PRODUCTION OF SYNGAS BY METHANE AND COAL CO-CONVERSION IN FLUIDIZED BED REACTOR

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Abstract

In this paper we report the concept of coal and natural gas co-conversion operations in a fluidised-bed reactor, which was conceived by the Institute of Coal Chemistry, Chinese Academy of Sciences (ICCCAS). Based on the features of natural gas reforming and steam gasification of coal, it was suspected that the partially reacted coal char might exert a catalytic effect on the partial oxidation of the gas. This may be best effected in a fluidized-bed reactor operating at about 1000? , eliminating the use of the expensive metal catalyst commonly used for gas reforming. The feedstock of methane needs not to be treated specially, which is most important for drainage-methane utilization because its small quantity oxygen content makes it difficult to concentrate methane. This would enable effective utilization of coal-bed methane, drastically reducing the environmental impact of coal mining and enhancing the utilization of available resources. In addition, the integrated coal gasification and gas reforming offers a further advantage that the H_2/CO ratio in the syngas produced can be adjusted between 1 and 3, by varying the ratio of coal/gas in the feedstock, to tailor the syngas to suit downstream processing requirement. The preliminary experiments in a laboratory-scale fluidized-bed reactor has proven the concept to be feasible, achieving over 90% natural gas conversion with favourable quality of the syngas produced (high H_2 and CO content and low CH_4 and CO_2).

Keywords: **Fluidized-bed, Co-conversion, Coal, Natural Gas, Syngas, Adjustable H_2/CO Ratio**

1.0 INTRODUCTION

The production of syngas from fossil fuel is the first step of chemical synthesis. Nowadays the dominant syn-gas production process is coal gasification and methane reforming. From the component point of view, coal contains more carbon and less hydrogen, methane contains more hydrogen and less carbon, as shows in Table 1. Methane has the highest H/C atomic ratio, which is several times higher than coal. So ordinarily speaking, with same reaction agent, the H_2/CO ratio in the syn-gas from methane is much higher than from coal. But when considering downstream synthesis, different desired products require different H_2/CO ratio in the syn-gas, as show in Table

2.

Table 1. H/C atomic ratio of typical feedstock [1]

Material	H/C
Coke	0.13
Charcoal	0.32
Anthracite	0.38
Bituminous coal	0.80
Lignite	0.86
Peat	1.15
Heavy and residual oil	1.41
Wood	1.44
Crude oil	1.71
Lignite fuel oil	2.00
Naphtha (light distillate feedstock)	2.18
Liquefied petroleum gases (LPG)	2.67
Liquefied nature gases (LNG)	3.43
Methane	4.00

Table 2. Required H_2/CO ratio of different desired products

Desired product	Required H_2/CO ratio
Synthetic Oil	1/2~ 2/1
Methanol	2/1
Acetic Acid	1/1
Glycol	3/2
Acetyloxide	1/1
Propionic Acid	4/3
Methacrylic Acid	5/4
Ethanol	2/1
Acetaldehyde	3/2
Acetic Ethene	5/4
Acetic Ether	3/2
Ethene	2/1

The production of syn-gas from methane can be realized by the following 3 reactions:

$CH_4+H_2O=CO+3H_2$? H^0_{298K}=205.9kJ/mol (1)

$$CH_4+CO_2=2CO+2H_2 \qquad ?H^0_{298K}=247.1kJ/mol \qquad (2)$$

$$CH_4+0.5O_2=CO+2H_2 \qquad ?H^0_{298K}= -35.9kJ/mol \qquad (3)$$

The reactions (1), (2), (3) are known as steam reforming, CO_2 reforming and partial oxidation 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 syn-gas production. But this process exists some unavoidable drawbacks. As show in reaction (1), the H_2/CO ratio in the syngas is theoretically 3. It is normally too high compared with what is required by many downstream synthesis processes, such as shown in Table 2. 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 recent years, a lot of attention has been paid on CO_2 reforming because it has the potential advantages of lower theoretical H_2/CO ratio and reuse of CO_2, as show in the above reaction (3). But the most difficult problem of this process is the greater potential of carbon deposition, which rapidly deactivates the catalyst. The R&D of CO_2 reforming is now only at the laboratory stage.

The CH_4 partial oxidation reforming, as show in reaction (2), can theoretically yields syn-gas with a H_2/CO ratio of 2, which is suit for many downstream synthesis. There are 2 ways to reforming CH_4 to syn-gas, 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. 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 CH_4 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.

In this paper we report the concept of coal and natural gas co-conversion operations in a fluidized-bed reactor, which was conceived by the Institute of Coal Chemistry, Chinese Academy of Sciences (ICCCAS). Based on the features of natural gas reforming and steam gasification of coal, it was suspected that the partially reacted coal char might exert a catalytic effect on the partial oxidation of the gas. This may be best effected in a fluidized-bed reactor operating at about 1000? , eliminating the use of the expensive metal catalyst commonly used for gas reforming. Based on this idea, some preliminary tests were carried out in a lab-scale fluidized bed reactor. Some typical results of pure methane-coal and simulated coal mine drainage-methane are introduced, which proved the concept to be feasible.

2.0 EXPERIMENTAL

2.1 APPRATUS

The coal & methane co-conversion experiments were carried out on a ϕ145mm (I.D.) auto-thermal fluidized bed reactor. The height of the reactor is about 1500mm. The system includes coal feeding, gas distributing, reactor, de-dusting, flow measurement and controlling, etc. (see the flow chart in Figure 1).

- Coal Preparation

Raw coal is crushed to the size of 0~1mm diameter with a jaw crusher and then put into the coal hopper after be dried.

- Feeding System

The dried coal is continuously fed by an adjustable screw feeder, then is pushed into the reactor by another screw feeder.

- Reaction gas supply unit

The reaction gases (oxygen, steam & methane) are fed through gas distributor and ash discharging pipe.

- Co-conversion reactor

The coal & methane co-conversion reactor is a fluidized bed. Dry coal reacts with methane, oxygen and steam in the reactor, producing CO, H_2, N_2 CH_4, CO_2 and H_2S. In the reaction rejion, part of oxygen and steam enters the reactor through the inverse-cone-shaped gas distributor to keep the particle fluidizing, and the remaining part and methane enters through the ash discharging pipe into the reactor. Certain amount of N_2 enters reactor also through ash discharging pipe in order to adjust temperature and to prevent ash sintering. The ash is removed through ash discharging pipe to ash hopper system and withdraw out of the reactor.

The produced gas exits from the top of reactor and then enters into cyclone.

- De-dusting, Gas Cooling/Cleaning System

High temperature gas from the top of reactor firstly enters cyclone by which the fine is separated. Then passes through the water scrubbing system. The remaining fly ash in the gas is further captured and in the mean time the gas is cooled. The cleaned gas is withdrawn out of system after measuring and analyzing.

- Operating and Controlling System

The co-conversion system is equipped with necessary measuring instruments (temperature, pressure, flow rate, etc). The reaction temperature is controlled manually by adjusting reacting agent flow rate or coal feed rate.

2.2 COAL TESTED

Two coals were selected in the experiments. Type A was bituminous coal and Type B was anthracite. The analysis data are given in Table 3.

Table. 3 Coal analysis data

Coal type	A	B
Proximate analysis (as received) wt%		
Moisture	2.52	2.06
Ash	10.14	27.82
Volatile	24.43	8.93
Ultimate analysis (as received) wt%		
C	69.94	61.49
H	3.85	2.83
O	12.73	3.45
N	0.36	0.89
S	0.46	1.46
Ash melting point, ?		
DT	1160	1500
ST	1210	>1500
FT	1300	>1500
Heating value, MJ/kg		
Q, net.v	29.09	22.84

2.3 RESULTS

Besides natural gas, there are also other gases that contain rich methane, such as coke oven gas, coal bed methane and coalmine drainage gas. Among these gases, the coalmine drainage gas approximately can be considered as the mixture of air and pure methane. The concentration of oxygen is about 10%. So it’s dangerous to separate methane from coalmine drainage gas with traditional PSA process. Therefore besides coal & methane co-conversion we also investigated the co-conversion of coal & simulated coalmine drainage gas. Table. 4 show the typical results of coal & methane co-conversion and Table. 5 give the typical results of coal & simulated coalmine drainage gas (air + methane) co-conversion in this small-scale fluidized bed reactor. From these tables one can see: 1) Pure CH_4 co-conversions with bituminous coal, the highest conversion reaches more than 90% and the concentration of $CO+H_2$ in the product gas reaches more than 70%; 2) Simulated coalmine drainage gas co-conversions with anthracite, the conversion is close to 80% and the concentration of $CO+H_2$ in the product gas is about 70%; 3) The feedstock rate of CH_4 to coal and Simulated coalmine drainage gas to coal is about $0.3Nm^3/kg$, respectively; 4) The co-conversion results of the bituminous coal is better than the anthracite.

3.0 CONCLUSIONS

The preliminary experiments in the laboratory-scale fluidized-bed reactor have proven the concept to be feasible. Under moderate temperature (about 1000?), it achieves enough methane conversion within once through with favorable quality of the syngas produced (high H_2 and CO content and low CH_4 and CO_2), eliminating the use of the expensive metal catalyst commonly used for gas reforming. The feedstock of methane needs not to be treated specially, which is most important for drainage-methane utilization. This would enable effective utilization of coal-bed methane, drastically reducing the environmental impact of coal mining and enhancing the utilization of available resources. In addition, the integrated coal gasification and gas reforming offers a further advantage that the H_2/CO ratio in the syngas produced can be adjusted by varying the ratio of coal/gas in the feedstock, to tailor the syngas to suit downstream processing requirement.

Table. 4 Typical results of coal & methane co-conversion (A coal)

Experiment No.	1- 1	1- 2	1- 3
Coal feed rate kg/h	1.54	1.58	1.58
CH_4 flow rate Nm^3/h	0.5	0.5	0.5
CH_4/coal Nm^3/kg	0.3	0.3	0.3
N_2 flow rate Nm^3/h	0.30	0.30	0.31
O_2 flow rate Nm^3/h	1.65	1.55	1.45
O_2/coal Nm^3/kg	1.07	0.98	0.92
Steam flow rate kg/h	2.4	2.4	2.4
Steam/coal kg/kg	1.56	1.52	1.52
Temperature °C	1000	1007	1021
Gas producing rate Nm^3/kg	2.82	2.62	2.73
Gas compositions (dry basis, vol%)			
CO_2	20.78	20.74	20.70
H_2	37.43	37.89	39.18
N_2	7.15	7.48	7.42
CO	32.52	32.09	31.73
CH_4	2.12	1.79	0.96
Gas heating value (LHV) $Kcal/Nm^3$	2329	2298	2248
CH_4 conversion ％	78.4	82.5	90.3
Carbon conversion ％	68.05		

4.0 FUTURE WORKS

Early in 1980s, the ICC, CAS started a series research and development on ash agglomerating fluidized bed gasification process. A 1m (I. D.) pilot plant with a capacity of 24 tons of coal per day was set up and put into test by the end of 1990 and a series test of air/steam, enriched air/steam and oxygen/steam blown gasification have been carried out. A wide variety of feedstock including lignite, bituminous coal, sub-bituminous coal, anthracite, char and petroleum coke were successfully gasified. In 2001, a 2.4m (I. D.) industrial demonstration gasifier with a capacity of 100 tons of coal per day was set up and successfully put into application. Possessing such experience in R&D of coal gasification, it is of confidence that the new concept introduced here can be quickly put into industrial application. To accelerate this process, further works will be focused on reaction mechanism research and parameters optimization in order to further improve the conversion of CH_4.

Table. 5 Typical results of coal & drainage gas co-conversion (B coal)

No.	2002- 8- 14			2002- 8- 16		
Coal feed rate kg/h	2.5	2.5	2.5	2.5	2.5	2.5
CH_4 flow rate Nm^3/h	0.4	0.4	0.4	0.4	0.4	0.4
CH_4/coal Nm^3/kg	0.16	0.16	0.16	0.16	0.16	0.16
Air flow rate Nm^3/h	0.4	0.4	0.4	0.4	0.4	0.4
O_2 flow rate Nm^3/h	2.0	2.0	2.0	2.0	2.0	2.0
O_2/coal Nm^3/kg	0.8	0.8	0.8	0.8	0.8	0.8
Steam flow rate kg/h	2.0	2.0	2.0	2.0	2.0	2.0
Steam/coal kg/kg	0.8	0.8	0.8	0.8	0.8	0.8
Temperature °C	968	971	968	966	970	970
Gas producing rate Nm^3/kg	2.22	2.2	2.13	2.2	2.38	2.38
Gas compositions (dry basis, vol%)						
CO_2	22.39	17.89	21.56	20.48	21.16	20.5
H_2	35.49	39.01	36.27	36.78	36.61	37.63
N_2	6.327	6.523	6.59	6.369	5.892	6.352
CO	33.46	33.63	32.96	33.99	33.53	32.48
CH_4	2.337	2.954	2.624	2.38	2.806	3.041
Gas heating value (LHV) $Kcal/Nm^3$	2314	2485	2350	2373	2395	2416
CH_4 conversion %	78.2	70.9	75.7	78	69	68.7
Carbon conversion %	70			71		

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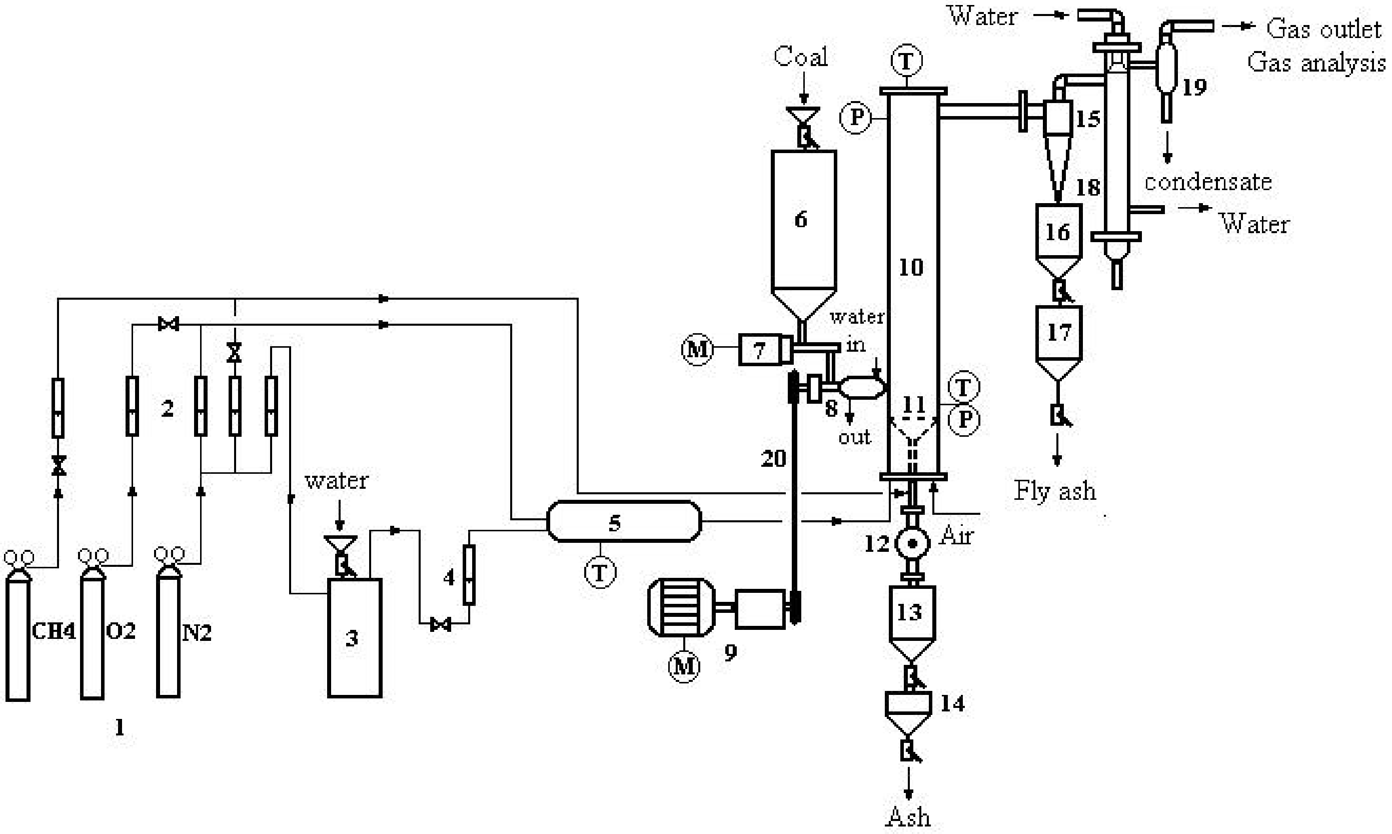

1. gas cylinder 2.gas rotameters 3.distill water tank 4.water rotameter 5. steam evaporator and mixer 6.coal hopper 7. measuring screw feeder 8. pushing feeder 9.motor 10.gasifier 11.gas distributor 12. ash discharger 13. 1st ash hopper 14. 2nd ash hopper 15. cyclone 16.1st fly ash hopper 17. 2nd fly ash hopper 18.gas cleaner/cooler 19.liquid and gas separator 20. driving band

Fig. 1 Flow sheet of bench-scale fluidized bed coal & methane co-conversion system