temperature of 602°C and outlet temperature of 894°C, under which H$_2$/CO is 1.41 and slip methane of 0.09.%.

The results in Table 10 also suggests that decreasing H$_2$O/methane ratio to as low as 1.3 with co-feeding CO$_2$ can effectively depress the carbon formation, and give a stable catalyst performance. This can significantly reduce the steam feeding in the conventional steam reforming process, which would save energy and simplify the hydrogen plant, also it can make use of CO$_2$ in the gas stream.

It is seen from Table 10 that when fixing the reaction pressure and CO$_2$/CH$_4$ ratio while increasing H$_2$O/methane ratios, H$_2$ and H$_2$/CO increase in the products. Increasing CO$_2$/CH$_4$ ratio favors the CO production, giving desirable product compositions for the process where more or pure CO is required.

When the pressure was increased to 0.6Mpa from 0.3Mpa, the slip CH$_4$ concentration increased more significantly. This can be explained by the thermodynamic model, due to the reforming reaction is volume expansion, while CO WGS is identical volume process (Steinfeld, Kuhn et al. 1993; Tsai and Wang 2008; Maestri, Vlachos et al. 2009).

4.1.6 Effect of lower H$_2$O/methane ratio on the reactions

At P of 0.3Mpa，and CH$_4$ GHSV of 2561h^{-1}，CO$_2$/CH$_4$ of 1 when decreasing H$_2$O/methane to as low as 1.0 and 0.8, the catalyst has run for more than 50 hours each , a little carbon deposition were observed in the inlet of the catalyst at H$_2$O/C at 0.8, but much more carbon

deposition in the exit reactor tube has been observed, which caused big pressure drop. This suggests that the steam is very important and essential to depress the carbon formation. A further experiment also proves this. When the pressure drop increased to 2 bars during the reaction with H_2O/CH_4 0.8 for 60hours, the steam feeding was increased to H_2O/CH_4 at 2 with the CH_4 and CO_2 feeding rate unchanging, we can see that the H_2/CO ratio increased to 1.92, and slip methane decreased to 0.05%, also the pressure drop decreased from 2 bar to 0.1bar after 95 hours operation. This suggests that the deposited carbon in the catalyst bed can be removed through adjusting the $H_2O/methane$ ratios.

5. Catalyst deactivation and regeneration study

During the catalyst pilot test, it is found that when the CO_2 is co-fed with the steam at $H_2O/CH_4>1$, the catalyst can effectively convert natural gas and CO_2 into syngas with various H_2/CO ratio, and no pressure drops were observed during the test. However, when the H_2O/CH_4 is decreased to less than 1, pressure drop occurs in the reactor, and increased with the time on stream, but the products distribution and methane conversion remained unchanged. This suggests that even with some carbon deposition, the catalyst active sites can still catalyze the reactions.

Here we collected the carbon deposited catalyst sample and characterized them using XRD, TG and laser Raman. The XRD results showed that nickel is present in highly dispersed metallic metal, while a small amount of crystalline carbon is detected, which show a very small diffraction peak at 28.9o, which is tentatively assigned to the carbon deposition.

The used catalyst has been measured using TG-DTA-MS, the weight change, heat flow and the emitted products were monitored using MS during the thermal analysis. For comparison, a fresh H_2/H_2O reduced Ni catalyst has also been characterised using TG-DTA-MS. The results are shown in Fig. 12. It is clearly shown that with the increase of
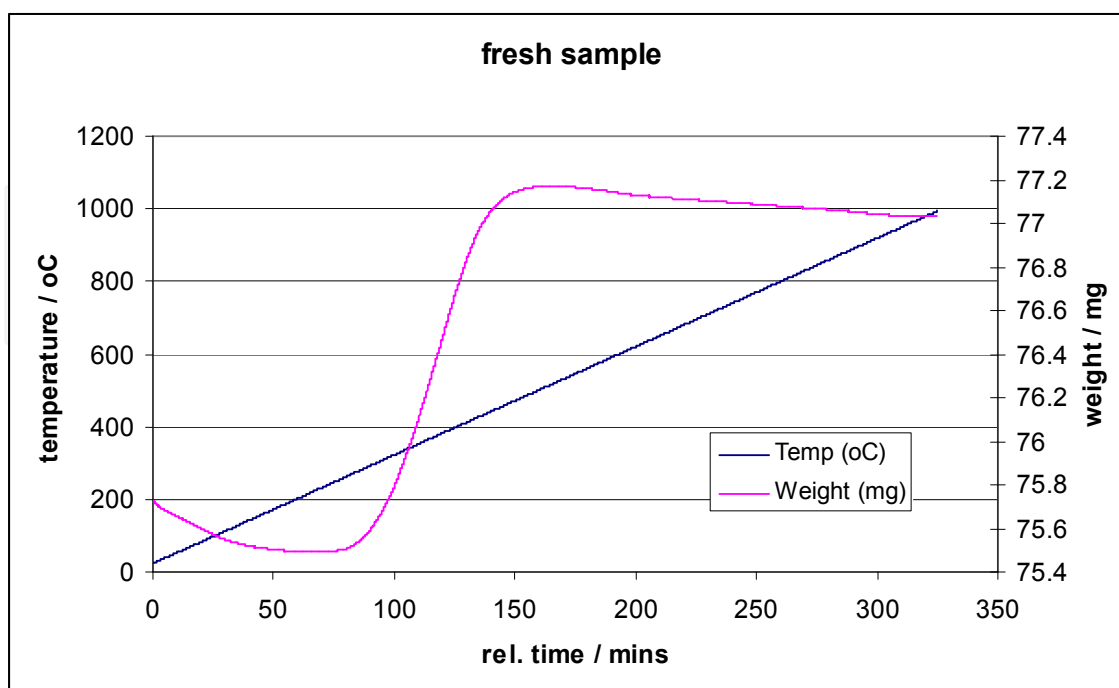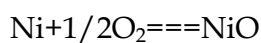

Fig. 12. TG-DTA-MS of the fresh reduced Ni/Al_2O_3 reforming catalyst

temperature, the weight of catalyst sample increase, which can be explained by the oxidation of nickel metal into nickel oxide. (Bhattacharyya and Chang 1994; Gonzalez-Delacruz, Pereniguez et al. 2011).

$$Ni+1/2O_2===NiO$$

Because the nickel metal particles uniformly dispersed over the support, the oxidation occurs in a very narrow range of the temperature from 230°C to 400°C. The weight loss after 500°C may be due to the decomposition of the resultant NiO.
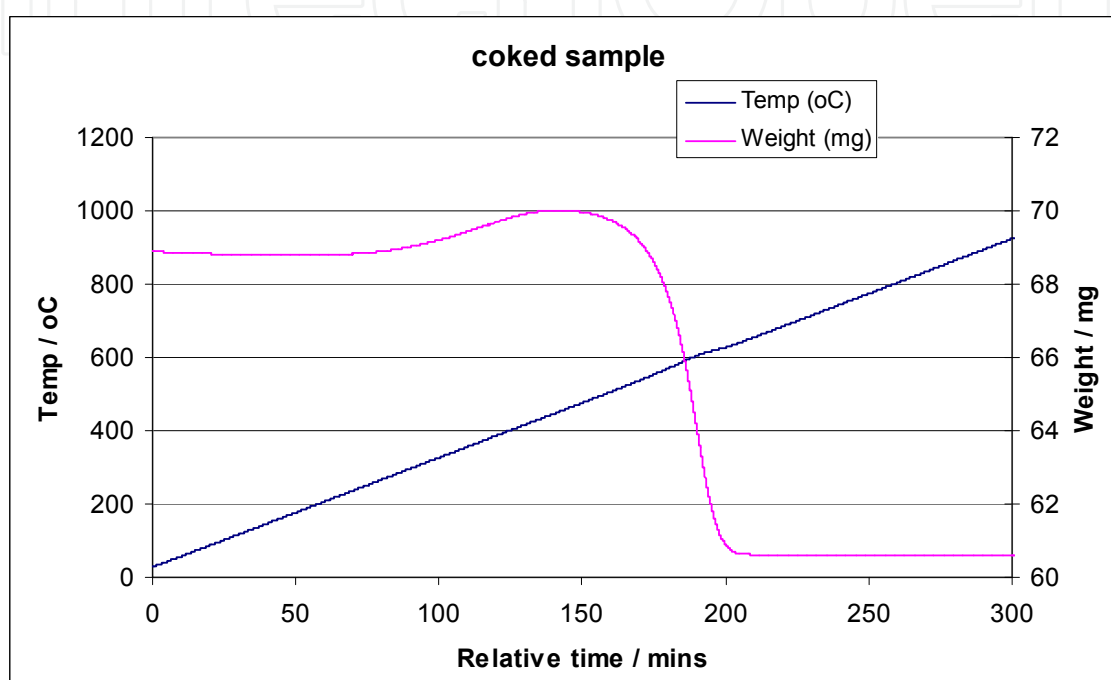

Fig. 13. TG-DTA of the used BOXE reforming catalyst

TG results of the used catalyst (unloaded from the reforming reactor where H_2O/methane=0.5 and operated for 50 hours), It is interesting to see that the catalyst weight started to increase at 210°C until 405°C, this is in agreement with the fresh catalyst sample, which can be explained by the oxidation of nickel metal particles into oxide. When the temperature is increased to 450°C, an abrupt weightloss occurs, with the weight of the sample change from 70mg to 60.5mg, equivalent the weighloss ratio of 13.8wt%. (Riensche and Fedders 1991; Claridge, Green et al. 1994; Verykios 2003; Adachi, Ahmed et al. 2009) Because the TG is carried in static air where oxygen is present, hence the deposited carbon is converted into CO_2 and evolved into the gas products, thus leading to the weightloss. This is further supported by the TG-DTA results as shown in Fig.14.

The TG-DTA results showed that the weighloss of the catalyst corresponds to a strong exothermic reaction, which is due to the oxidation of the carbon, as oxidation reaction gives heat. Also the carbon formation may be present in different forms, so the oxidation reaction is in a broad temperature ranges.

The MS results (Fig. 15) of the burnt gas suggest that only CO_2 is detected, which is in the same temperature for the weighloss of the catalyst sample as shown in Fig 13. No other gas
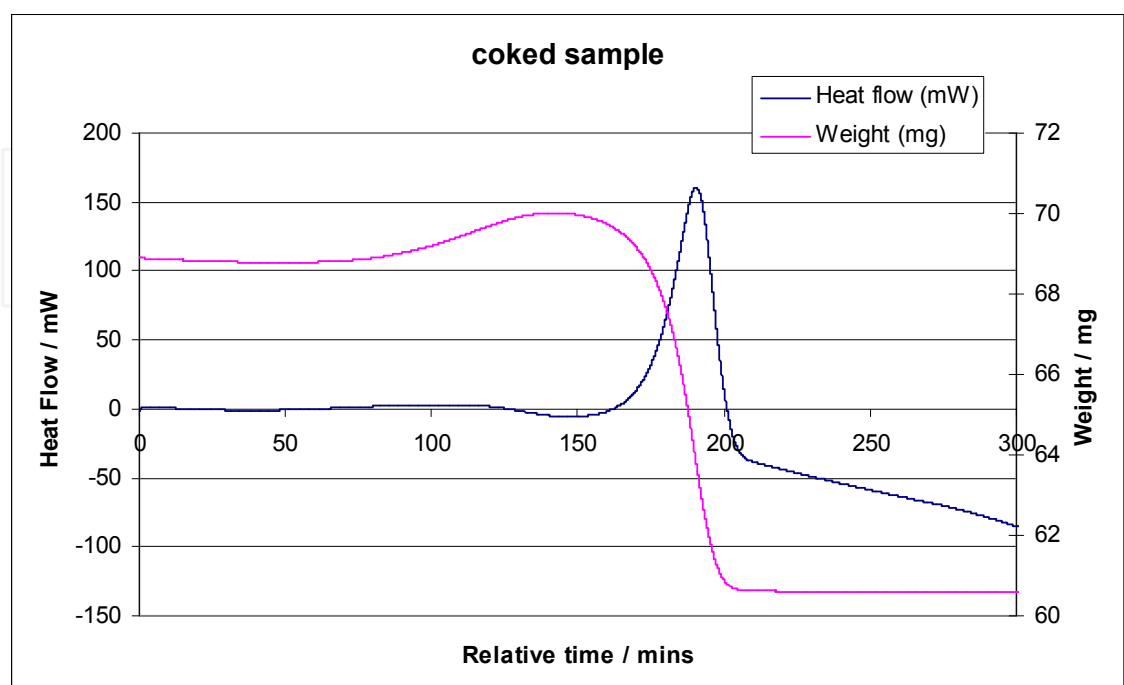
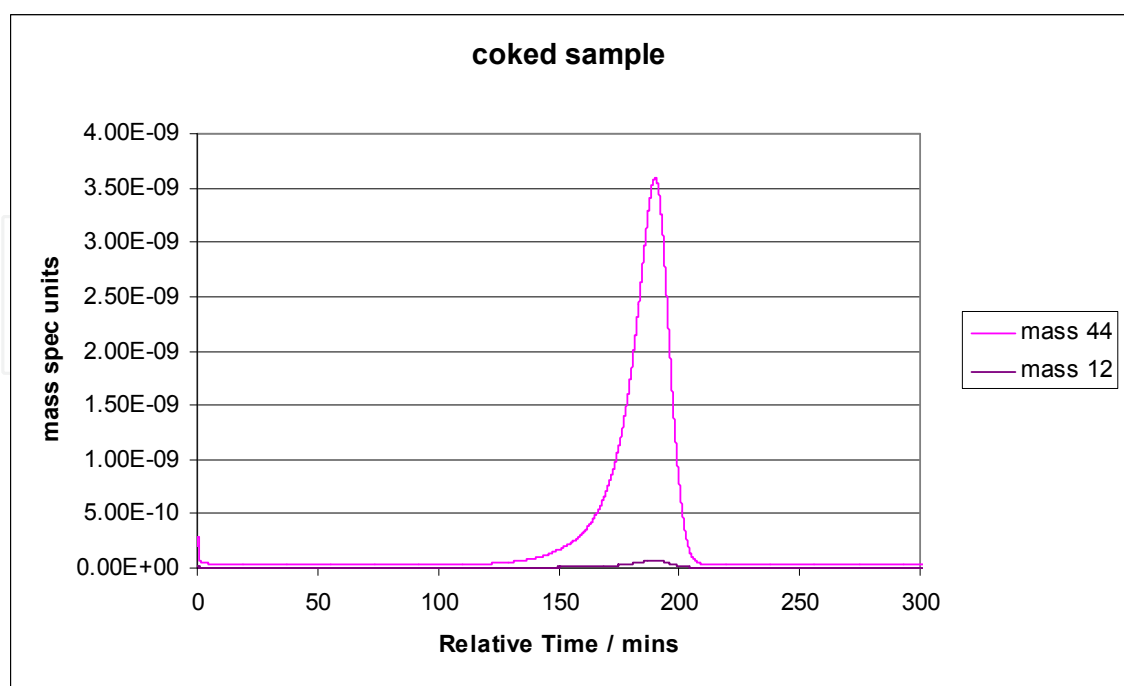Fig. 14. TG-DTA result of the used BOXE reforming catalysts

Fig. 15. The evolution of CO_2 from the used reforming catalysts during the thermal analysis

like methane or ethane is detected from the MS, also no aromatics, suggesting that the carbon formation over the BOXE catalyst is though nickel active site, not through the acid site, where aromatic carbon is the coke precursors.

6. Conclusion

6.1 Carbon dioxide is present in most natural gas field, separating CO_2 and transporting the natural gas into market may be more suitable for large gas field, but not economical for small gas field or high CO_2 containing gas field.

6.2 Converting the gas into liquid and transportation together with oil maybe an economical way to utilize the gas, but the conventional steam reforming catalyst requires high H_2O/CH_4 ratio to avoid carbon deposition, however, the resultant syngas has much higher H_2/CO ratio in the gas products.

6.3 BOXE reforming catalysts have been tested in dual reforming reaction to make use of both CO_2 and methane in the gas field, which showed a broad operation window for utilize the CH_4 and CO_2.

6.4 Under proper pressure, $H_2O/C \cdot CO_2/CH_4$ ratios, reforming CH_4 using both H_2O and CO_2 at high temperature to generate syngas with low H_2/CO ratio is feasible. The catalysts showed stable good performance.

6.5 At temperature from inlet of 600°C and outlet of 900°C, given $H_2O/C=1.5$ to get $H_2/CO=1.5$ in the gas products is easy to obtain through adjusting GHSV and pressure and adding the amount of CO_2.

6.6 Reforming CH_4 at H_2O/C as low as 1.0 in the feedstock experience carbon deposition, especially in the reactor wall end. Hence it is not recommended to use the feedstock with low H_2O/C ratio in feedstock.

6.7 To reach long-term stable industrial operation, it is recommended to adopt relatively mild conditions such as lower outlet temperature (<870°C) relative high H_2O/C ratio (ca.1.4-1.5) to do the pilot test.

6.8 Dual reforming with CO_2 and H_2O not only helps to give the desirable H_2/CO ratio for the reformed gas products, but also helps to make use of the CO_2 in the gas fields and reduces GHG emission, The BOXE reforming catalyst showed high activity and selectivity to the syngas production at a very broad operating window.

6.9 The low $H_2O/$methane feed may result in carbon deposition when CO_2/CH_4 ratio is not high enough. However, the results carbon can be converted into CO through increasing the H_2O feeding during the operation.

6.10 The carbon formation under lean steam/carbon ratio is due to the nickel decomposition of the methane over the catalysts, it can be converted into CO_2 when oxygen is present, this can be another way for the catalyst regeneration outside of the reactor.

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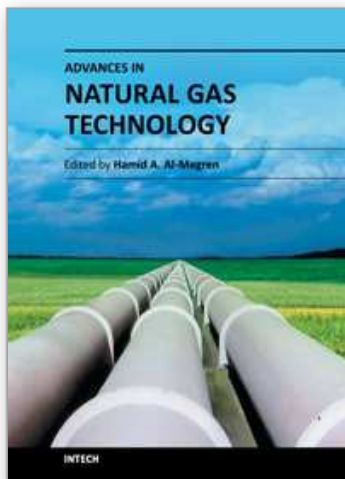
Advances in Natural Gas Technology

Edited by Dr. Hamid Al-Megren

Natural gas is a vital component of the world's supply of energy and an important source of many bulk chemicals and speciality chemicals. It is one of the cleanest, safest, and most useful of all energy sources, and helps to meet the world's rising demand for cleaner energy into the future. However, exploring, producing and bringing gas to the user or converting gas into desired chemicals is a systematical engineering project, and every step requires thorough understanding of gas and the surrounding environment. Any advances in the process link could make a step change in gas industry. There have been increasing efforts in gas industry in recent years. With state-of-the-art contributions by leading experts in the field, this book addressed the technology advances in natural gas industry.

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