

Synthesis Gas Production with an Adjustable H₂/CO Ratio through the Coal Gasification Process: Effects of Coal Ranks And Methane Addition

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With the decline of oil reserves and production, the gas-to-liquids (GTL) part of Fischer–Tropsch (F–T) synthesis technology has become increasing important. Synthesis gas (H₂ + CO) with a stoichiometric ratio (H₂/CO) at 2 or ranging from 1 to 2 is generally used in major synthesis-gas-based chemicals production. There are growing interests in the development of an alternative technology, other than the expensive natural-gas-based catalytic process, for cost-effective production of synthesis gas with a flexible hydrogen/carbon monoxide (H₂/CO) ratio. Direct production of synthesis gas using coal as a cheap feedstock is attractive but challenging due to its low H₂/CO ratio of generated synthesis gas. Three typical U.S. coals of different ranks were tested in a 2.5 in. coal gasifier to investigate their gasification reactivity and adjustability on H₂/CO ratio of generated synthesis gas with or without the addition of methane. Tests indicated that lower-rank coals (lignite and sub-bituminous) have higher gasification reactivity than bituminous coals. The coal gasification reactivity is correlated to its synthesis-gas yield and the total percentage of H₂ and CO in the synthesis gas, but not to the H₂/CO ratio. The H₂/CO ratio of coal gasification was found to be correlated to the rank of coals, especially the H/C ratio of coals. Methane addition into the dense phase of the pyrolysis and gasification zone of the cogasification reactor could make the best use of methane in adjusting the H₂/CO ratio of the generated synthesis gas. The maximum methane conversion efficiency, which was likely correlated to its gasification reactivity, could be achieved by 70% on average for all tested coals. The actual catalytic effect of generated coal chars on methane conversion seemed coal-dependent. The coal-gasification process benefits from methane addition and subsequent conversion on the adjustment of the H₂/CO ratio of synthesis gas. The methane conversion process benefits from the use of coal chars due to their catalytic effects. This implies that there were likely synergistic effects on both.

1. Introduction

Gas-to-liquid (GTL) conversion is a well developed and proven technology, which is capable of converting gas to clean liquid hydrocarbons and oxygenates, such as methanol, fuel additives (DME), and many other chemicals. The GTL process of Fischer–Tropsch (F–T) synthesis is one such technology, through which synthesis gas (CO + H₂) can be converted into liquid hydrocarbons.^{1,2} With the decline of oil resources (liquid hydrocarbon mixtures), the GTL of F–T synthesis technology

has become increasingly important and received much attention from both academic and industrial interests.^{3–5} The Sasol Company in South Africa is one such successful example of achieving the F–T synthesis process for the production of liquid fuels and chemicals using synthesis gas.⁶ The synthesis gas can be produced through reforming or the partial oxidation of methane.^{7,8} The methane source can be natural gas or coal-bed methane (CMB). However, economically viable processes for

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synthesis-gas production based on methane only typically produce a gas that is too rich in hydrogen ($H_2/CO = 3$) to meet the required stoichiometric ratio ($H_2/CO = 2$) in synthesis gas. Some other value-added chemicals may require the H_2/CO ratio of the synthesis gas to be varied between 1 and 2.^{9–12} Consequently, a downstream facility to adjust the H_2/CO ratio is generally necessary prior to the chemical synthesis. The synthesis gas manufacturing systems based on natural gas are also capital intensive due to the presence of an expensive catalyst and higher energy consumption. Hence, there is growing interest in the development of an alternative technology for cost-effective production of synthesis gas.

Coal can be a cheap feedstock to produce synthesis gas though the gasification process. However, coal-derived synthesis gas production is generally not the dominant process on an industrial scale when natural gas is available. There is a technical challenge in decreasing the capital investment and the operating cost to direct production of synthesis gas with a flexible H_2/CO ratio using the coal gasification process. The first technical challenge is that coal gasification provides synthesis gas with a H_2/CO ratio close to 1. To adjust the H_2/CO ratio of coal-derived synthesis gas, the water-gas-shift reaction is required after coal gasification. The water-gas-shift reaction is a feasible process, but its lower kinetics requires catalyst promotion, which increases capital and operational costs. Second, the process economics of coal-derived synthesis gas production is largely dependent on the gasification reactivity of coal. Coal reactivity determines the coal-carbon conversion efficiency and the synthesis gas yield and, consequently, the capital cost of a coal gasifier. Thus, coal reactivity and the H_2/CO ratio are two important parameters used to determine the economics of the synthesis gas process. Coal gasification reactivity is likely correlated to coal ranks. According to the definition of coal ranks, there are three main coals of different ranks in the U.S. In order of increasing coal rank, they are the following: lignite, sub-bituminous, and bituminous coal. The Department of Energy (DOE) Energy Information Administration (EIA) estimates that over 50% of the coal reserve base in the United States (U.S.) is bituminous coal, about 30% is sub-bituminous, and 9% is lignite.¹³

Methane could be a H_2 source for synthesis gas production, while coal-bed methane (CBM) seems a good selection as a methane source since it is cheap and available during coal production.¹⁴ In the United States, conservative estimates suggest that more than 700 trillion cubic feet (TCF) of coal-bed methane exists in place, with 100 TCF economically recoverable with existing technology—equivalent to about a 5-year supply at

present rates of use.¹⁵ So far, CBM has accounted for about 7.5% of total natural gas production in the U.S. Coal-bed methane is coproduced in many coal mines, including those of lignite, sub-bituminous coal, and bituminous coal. Among them, the Powder River Basin (PRB) area of the U.S., which is also the top producer of PRB sub-bituminous coal, is one of the newest, most productive areas of CBM. Another major coal-bed methane production area in the U.S. is in the Black Warrior Basin in Alabama, which is close to the geological reserve of Texas lignite.¹⁶ Methane release from coal mining accounts for approximately 10% of methane emissions in the U.S.¹⁷ Utilization of CBM also helps to preserve the nation's environmental quality since methane is a greenhouse gas, with 21 times the global warming potential of carbon dioxide.⁵

Cogasification of coal and methane to produce synthesis gas has been evaluated and developed in recent years.^{18–21} Cao and Wu cogasified coal and methane to produce hydrogen-rich synthesis gas (H_2/CO ratio greater than 1) in a fluidized-bed reactor.^{18,19} Cao focused on the behavior of coal's sulfur release under a hydrogen-rich environment during cogasification. Simultaneously, tests indicated that the achievable H_2/CO ratio of the produced synthesis gas was about 1.5–2 under the air blown condition.¹⁸ Wu achieved higher than 75% methane conversion efficiency in the cogasification process in an oxygen-blown mode. Unfortunately, the adjustability of methane addition on the H_2/CO ratio was not focused.¹⁹ It is possible the partial oxidation or burnout of methane occurred during his test. Other researchers^{20,21} also tested higher methane/coal ratios to achieve the adjustability of the H_2/CO ratio in a fixed bed or moving bed by cogasification technologies. It seemed that the location of methane introduced into the gasifier and coal ranks have major impacts on methane conversion and the H_2/CO ratio of synthesis gas. There are also some investigations on the synergistic interaction between coal gasification and methane conversion under the conventional coal gasification process.^{22,23} This paper focuses on the effects of coal rank and the adjustability of methane addition on the quality of synthesis gas under conditions of conventional coal gasification and cogasification. The reactivity of coals of different ranks (two bituminous coals, one sub-bituminous, and one lignite) was first evaluated in a thermogravimetric (TG) analyzer using water or

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Table 1. Proximate and Ultimate Analyses and Major Oxides of Coal Samples (on a Dry Basis)

sample name	dry basis, by weight												
	moisture (%)	ash (%)	vol. mat (%)	sulfur (%)	btu (kJ/(K g))	carbon (%)	hydrogen (%)	nitrogen (%)	oxygen (%)	chloride (ppm)	mercury (ppm)	fluoride (ppm)	bromide (ppm)
lignite (0.1–0.5 mm)	24.41	22.51	30.21	1.34	18745	46.17	5.76	0.54	23.68	139	0.25	62	nd
sub-bitu (0.35–0.8 mm)	11.47	4.87	40.99	0.38	24316	62.04	5.43	0.74	26.54	200	0.06	98	nd
bit-1 (0.5–0.85 mm)	1.50	11.23	35.34	0.90	29717	69.98	5.24	1.46	11.19	468	0.10	475	nd
bit-2 (0.5–0.85 mm)	2.57	7.02	33.46	0.55	32490	76.56	5.33	1.57	8.97	1637	0.07	204	nd

in percent by weight and after normalization													
	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	CaO	K ₂ O	SO ₃	P ₂ O ₅	BaO	SrO	Fe ₂ O ₃	MnO	TiO ₂
lignite (0.1–0.5 mm)	<0.01	1.33	22.28	52.64	7.44	0.85	8.45	0.05	0.11	0.06	5.39	0.04	1.36
sub-bitu (0.35–0.8 mm)	0.40	3.79	13.10	23.69	23.20	0.27	27.84	0.82	0.44	0.34	4.89	0.02	1.19
bit-1 (0.5–0.85 mm)	<0.01	0.60	31.75	53.06	0.74	1.77	0.88	0.59	0.14	0.25	8.13	0.01	2.08
bit-2 (0.5–0.85 mm)	<0.01	0.85	31.83	50.44	1.71	2.48	1.86	0.22	0.19	0.28	8.09	0.01	2.04

carbon dioxide as gasification agents. The TG results, together with a proximate theoretical analysis, were used to determine the actual operational conditions in the follow-up experiments of gasification and cogasification. The experiments in the 2.5 in. coal gasifier were conducted to determine the actual synthesis gas yield, carbon conversion efficiency, and the H₂/CO ratio of the produced synthesis gas.

2. Methods

2.1. Preparation of Coal Samples. A total of four coal samples of different ranks, including two bituminous coals (bit-1 and bit-2), one sub-bituminous coal, and one lignite were tested in this study. Samples of raw coals were purchased from four coal-fired power plants. Each raw coal sample was first pulverized and sieved into several size categories of coal particles. Generally, low-rank coals need fewer amounts of the gasification agent during their gasification process due to their lower carbon content. This will possibly decrease fluidization velocity and increase the residence time of low-rank coal in the coal gasifier. Thus, coal samples with smaller particle sizes were chosen for testing the two low-rank coals. The particle size of lignite was in the range of 100–500 μm and that of sub-bituminous coal was in a range of 350–800 μm . For two high-rank coals (bit-1 and bit-2), coal samples for testing were slightly larger, in the range of 500–850 μm . Coal samples were dried in an oven, whose temperature was maintained at about 100 °C overnight before testing.

Analysis of coal samples in this study follows ASTM standard methods. The detail description of these ASTM methods is shown in Supporting Information S1. Analysis results of all tested coals in this study are presented in Table 1. All tested coals have high volatile contents, which are above 30% on a dry basis. The moisture content of lignite and sub-bituminous coal are as high as 24% and 10%, respectively. The moisture contents of two bituminous coals are lower at about 2%. Both bituminous coals have a slightly higher ash content (about 8%) than that of sub-bituminous coal (about 4%), but much lower than that of lignite (above 20%). Higher moisture and ash content of lignite results in its lowest heating value among all tested coals in this study, which is 18 745 kJ/(K g) on a dry basis. Sub-bituminous coal has the medium heating value at 24 316 kJ/(K g) on a dry basis, and two bituminous coals have a higher heating value at about 31 000 kJ/(K g) on a dry basis. The ratios of carbon and hydrogen contents in tested coals on a dry basis, in increasing order, are about 0.125 for lignite, 0.088 for sub-bituminous coal, and about 0.07 for two bituminous coals. The major metal oxides in tested coals are shown in the same table. It is indicated that sub-bituminous coal has a relatively high content of CaO and MgO, which is about 25%. The lignite and other two bituminous coals have similar ash constituents, which are about 80% of Al₂O₃ and SiO₂.

2.2. Test Facilities. TGA. Evaluation of pyrolysis and the gasification reactivity of coal chars were carried out in a TA Instruments model 2950 TGA, under an ultrahigh purity (UHP)

nitrogen (N₂) atmosphere or under a CO₂ or H₂O atmosphere. Coal-char samples are derived from the coal pyrolysis process under a nitrogen atmosphere at 900 °C. The concentrations of CO₂ and H₂O in TG tests were 10% and 20%, respectively, which match actual feeding CO₂ and H₂O concentrations in the coal gasification process. Each coal sample of approximately 30–50 mg was placed in a ceramic pan of the 2950 TGA and heated from an ambient temperature at 30 °C/min to a range of about 1000 °C in a nonisothermal mode. The following parameters were measured: time (min), weight (%), and weight loss rate (%/min). The calcium oxalate was used as reference to confirm the correct operation of the TGA. Test results indicated that higher reactivity of pyrolysis and gasification processes were found for both low-rank coals (lignite and PRB) in comparison to those of high-rank coal (bit-1 and bit-2). The detailed description of tests using TG is given in Supporting Information S2.

Fluidized Bed Coal Gasification System and Test Procedure. The fluidized bed coal gasifier system, which was used in this study, has seven major components, as shown in Figure 1. It includes an electrically heated main body of the gasification reactor; two coal hoppers and one coal screw feeder; a steam generator and a gasification agent (air or oxygen, steam) metering and feeding system; an ash discharging piping and two collecting hoppers; a synthesis gas cleanup unit including a cyclone, a high temperature metal filter, and water cooling tube; and a wet scrubber. The inside diameter (i.d.) of the low part of the gasifier is about 2.5 in. and is enlarged to be 4 in. in the upper part of the gasifier, which makes the ash entrainment largely controlled. The total height of the gasifier is 65 in.. There is a corn-shaped gas distributor at its bottom with a percentage of total opening at 1% in order to achieve a good fluidization performance. The gasifier temperatures are monitored by a platinum–rhodium thermocouple, which is sealed into a stainless steel tube in the gasifier. The thermocouple could be movable inside this tube to monitor temperature variation along the height of the gasifier. Temperatures of the gasifier were found to be evenly distributed along the height of the gasifier except the coal feeding area, where the temperature was generally 50 °C lower than those at other parts of the gasifier. The pressure drop between the bottom and top of the gasifier is monitored by a U-shaped water column tube.

The gasification agent streams were preheated and continuously fed into the gasifier unit through the cone-shaped gas distributor. Flow meters were used for controlling flow rate of air or oxygen injection, which were calibrated before tests began. Air supply was obtained from a compressed air line. The steam was generated by a water-injection pump coupled with an oven, which was operated at 300 °C and about 1.03×10^5 Pa. It was monitored by a steam orifice meter together with the pressure drop meter and controlled by a needle valve. The nitrogen stream from a N₂ cylinder was used for system startup and shutdown. The coal gasification system in this study was operated at two modes, the air-blown mode and the oxygen-blown mode. Under the oxygen-blown mode, the 100% pure oxygen stream was supplied by an oxygen cylinder. A trace of nitrogen stream (in 20% of N₂/O₂), which is inert in the

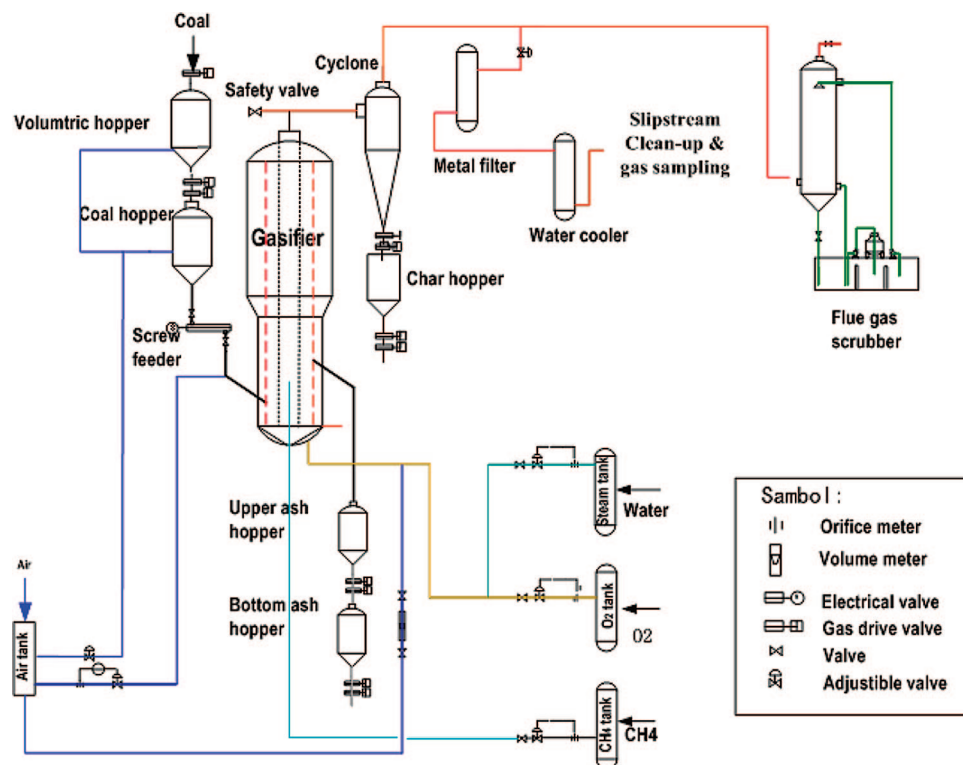


Figure 1. Coal gasifier test system (2.5 in.).

gasification process and also accurately detected, was used in the oxygen-blown mode to calculate the dry synthesis gas yield. The concentration of nitrogen tracer in the produced synthesis gas was only about 3% so that it did not impact the coal gasification process under the oxygen-blown mode. The fluidized bed gasifier was generally operated at a velocity of $3\text{--}10U_{mf}$ (the minimum fluidization velocity), depending on feeding rates of air (or oxygen) and steam and operation temperature. Coal feeding is controlled by a volumetric screw feeder, which is connected closely to the bottom of the low portion of the gasifier. There were two outlets for coal char collection. Except for a common outlet for fine-char-laden synthesis gas, there was a special port for char overflow on the top of the dense phase of the fluidized bed. During tests, coal is continuously fed in and coal char is continuously discharged out to maintain the height of the dense phase of the bed material in the gasifier. It is used to control the residence time of the coal char in the gasifier. The adjustability of the residence time of coal char in the gasifier could be achieved by changing the coal-feeding rate, since the amount of coal char inside the gasifier remained constant during the test. The produced synthesis gas with the char residue at the top outlet of the gasifier is collected by combining the cyclone and a high-temperature porous metal filter. The cleaned and cooled synthesis gas is collected by a sampling bag and is delivered to gas analyzers.

At the beginning of the test, the coal char from previous test runs was used as bed material to be fed into the gasifier, and then, the fluidized bed gasifier was electrically heated to the desired temperature under the protection of the nitrogen. When the temperatures began to approach the desired point, air or oxygen and steam, together with coal particles, were fed into the gasifier. Fed air or oxygen, steam, and coal were adjusted to stabilize temperature and pressure drop across the gasifier. It generally takes several hours to finish the aforementioned stabilization steps. Upon the stabilization of temperature and the pressure drop of the gasifier, the gas sampling was started every 10 min. After finishing the test, nitrogen was again fed into the bed to replace the gasification agents. The char produced was discharged from the bed and collected when the bed temperature was below $150\text{ }^{\circ}\text{C}$. For every testing condition, one test was repeated. If no abnormal results were found, the average data was accepted for certain testing conditions. Collected

coal char samples were analyzed three times to obtain the average analysis results. The synthesis gas yield on a dry basis was calculated based on a nitrogen balance of the system, which is indicated in eq 1.1 for the air-blown mode and eq 1.2 for the oxygen-blown mode. The carbon conversion efficiency was calculated based on the carbon balance of the system, which is indicated in eq 2.

$$\text{the synthesis gas yield (N m}^3\text{/kg)} = \frac{\text{the air/coal ratio} \times 79\%}{\text{N}_2 \text{ concentration in synthesis gas (\%)}} \quad (1.1)$$

$$\text{the synthesis gas yield (N m}^3\text{/kg)} = \frac{\text{the oxygen/coal ratio} \times \text{nitrogen/oxygen ratio}}{\text{N}_2 \text{ concentration in synthesis gas (\%)}} \quad (1.2)$$

$$\text{the carbon conversion efficiency (\%)} = \frac{\text{the total carbon in coal} - \text{the total carbon in char}}{\text{the total carbon in coal}} \quad (2)$$

For the cogasification tests with selected coals and methane, an additional methane injection pipe was made to deliver methane to the gasifier for safety considerations of possible explosions after directly mixing with air or oxygen. Its height could be adjusted to accommodate the availability of methane at different zones in the gasifier, such as the dense phase oxidation zone, dense phase pyrolysis and gasification zone, and diluted phase gasification zone. Adjustment of the methane feeding location was performed to simulate its impacts on variations of methane conversion efficiency and the H_2/CO ratio of the produced synthesis gas. A detailed description and figure concerning methane injection locations were included in Supporting Information S3. Simulated methane of 100% purity is supplied by a methane-cylinder tank. Air or oxygen, after mixing with steam, was fed into the gasifier through their original locations as tests in coal gasification. During each test, the air/coal ratio, steam/coal ratio, and CH_4/coal ratio were controlled, and synthesis gas samples were collected and delivered to the gas chromatograph (GC) for analysis by performing three runs. The dry synthesis-gas yield and the conversion efficiency of coal carbon were calculated based on eqs 1.1, 1.2, and 2 mentioned above. The CH_4 conversion efficiency is approximately based on the following equation, as indicated in eq 3.

the CH₄ conversion efficiency (%) =

$$(\text{CH}_{4\text{injection}} - \text{CH}_{4\text{in_synthesis_gas}}) / \text{CH}_{4\text{injection}} \quad (3)$$

Where, CH_{4injection} represents the total flow rate of methane injection in the cogasifier, and CH_{4in_synthesis_gas} is the total flow rate of methane in the synthesis gas.

2.3. Synthesis Gas Sampling and Measurement. Dry, clean synthesis gas from gasification or cogasification tests was sampled by a gas sampling bag every 10 min (generally three gas samples for each test condition) after a stable condition was reached. The synthesis gas samples were analyzed by a gas chromatography (Shimadzu Model GC-8A) with a thermal conductivity detector (TCD) and an injector connected to a Carboxen-1000 column which was loaded with a SUPLECO in 60 to 80 meshes. The temperature of the chromatography column was 70 °C, and the temperature of the TCD was 110 °C. Argon was used as carrier gas at a flow rate of 40 mL/min. Chromatography calibration was done with standard gas mixtures of H₂, CO, O₂, N₂, CO₂, and CH₄. The same GC was also used for the analysis of light hydrocarbon constituents (mainly C₂–C₄) in the synthesis gas through a Porapak R column using argon as a carrier gas. The total percentage of these light hydrocarbon constituents in the dry synthesis gas was found to be generally lower than 1% and, thus, could be ignored.

3. Results and Discussion

3.1. Coal Gasification Tests in a 2.5 in. Coal Gasifier.

Actual operational conditions and test results in a 2.5 in. coal gasifier are shown in Table 2(a) through Table 2(b) for four tested coals. Operation conditions (air/coal ratio or oxygen/coal ratio, and H₂O/coal ratio) for two coals of low ranks are similar to those theoretical values, which are included in Supporting Information S4 in Table S1. Considering coal reactivity and lower actual carbon conversion efficiency of two bituminous coals, the H₂O/coal ratios were set generally higher than its theoretical values, which are also indicated in Supporting Information S4 in Table S1. The higher H₂O partial pressure could help with the reactivity promotion in the char steam gasification process.

Table 2 (bit-1 and bit-2) shows the variation of typical test results with their operational conditions during tests with bit-1 and bit-2 in the 2.5 in. coal gasifier. Test results with normal gasification operations of bit-1 coal are shown in the same table as test nos. 1–3 under the air-blown mode. Under the air-blown mode, the synthesis gas yield in the dry basis varied between 2.99 and 3.05 N m³/kg, which were dependent on their carbon conversion efficiency between 68.3% and 73.9%. The total percentage of H₂ and CO on a dry basis varied between about 42% and 45%. The synthesis-gas yield and the total percentage of H₂ and CO is lower than their theoretical values, which are about 3.57 N m³/kg and 55% (see Supporting Information Table S1). This is due to a lower carbon conversion efficiency at about 70% in test runs with bit-1 than that of 100% during the theoretical calculation. However, the H₂/CO ratios of synthesis gas by bit-1, which varied between about 0.9 and 1.4, were close to their theoretical value at about 1.05 (see Supporting Information Table S1). Test results with bit-1 under the oxygen-blown mode are also shown in the Table 2 (bit-1 and bit-2) as test nos. 4 and 5. Under the oxygen-blown mode, the synthesis gas yield on a dry basis varied between 1.9 and 1.95 N m³/kg, which was close to but lower than its theoretical value of about 2.34 N m³/kg due to its lower carbon conversion efficiency at about 80%. The average total percentage of H₂ and CO in the dry basis was about 75%, which was also low at about 88% compared with its theoretical value due to similar reasoning of lower carbon conversion efficiency. However, the H₂/CO ratio varied between 0.94 to 1.03, which was close to its theoretical

value of about 1.05. Higher CO₂ concentrations were found in the actual coal gasification process by bit-1 than the theoretical values under both the air-blown mode and the oxygen-blown mode. It is apparent that some CO was burned out during the actual gasification process since CO was decreased in the synthesis gas and the CO₂ concentration was increased in the synthesis gas. Hydrogen may experience burnout since H₂ can burn under an oxygen atmosphere at lower initial temperatures and have a lower active energy of burnout than CO.²⁵ This partial burnout of generated synthesis gas (H₂ and CO) was not considered as part of the theoretical calculation. The oxygen consumption by partial burnout of synthesis gas must decrease the consumption of carbon by reacting with oxygen and, thus, decrease carbon conversion efficiency. This was confirmed by comparing the theoretical and actual carbon conversion efficiency. Following up aforementioned reasoning, the H₂/CO ratio should be lower than expected based on theoretical calculations. However, the H₂/CO ratio in the actual gasification process by bit-1 is slightly higher or close to its theoretical value at about 1. This may imply some processes other than the char gasification process (e.g., coal pyrolysis) may generate more H₂ than CO. This was not considered in the theoretical calculation. It seemed that the burnout of H₂ and CO was not affected by operation modes, either under the air-blown mode or the oxygen-blown mode. Another mechanism was possibly relative to the water-gas-shift reaction, where the H₂ could be generated by consumption of CO in the synthesis gas and the simultaneous generation of CO₂.

Test results of bit-2 are also shown in Table 2 (bit-1 and bit-2) as test nos. 1–3 under operation of the air-blown mode and with tests nos. 4 and 5 being of the oxygen-blown mode. Under the air-blown mode, the synthesis gas yield on a dry basis improved and varied between 3.24 and 3.58 N m³/kg due to the improvement of carbon conversion efficiency of bit-2. The total percentage of H₂ and CO on a dry basis was also slightly improved at about 48%. The reason for the increase of synthesis gas yield and the total percentage of H₂ and CO was due to the higher gasification reactivity of bit-2 over that of bit-1, as indicated in aforementioned reactivity evaluation tests by TG (see Supporting Information S2). The H₂/CO ratio was slightly above 1 due to similar reasons as those for bit-1. Under the oxygen-blown mode, the synthesis gas yield on a dry basis varied between 2.11 and 2.25 N m³/kg, which was higher than that of bit-1 for the same reason. The total percentage of H₂ and CO on a dry basis improved by about 82% on average, which was better than that of gasification with bit-1 under the same conditions. The H₂/CO ratio under the oxygen-blown mode was similar to that under the air-blown mode. Both were close to 1. The improved carbon conversion efficiency for bit-2, due to enhanced char gasification reactivity, was responsible for increases of dry synthesis gas yield, carbon conversion efficiency, and the total percentage of H₂ and CO. However, it seemed the enhancement of char gasification reactivity did not help with the increase of the H₂/CO ratio by comparing these two coals of the same rank.

Test results with two low-rank coals in the 2.5 in. coal gasifier are shown in Table 2 (lignite and sub-bit). The two low-rank tested coals showed good gasification reactivity under both air-blown and oxygen-blown modes because above 90% carbon conversion efficiency could be achieved for both of these two types of coals in tests with a 2.5 in. coal gasifier. The synthesis

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Table 2. Operational Parameters and Test Results of Synthesis Gas Produced in a Coal Gasifier

Bit-1 and Bit-2													
test no.	1	2	3	4	5	1	2	3	5	6			
operation mode	air-blown			bit-1		oxygen-blown		operational conditions		air-blown		bit-2	
coal													
air or oxygen/coal ratio, N m ³ /kg	1.51	1.65	1.57	O ₂ : 0.305 (O ₂ + N ₂ : 0.365)		O ₂ : 0.315 (O ₂ + N ₂ : 0.367)		1.65	1.65	1.73	O ₂ : 0.312 (O ₂ + N ₂ : 0.382)		O ₂ : 0.315 (O ₂ + N ₂ : 0.387)
steam/coal ratio, kg/kg	0.8	0.8	0.8	0.8		0.8		0.8	0.8	0.8	0.8		0.8
particle size, mm	0.5–0.85	0.5–0.85	0.5–0.85	0.5–0.85		0.5–0.85		0.5–0.85	0.5–0.85	0.5–0.85	0.5–0.85		0.5–0.85
bed temp, °C	985	989	980	1035		1043		970	990	980	1035		1035
pressure, bar	1	1	1	1		1		1	1	1	1		1
synthesis gas compositions (%)													
H ₂	23.83	20.77	26.03	38.16		35.48		25.41	25.23	26.23	42.36		43.02
CO	20.94	21.52	18.05	37.03		37.81		23.39	22.68	23.11	39.3		40.66
CH ₄	2.87	1.98	1.68	1.32		1.11		1.37	1.01	1.3	1.07		0.87
CO ₂	12.46	12.75	13.6	20.42		22.86		10.63	10.9	11.21	14.16		12.04
N ₂	39.9	42.98	40.64	3.07		2.74		39.2	40.18	38.15	3.11		3.41
O ₂	0	0	0	0		0		0	0	0	0		0
synthesis gas index													
dry synthesis gas production, N m ³ /kg coal	2.99	3.03	3.05	1.95		1.90		3.33	3.24	3.58	2.25		2.11
carbon conversion efficiency, %	68.3	71.3	73.9	78.2		80.4		78.9	81.7	82.6	84.5		83.7
(CO + H ₂), %	44.77	42.29	44.08	75.19		73.29		48.80	47.91	49.34	81.66		83.68
H ₂ /CO	1.14	0.97	1.44	1.03		0.94		1.09	1.11	1.14	1.08		1.06

Lignite and Sub-bituminous													
test no.	1	2	3	4	5	6	7	1	2	3	4	5	
operation mode	air-blown			lignite		oxygen-blown		operational parameters		air-blown		sub-bit	
coal													
air (oxygen)/coal ratio, N m ³ /kg	0.796	0.797	0.905	1.1	O ₂ : 0.28 (O ₂ + N ₂ : 0.34)		O ₂ : 0.29 (O ₂ + N ₂ : 0.34)		1.33	1.33	1.33	O ₂ : 0.35 (O ₂ + N ₂ : 0.40)	O ₂ : 0.39 (O ₂ + N ₂ : 0.345)
steam/coal ratio, kg/kg	0.421	0.418	0.45	0.466	0.412		0.483		0.519	0.5	0.5	0.58	0.5
particle size, mm	0.1–0.5	0.1–0.5	0.1–0.5	0.1–0.5	0.1–0.5		0.1–0.5		0.1–0.5	0.35–0.8	0.35–0.8	0.35–0.8	0.35–0.8
bed temp, °C	900	900	910	950	900		950		950	940	928	950	940
pressure, bar	1	1	1	1	1		1		1	1	1	1	1
synthesis gas compositions (%)													
H ₂	32.52	33.25	32.18	27.19	45.6		40.89		42.54	32.88	29.26	45	46.74
CO	23.06	24.7	21.56	19.71	31.12		34.27		32.82	27.75	30.74	37.72	40.21
CH ₄	2.8	2.72	2.67	1.41	2.2		2.36		1.78	2.89	1.9	2.14	1.79
CO ₂	8.73	8.05	9.04	10.53	17.29		19.58		18.76	5.72	3.5	12.7	9.08
N ₂	32.89	31.28	34.55	41.16	3.79		2.9		4.1	30.76	34.6	2.45	2.17
O ₂	0	0	0	0	0		0		0	0	0	0	0
synthesis gas index													
dry synthesis gas production, N m ³ /kg coal	1.91	2.01	2.07	2.11	1.58		1.72		1.37	3.42	3.04	2.04	2.07
carbon conversion efficiency, %	92.6	91.7	92.3	90.5	95.1		98.2		98.6	91.2	85.7	95.2	94.5
(CO + H ₂), %	55.58	57.95	53.74	46.90	76.72		75.16		75.36	60.63	60.00	82.72	86.95
H ₂ /CO	1.41	1.35	1.49	1.38	1.47		1.19		1.30	1.18	0.95	1.19	1.16

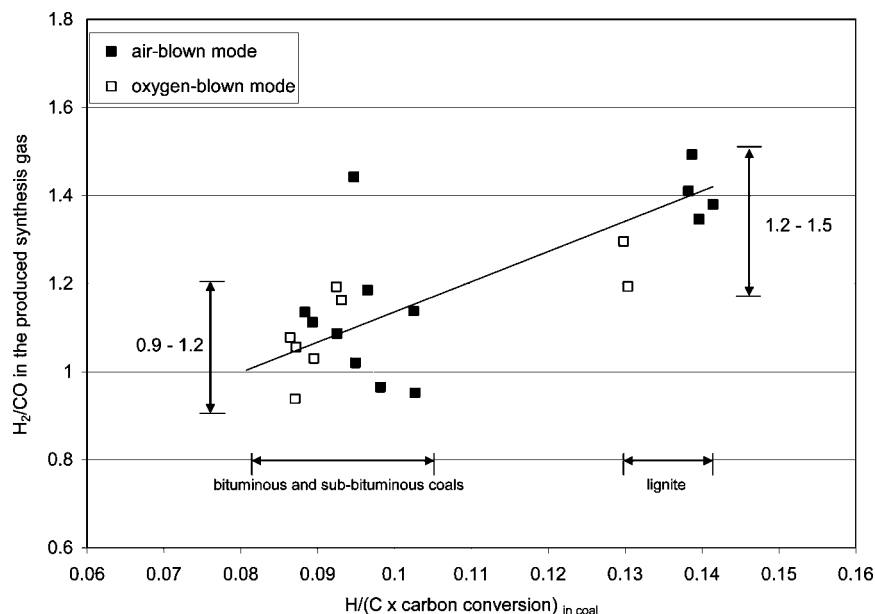


Figure 2. Correlation between H/C ratio in coal and H_2/CO ratio in the produced synthesis gas.

gas quality, in view of the synthesis gas yield and the total percentage of H_2 and CO, perfectly matched the theoretical calculation predictions (see Supporting Information S4 in Table S1) compared to those of the two high-rank bituminous coals, except for the H_2/CO ratio. For sub-bituminous, the synthesis gas yields were about $3.4 \text{ N m}^3/\text{kg}$ under the air-blown mode and $2.05 \text{ N m}^3/\text{kg}$ under the oxygen-blown mode, respectively. The total percentage of H_2 and CO was about 60% under the air-blown mode and 84% under the oxygen-blown mode. The H_2/CO ratios of synthesis gas by sub-bituminous coal were close to their theoretical predictions, which were about 1 for both operation modes by air or oxygen. Several basic parameters of synthesis gas by sub-bituminous coals were close to those of two bituminous coals due to its actual carbon consumption per kilogram of coal in the gasification process being close to those of the two bituminous coals.

For tests with lignite, the synthesis gas yields were about $1.95 \text{ N m}^3/\text{kg}$ in the air-blown mode and $1.65 \text{ N m}^3/\text{kg}$ in the oxygen-blown mode, respectively. The lower synthesis gas yield was found for lignite compared to the bituminous coals and sub-bituminous coals due to its higher moisture and ash content, which resulted in its lower carbon content. However, it seemed that lower carbon content in lignite did not make the total percentage of H_2 and CO of synthesis gas decrease. The H_2/CO ratio of synthesis gas by lignite was found to increase to about 1.4 during gasification tests with lignite under the air-blown mode and also to about 1.3 on average under the oxygen-blown mode. Gasification reactivity seemed not to be responsible for the higher H_2/CO ratio of synthesis gas by lignite since sub-bituminous coal had similarly higher gasification reactivity, but lower H_2/CO ratio which was the same as that of bituminous coals with lower gasification reactivity. It seemed the H_2/CO ratio of synthesis gases was strongly correlated with the H/C ratio in tested coals, as indicated in Figure 2. In Figure 2, the corrected carbon content in coal by the carbon conversion efficiency ($C_{\text{in, coal}} \times \text{carbon conversion efficiency}$) was used to replace the actual carbon content in coal to calculate the H/C ratio. The higher corrected H/C ratio was in coal, synthesis gas with the higher H_2/CO ratio could be obtained through gasification of such coal. The bit-1, bit-2, and sub-bituminous coal in this study have a similar lower corrected H/C ratio, which varied between 0.085 and 0.105. They could generate the synthesis

gas with a similarly lower H_2/CO ratio although their gasification reactivity was quite different. The corrected H/C ratio of lignite was as high as 0.135. Consequently, the H_2/CO ratio of synthesis gas was as high as 1.4 on an average when comparing the H_2/CO ratio of synthesis gas from gasification of bituminous and sub-bituminous coals.

3.2. Effects of the Methane Injection Location on Methane Conversion Efficiency and the H_2/CO Ratio of Synthesis Gas. The variations of the CH_4 conversion efficiency and the H_2/CO ratio of the produced synthesis gas, by moving the methane injection pipe into different locations in the cogasifier by three tested coals, are shown in the Figure 3. The air/coal ratios were controlled in the same way as those in the conventional gasification process for three tested coals. However, more steam was introduced in the cogasification process in comparison to their corresponding coal gasification process, in order to promote the conversion of methane in the cogasifier. Considering the differences in the synthesis gas yield and H_2/CO ratio in gasification of the different ranks of coals, the injection rates of methane into the gasification process of these coals are varied. The methane injection rate is controlled to be $0.3 \text{ N m}^3/\text{kg}$ of coal for two bituminous coals, $0.25 \text{ N m}^3/\text{kg}$ coal for sub-bituminous coal, and $0.15 \text{ N m}^3/\text{kg}$ coal for lignite.

As indicated in Figure 3, three tested coals of different ranks presented similar trends in methane conversion efficiency and in the H_2/CO ratio by moving methane injection locations in the cogasifier. The CH_4 conversion efficiency could reach above 90% for all three tested coals when the methane injection pipe was in location no. 1, which is the dense phase oxidation zone. However, the corresponding H_2/CO ratios in produced-synthesis gases were lower for all tested coals, which were coal-dependent and varied between 1.2 and 1.6. The CH_4 conversion efficiency was quickly decreased by switching the methane injection pipe from location no. 1 to location no. 2, where the dense phase pyrolysis and gasification zone was. But, the H_2/CO ratios were ideal and sharply increased to close to 2 for all three tested coals. There was another quick decrease of the CH_4 conversion efficiency when the methane injection pipe was switched from location no. 2 to location no. 3, where the border of the dense phase and the diluted phase of the cogasifier was. The H_2/CO ratio was decreased consequently due to the decrease of the

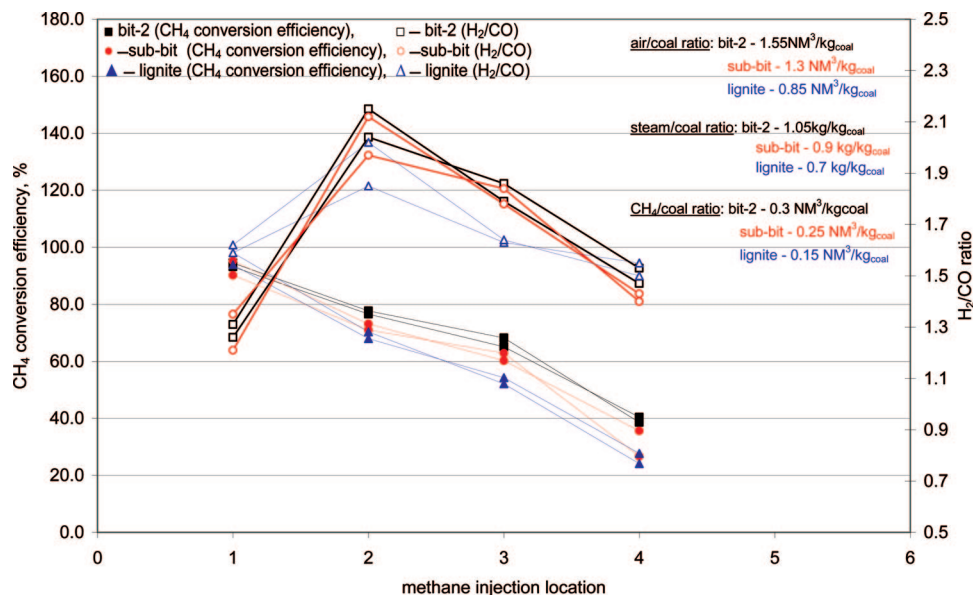


Figure 3. Variation of parameters of produced synthesis gas versus methane injection locations.

CH₄ conversion efficiency. Both the CH₄ conversion efficiencies and the H₂/CO ratios experienced a continuous decrease after the methane injection pipe was finally moved further up to location no. 4, which was deep into the diluted phase.

The higher methane conversion efficiency and lower H₂/CO ratio of the synthesis gas produced when the methane injection pipe was in the dense phase oxidation zone, might be attributed to the quick burnout of methane with available oxygen in this zone. In this case, the majority of injected methane was consumed by the reaction between the methane and supplied oxygen. Thus, very little methane could further react with H₂O and CO₂ to generate H₂ and CO. Moving the methane injection pipe into the dense phase pyrolysis and gasification zone could prevent the methane from coming in contact with the oxygen to be burned out by the oxygen. This is due to the oxygen being quickly consumed by coal char in the dense phase oxidation zone of the cogasifier. In this case, the maximum residence time of methane and the strong mixing between methane and coal char in the cogasifier could ensure the highest methane conversion efficiency and H₂/CO ratio. This was also confirmed by the next two steps to move the methane injection location up and into the diluted phase zone of the cogasifier. Injecting methane at location no. 3 decreases the methane conversion efficiency and H₂/CO ratio of synthesis gas due to the decreases of methane residence time in the cogasifier and simultaneous loss of more intensive mixing between methane and coal char in the diluted phase of the cogasifier. Continuously moving the methane injection pipe farther into the diluted phase caused decreases of methane conversion efficiency and the H₂/CO ratio of synthesis gas.

On the basis of this study, one would predict that addition of methane at suitable conditions inside the cogasifier could increase the H₂/CO ratio of produced synthesis gas, compared to the H₂/CO ratios of produced synthesis gas in the conventional coal gasification process by the same coals. This outcome must be due to the H₂/CO ratio by conversion reactions of methane in the cogasifier being higher than 1. This might result from different properties of ashes or coal chars generated during the cogasification process by the tested coals. A higher ash content and lower char content (higher carbon conversion efficiency) is available in cogasification by lignite. Correspondingly, the methane conversion efficiency during the cogasification of methane and lignite is lower than those of other tested coals.

This may indicate that the active site in methane reactions in the cogasification of lignite and methane is most likely correlated to lignite char, rather than its ash. Similar reasoning could explain why there is a lower CH₄ conversion efficiency during tests with one low-reactivity bituminous coal (bit-1) than that with one high-reactivity bituminous coal (bit-2). It seemed that coal char was the main medium to promote methane conversion reactions in the cogasifier. Trying to minimize the additional amount of methane inside the cogasifier, the methane injection pipe was fixed at location no. 2 in the follow-up tests, where the CH₄ conversion efficiency and adjustable capability of the H₂/CO ratio of synthesis gas could be maximized.

3.3. Cogasification Tests of Coal and Methane in a 2.5 in. Cogasifier. For the two bituminous coals and two low-rank coals tested, the synthesis gases with the expected H₂/CO ratios at about 2 could be produced by addition of the minimum amount of methane into the pyrolysis and gasification zone of the 2.5 in. cogasification demonstration unit under both air-blown and oxygen-blown operation modes. Test results of cogasification of methane and bit-1 or bit-2 are shown in Table 3 (bit-1 and bit-2) and those of sub-bituminous coal and lignite are in Table 3 (lignite and sub-bit).

For bit-1 under the air-blown mode, addition of methane into the cogasifier by a minimum ratio at about 0.3 N m³/kg could make the H₂/CO ratio of synthesis gas vary between 1.98 and 2.14 if the feeding ratios of air/coal and steam/coal were similar to those used in the coal gasification tests. At this minimum addition ratio of methane, the dry synthesis gas yield increased to about 3.4 N m³/kg coal in comparison to that without methane addition in the gasification process by bit-1. The total percentage of H₂ and CO was about 47% in the cogasification process, compared to 44% in the coal gasification process at similar conditions. The methane concentration in synthesis gas could be controlled at about 2.5%, which was similar to methane concentration of synthesis gas in the gasification process of the same coal. The methane conversion efficiency was slightly lower at about 70% under the air-blown mode. Under the oxygen-blown mode with similar feeding conditions of oxygen, steam, and coal with those in the coal gasification process, the methane conversion efficiency could be increased to about 80% with the addition at a minimum ratio of methane by 0.25 N m³/kg in the cogasifier. The methane content in the produced synthesis gas

Table 3. Operational Parameters and Test Results of Synthesis Gas in the Cogasification Process of Coal and Methane

Bit-1 and Bit-2										
test no.	1	2	3	4	5	1	2	3	4	
operation mode	air-blown				oxygen-blown		air-blown		oxygen-blown	
coal	bit-1				bit-2		bit-2			
operation parameters										
air or oxygen/coal ratio, N m³/kg	1.55	1.55	1.55	O₂: 0.326 (O₂ + N₂: 0.42)	O₂: 0.315 (O₂ + N₂: 0.43)	1.55	1.55	O₂: 0.315 (O₂ + N₂: 0.42)	O₂: 0.315 (O₂ + N₂: 0.41)	
steam/coal ratio, kg/kg	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05	
CH₄/coal ratio, N m³/kg	0.3	0.3	0.3	0.25	0.25	0.3	0.3	0.25	0.25	
bed temp, °C	983	995	974	1045	1040	993	998	1027	1043	
pressure, bar	1	1	1	1	1	1	1	1	1	
syngas compositions (%)										
H₂	32.79	31.57	30.7	50.07	49.85	32.59	36.7	50.21	51.91	
CO	15.3	15.98	14.91	25.22	23.82	16.48	17.1	24.76	25.39	
CH₄	2.52	2.73	2.39	1.96	1.96	2.03	1.88	1.98	1.69	
CO₂	14.14	12.97	14.97	18.87	19.91	13.67	11.58	19.21	17.54	
N₂	35.25	36.75	37.03	3.88	4.46	35.23	32.74	3.84	3.47	
O₂	0	0	0	0	0	0	0			
syngas index										
dry synthesis gas production, N m³/kg coal	3.47	3.33	3.31	2.42	2.58	3.49	3.74	2.73	2.74	
conversion efficiency of coal carbon, %	68.7	65.2	61.1	69.2	68.5	78.2	77.9	82.9	82.9	
CH₄ conversion efficiency, %	70.8	69.7	73.7	81.0	79.8	77.7	76.6	78.3	81.5	
(CO + H₂), %	48.09	47.55	45.61	75.29	73.67	49.07	53.8	74.97	77.3	
H₂/CO	2.14	1.98	2.06	1.99	2.09	1.98	2.15	2.03	2.04	

Lignite and Sub-bit										
test no.	1	2	3	4	1	2	3	4	5	
operatio mode	air-blown				oxygen-blown		air-blown		oxygen-blown	
coal	lignite				sub-bit		sub-bit			
operation parameters										
air or oxygen/coal ratio, N m³/kg	0.85	0.85	O₂: 0.28 (O₂ + N₂: 0.34)	O₂: 0.28 (O₂ + N₂: 0.34)	1.3	1.3	1.3	O₂: 0.35 (O₂ + N₂: 0.42)	O₂: 0.35 (O₂ + N₂: 0.42)	
steam/coal ratio, kg/kg	0.7	0.7	0.7	0.7	0.9	0.9	0.9	0.9	0.9	
CH₄/coal ratio, N m³/kg	0.15	0.15	0.15	0.15	0.25	0.25	0.25	0.25	0.25	
bed temp, °C	950	947	996	1026	970	985	990	1050	1038	
pressure, bar	1	1	1	1	1	1	1	1	1	
syngas compositions (%)										
H₂	35.95	36.9	49.23	48.65	41.2	39.34	39.43	52.75	54.27	
CO	19.42	18.26	25.24	25.81	19.42	19.99	20.04	24.17	26.82	
CH₄	2.21	1.99	2.15	2.39	1.87	1.97	1.86	2.04	2.39	
CO₂	11.51	12.84	19.88	19.35	8.95	10.77	10.46	18.33	13.59	
N₂	30.91	30.01	3.5	3.8	28.56	27.93	28.21	2.71	2.93	
O₂	0	0	0	0	0	0	0	0	0	
syngas index										
dry synthesis gas production, N m³/kg coal	2.17	2.24	1.71	1.58	3.60	3.68	3.64	2.58	2.39	
conversion efficiency of coal carbon, %	93.1	92.8	94.1	94.7	93.7	91.9	95.6	96.2	93.6	
CH₄ conversion efficiency, %	67.99	70.31	75.43	74.84	73.10	71.02	72.91	78.92	77.16	
(CO + H₂), %	55.37	55.16	74.47	74.46	60.62	59.33	59.47	76.92	81.09	
H₂/CO	1.85	2.02	1.95	1.88	2.12	1.97	1.97	2.18	2.02	

was still lower at about 2%. The dry synthesis gas yield was increased to about 2.5 N m³/kg, and the total percentage of H₂ and CO was about 75% compared to those in the coal gasification process. As expected, the H₂/CO ratio could reach to about 2.

Similar operation conditions to those of bit-1 were used to conduct cogasification tests using bit-2. The expected H₂/CO ratios (about 2) could be achieved by minimum methane addition at 0.3 N m³/kg under the air-blown mode and by the minimum methane addition at 0.25 N m³/kg under the oxygen-blown

mode. Due to the higher gasification reactivity of bit-2 than that of bit-1, the carbon conversion efficiency of the cogasification process by bit-2 was increased to about 78%, compared to that of bit-1 at about 65%. The direct consequence of improved carbon conversion efficiency was to increase the dry synthesis gas yield during the cogasification process by bit-2, which was about 3.6 N m³/kg coal. However, the increase of carbon conversion did not impact the total percentage of H₂ and CO in the produced synthesis gas by bit-2. Under the oxygen-blown mode, the carbon conversion efficiency and

methane conversion efficiency were even higher than those under the air-blown mode. This might result from the fact that there is higher operational temperature under the oxygen-blown mode to promote conversion of coal carbon and methane than that under the air-blown mode. O₂-blown conditions also mean that there is a higher combustion rate and higher heat release rate without the dilution effect of N₂. Thus, higher kinetics of cogasification could be expected under the oxygen-blown mode than that under the air-blown mode due to the occurrence of higher temperatures under the oxygen-blown operational mode. In comparison to bit-1, the higher gasification reactivity of bit-2 possibly resulted in more activated char, which simultaneously catalyzed the methane reforming and partial oxidation process in cogasification.

For the two low-rank coals, the expected H₂/CO ratio (about 2) could also be achieved by adding methane in the 2.5 in. cogasifier. The feeding ratios of air/coal and steam/coal are the same as those in the gasification process using the same low-rank coals. A ratio of sub-bituminous coal and methane was controlled at 0.25 N m³/kg coal, and a ratio of lignite and methane was controlled even lower at 0.15 N m³/kg. Operational temperatures were about 950 °C for the air-blown mode and slightly higher at 1050 °C under the oxygen-blown mode for both low-rank coals. Both coals of low ranks were higher in their gasification reactivity. Consequently, the carbon conversion efficiencies of these two low-rank coals were above 90% under both the air-blown mode and the oxygen-blown mode, which were similar to those in the gasification of the same coals.

For sub-bituminous coal, the dry synthesis gas yield and the total percentage of H₂ and CO were about 3.6 N m³/kg coal and about 60% under the air-blown mode, respectively. Under the oxygen-blown mode, the dry synthesis gas yield and the total percentage of H₂ and CO were about 2.5 N m³/kg coal and about 78%, respectively. The methane conversion efficiencies of sub-bituminous coal were 72% under the air-blown mode and 78% under the oxygen-blown mode. Higher methane conversion efficiency of cogasification of sub-bituminous coal and methane was due to a similar reason as that of bit-2, which was most likely relative to its catalytic characterization of activated char produced. For lignite, a lower methane addition ratio was needed to achieve the H₂/CO ratio in the synthesis gas during cogasification of lignite and methane. The carbon conversion efficiency of lignite was higher (over 90%), which was the same as that of sub-bituminous coal. However, methane conversion efficiency seems lower in the air-blown mode at about 68% and increased to about 75% under the oxygen-blown mode. Due to the lower carbon content of lignite, the synthesis gas yield was only 2.2 N m³/kg coal under the air-blown mode and 1.65 N m³/kg coal under the oxygen-blown mode on average. However, the total percentage of H₂ and CO could match sub-bituminous coal and bituminous coal. For both low-rank coals under both operational modes, the methane concentrations in the synthesis gas were better controlled close to 2%.

This study confirmed that the addition of methane into the coal-gasification process was effective in adjusting the H₂/CO ratio of synthesis gas produced by properly selecting injection locations. The total synthesis gas yield, which resulted from both methane conversion reactions and coal gasification reactions, was higher compared to that of coal gasification only. The H₂/CO ratio is varied between 1 and 1.5 in the conventional gasification process using coal as the only feedstock, but this ratio could be adjusted to about 2 in the cogasification with methane. Therefore, the H₂/CO ratio of synthesis gas by methane conversion reactions should be slightly higher than 2. Generally,

lower methane conversion efficiency occurs by methane conversion reactions if no catalyst is available. Our tests indicated the cogasification of coal and methane allowed the methane conversion efficiency to reach as high as 65% for low-reactivity bituminous coal and 75% for both high-reactivity sub-bituminous coal and one bituminous coal under test conditions in this study. Higher methane conversion efficiency may mean there is a catalytic effect on methane conversion from either coal ash or coal char, which is coal dependent. Coal char seems more important than coal ash in their catalytic effect on methane conversion. Methane addition benefits the adjustability of the H₂/CO ratio of synthesis gas in the coal gasification process. The catalytic effects of coal chars generated in coal gasification benefit the methane conversion process. This implies there were some synergistic effects on both processes. On the other hand, the H₂/CO ratio is not the only factor to consider in improving this cogasification process. The higher dry synthesis gas yield and the higher total percentage of H₂ and CO in the produced synthesis gas should also be considered to maximize process economics. Reactive coal gasification seemed a key factor in the coal gasification process because the gasification reactivity of coal may impact both the dry synthesis gas yield and the total percentage of synthesis gas, as well as methane conversion efficiency if methane is added. Coal with higher gasification reactivity and simultaneously higher carbon content, such as one bituminous coal and sub-bituminous coal used in this study, likely introduce more active coal chars for catalytic conversion of methane in the cogasification process of these two coals.

The follow-up kinetics study in the one inch testing rig also presented the likelihood of CH₄ reforming and partial oxidation with a favorable H₂/CO ratio, which is generally greater than 5.²⁶ The higher H₂/CO ratio of synthesis gas by CH₄ conversion reactions means that less CH₄ in mass is needed to adjust the H₂/CO ratio in the cogasification process of coal and methane. Ash failed to be a good catalyst candidate on CH₄ conversion reactions because of its very low specific surface area available for catalyst reactions.²⁶ However, coal chars present very promising catalytic performance on CH₄ conversion reactions because of their larger specific surface area. In this study, no other constituents in coal fly ash or special surface properties of coal chars were correlated with the enhanced CH₄ conversion efficiency. In the tests with a 2.5 in. cogasification facility, addition of methane was in the dense phase but above the area where the oxygen concentration is enriched so that the higher CH₄ conversion efficiency and selectivity could be achieved in this study. This indicated the coal dependence of methane conversion reactions in the cogasification process of coal and methane.

Conclusion

Three typical U.S. coals of different ranks were subjected to a conventional gasification test in this study. Evaluation of gasification reactivity of different ranked coals in a thermogravimetric analyzer (TG) indicated that coals of lower rank, such as lignite and sub-bituminous, have higher gasification reactivity than those of bituminous coals. In tests with a 2.5 in. coal gasifier, results indicated that the higher synthesis gas yield and the total percentage of H₂ and CO in the synthesis gas were attributed to higher gasification reactivity of coals. But, the H₂/CO ratio of synthesis gas was independent of coal gasification

(26) Zhou, H. C.; Wang, Q. H.; Cao, Y.; Zhao, H. Y.; Liu, H. Y.; Pan, W. P. Investigation of H₂O and CO₂ Reforming and Partial Oxidation of Methane: Catalytic effects of coal char and coal ash. *Energy Fuels*, submitted for publication.

reactivity. The H_2/CO ratio of synthesis gas produced in the coal gasification was found to be correlated to the rank of coals, more accurately to the H/C ratio of coals. The H_2/CO ratios of synthesis gas from all tested coals, except for that of lignite, were close to 1. The H_2/CO ratio of gasification of lignite reached 1.5. With the addition of methane, synthesis gas with the H_2/CO ratio at nearly 2.0 could be achieved for all four test coals of different ranks in the cogasification process. The most efficient location for methane injection and subsequent conversion is in the dense phase of the pyrolysis and gasification zone in the cogasification reactor. The maximum methane conversion efficiency that could be achieved was 70% on average for all tested coals. It seemed there were some synergistic interactions between methane conversion reactions and the coal gasification

reactions. Coal gasification benefits from the adjustment of the H_2/CO ratio of the synthesis gas by the addition of methane, while methane conversion benefits from the catalytic effect by coal chars.

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Supporting Information Available: Sections S1–S4. This material is available free of charge via the Internet at <http://pubs.acs.org>. EF7005707