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Experimental study of methane-oriented gasification of semi-anthracite and bituminous coals using oxygen and steam in the context of underground coal gasification (UCG): Effects of pressure, temperature, gasification reactant supply rates and coal rank

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Abstract:

The results of ex-situ small-scale laboratory tests performed in a bespoke batch reactor simulating coal gasification to find the most optimal experimental conditions for producing methane-rich syngas in the context of UCG are presented in this paper. The influence of gaseous reactants (oxygen and steam), their supply rates and thermodynamic conditions (temperatures of 650°C, 750°C, 850°C and pressures of 20 bar and 36 bar) on the gasification of semi-anthracite (South Wales coalfield) and bituminous (Silesian basin) coals is investigated. Increasing the gasification pressure from 20 bar to 36 bar and doubling the amount of steam with respect to oxygen benefit the methane generation. Although temperature increase from 650°C to 850°C also benefits methane generation, gasification at 750°C provides the most optimal conditions for methane-rich syngas production. Overall, the highest methane generation occurs at 750°C, 36 bar and H_2O:O_2=2:1 yielding peak methane concentrations of 44.00 vol.% and 35.55 vol.%, and average methane concentrations of 15.34 vol.% and 14.64 vol.% for the semi-anthracite and bituminous coals, respectively. These findings demonstrate that an increase in coal rank favours the methane generation. Owing to high methane content, the syngas produced at such conditions contains the highest calorific value, although the generation of hydrogen and carbon monoxide is reduced in comparison to the experiments conducted at 850°C. This study shows that gasification of bituminous and semi-anthracitic coals at elevated pressures can provide stable generation of methane-rich syngas whose quality can be controlled by the gasification temperature through the dynamics of steam and O_2 supply rates.

Keywords:

Underground coal gasification; Methane; Semi-anthracite; Bituminous coal; High pressure, High temperature.

1. Introduction

With an increasing global population, the society is faced with a dual challenge to produce more energy and less carbon. In 2018, the global energy consumption increased by 2.3%, i.e. at nearly twice the average rate of growth since 2010, while energy-related CO_2 emissions rose 1.7% [1]. Underground coal gasification (UCG) is a clean-coal technology that offers a prospect to be one of the solutions to such challenge, as it can safely harness the energy by utilising deep coal seams and convert them into a synthetic gas. Although coal reserves are the most abundant of all the fossil fuels, less than one sixth of the world's coal is economically accessible via conventional mining methods [2]. European coal reserves are mainly found in the UK, Germany, Poland, Netherlands, Ukraine and Turkey [3]. For instance, in the UK total coal resources could be 187 Btonnes with around 17 Btonnes suitable for UCG, representing a resource for almost 300 years [4, 5]. Similarly, Germany contains around 6.7 Btonnes of coal, while Poland has around 21 Btonnes of hard coal reserves alone [5]. As the global demand for gas is forecast to increase, with industry emerging as the main driver for such growth [6], utilisation of coal reserves through UCG offers a great prospect of increasing the efficiency of fossil fuel use and security of energy supply, and help moving towards low carbon emissions in Europe and worldwide.

The UCG process involves the reactions of oxygen, air or steam with coal carbon and other pyrolysis products producing a syngas which is mainly composed of methane, hydrogen, carbon monoxide, carbon dioxide and steam [7]. For example, hydrogen is a clean fuel that constitutes a valuable chemical feedstock for different chemical processes and syntheses [8]. The produced methane-rich syngas is compatible with natural gas and can be used as a synthetic natural gas (SNG) for power generation, raw material in industry or conversion into other fuels and chemicals [7, 9, 10]. In general, as a fuel, methane has a high economic value as well as the environmental, energy security and industrial safety benefits [11].

As coal is not a pure chemical species, but rather a heterogeneous and multispecies porous medium with large available internal surface area, its gasification involves a complex system of chemical reactions, with the main ones shown in Table 1 [7, 12-14]. In general, endothermic reactions are favoured at higher temperatures, at the expense of exothermic reactions [12]. Those reactions in which

63 the number of moles of products is less than the number of moles of reactants will be favoured at higher
64 pressures [12]. Thermodynamically, some CH_4 producing reactions, such as hydrogasification reaction
65 (no. 4) are favoured at high pressures and relatively lower temperatures [7].

66 Table 1. Main gasification reactions (after [13, 14])

No.	Reaction	Reaction enthalpy (MJ/kmol)
1	$C + O_2 \rightarrow CO_2$	-394.9
2	$2C + O_2 \rightarrow 2CO$	-226.0
3	$2CO + O_2 \rightarrow 2CO_2$	-563.8
4	$C + 2H_2 \rightarrow CH_4$	-87.5
5	$C + H_2O \rightarrow CO + H_2$	+135.7
6	$C + CO_2 \rightarrow 2CO$	+168.9
7	$CO + H_2O \rightarrow CO_2 + H_2$	-33.2
8	$CO + 3H_2 \rightarrow CH_4 + H_2O$	-206.2
9	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	-165.0

67 However, although carbon is the dominant species present in coal, the reactivity of coal may differ from
68 that of pure carbon [7]. Hence, the coal gasification process is complicated by a number of factors, such
69 as operational pressure, reaction temperature, coal rank and its composition and structure, and type of
70 oxidants used [7, 15-18]. For instance, bituminous and anthracite coals usually have low moisture and
71 volatile contents, hence less reactants available from within the coal available for gasification [19]. This
72 was confirmed by Stańczyk et al. [20] demonstrating that gasification of lignite and hard coal blocks
73 with air can lead to poor thermodynamic conditions and low process efficiency. Therefore, it is
74 recommended to use oxygen and steam as main gasification agents to achieve high reaction
75 temperatures and conversion of coal into syngas [19].
76 UCG experiments have been conducted worldwide for almost a century, both at in-situ and laboratory
77 scale. The former ones demonstrated the feasibility of the UCG process and challenges that need to be
78 overcome for successful commercialisation, such as process control, groundwater pollution and
79 subsidence [21-28]. The later ones gave further confidence on the effectiveness and stability of the UCG
80 process [8, 13, 14, 20, 29-38]. For instance, Stańczyk et al. [8] proved the feasibility of producing a H_2-
81 rich gas during the gasification of hard coal by alternating the injection of oxygen and steam. Liu et al.
82 [37] showed that oxygen enriched air gasification of lignite is superior compared with air gasification
83 producing a syngas with 2.4 higher calorific value. Similarly, higher flow rates of oxygen during the
84 gasification of low rank coals led to higher gasification efficiency by increasing the reaction temperature
85 and expansion of gasification area [35]. Overall, most laboratory studies have concentrated on the

86 influence of different gasification agents on the gasification of low and medium rank coals under
87 atmospheric pressure conditions, which is potentially attributable to the complexity of gasification
88 under high pressure regime but also limited reactivity and permeability of the high rank coals.
89 This paper therefore aims to provide further understanding of the effects of various operating conditions
90 on the CH_4 oriented coal gasification in the context of UCG by utilising two coals of different rank, i.e.
91 bituminous coal and semi-anthracite. The experimental plan involved testing the influence of gaseous
92 reactants (O_2 and steam), their supply rates (molar ratios of H_2O:O_2=1:1 and H_2O:O_2=2:1) and
93 thermodynamic conditions (temperatures of 650°C, 750°C, 850°C and pressures of 20 bar and 36 bar)
94 on the gasification process. In total, 20 gasification tests were conducted using a small-scale ex-situ
95 gasification reactor. Based on a detailed analysis of experimental data obtained, the most favourable
96 gasification conditions for CH_4-rich gas production are identified. According to the authors' knowledge,
97 no CH_4 focused gasification experiments in the context of UCG have been performed on coals of such
98 rank. Hence, the dataset presented here offers insights into the most favourable thermodynamic
99 conditions to maximise the CH_4 generation during gasification of bituminous and semi-anthracitic
100 coals.

101 ## 2. Materials and Methods

102 ### 2.1.Experimental facility

103 The experimental simulations of the gasification process involved the use of a bespoke small-scale ex-
104 situ high-pressure high-temperature gasification rig (Fig. 1). The rig can sustain maximum pressures
105 and temperatures up to 50 bar and 900°C, respectively. Air, O_2, CO_2 and N_2 can be used as reactant
106 gases under supply rates up to 10 L/min and H_2O under supply rates up to 9.99 mL/min.

107 The experimental setup consists of: 1) Gas cylinders with pressure regulators; 2) High Performance
108 Liquid Chromatography (HPLC) water pump which supplies de-ionised water in the system; 3) On/off
109 valves; 4) Mass flow controllers (MFC) with bypass on/off valve; 5) Filters; 6) Non-return valves; 7)
110 Pressure relief valves; 8) Pressure gauges; 9) Tubular reactor 33 cm in length, 2.54 cm internal diameter;
111 10) Horizontal split hinge furnace; 11) Temperature controller Carbolite 301; 12) Water cooler

condenser; 13) Gas liquid separator - tar trap; 14) Back-pressure regulator; 15) Digital mass flow meter (MFM); 16) Rotameter and 17) Gas analyser.

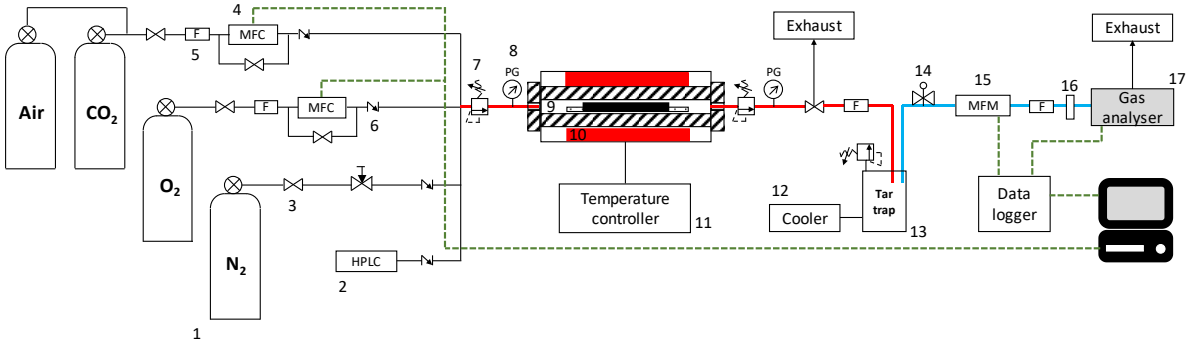


Fig. 1. Schematic of the bespoke high-pressure high-temperature ex-situ small-scale gasification rig.

2.2.Materials

Field specimens were gathered from two different locations. The first selection of coal blocks was obtained from an open cast coal mine in the South Wales Coalfield, UK. The sampling location is 88 m below the ground level, from a coal seam of an average thickness of 1.2 m. The seam name is "Six Feet", with a local name "Big". The second selection of blocks was obtained from an underground coal mine Wesoła in Poland. The sampling location is 950 m below the ground level from a coal seam of an average thickness of 5 m. Coal samples were cut out of the coal blocks using a saw with a diamond tipped saw blade. For the purpose of the gasification experiments, rectangular coal samples were cut to a length of 5-10 cm and a width of 1.5 cm (Fig. 2). Total mass of samples used in each experiment was approximately 30 g (Table 2). Crushed samples passed through a sieve size of 0.212 mm were used for the Proximate and Ultimate analyses [39-43], and the results are presented in Table 3. An air-drying method was applied to dry the samples prior to the experiments [44].

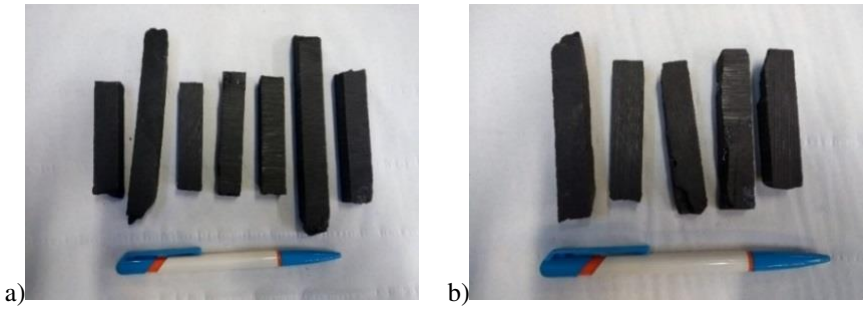


Fig. 2. Coal samples used in the gasification tests: a) "Six Feet" coal; b) "Wesoła" coal.

129 **Table 2.** Mass of coal samples used for ex-situ small-scale gasification tests.

Test number	Mass (g)	
	"Six Feet" coal (South Wales, UK)	" Wesoła" coal (Silesia, Poland)
Test 1	30.96	30.52
Test 2	30.31	30.67
Test 3	31.35	30.89
Test 4	30.86	30.95
Test 5	30.91	30.82
Test 6	30.78	30.81
Test 7	30.25	30.21
Test 8	30.21	30.55
Test 9	30.56	30.70
Test 10	30.88	30.94
Average	30.71	30.71

130 **Table 3.** Proximate and Ultimate characteristics of coals used for ex-situ small-scale gasification tests.

Parameter	Value (%)	
	"Six Feet" coal (South Wales, UK)	"Wesoła" coal (Silesia, Poland)
Moisture content	0.88	3.60
Ash content	2.99	8.74
Volatile matter	13.42	27.67
Total carbon content	89.06	75.35
Total sulphur content	0.70	0.31

131 ## 2.3.Experimental methodology

132 Ten tests on each coal were conducted using mixtures of O_2 and H_2O as the gasification media under
133 different molar ratios, pressure and temperature conditions. In particular, molar ratios of $H_2O:O_2$=1:1
134 and $H_2O:O_2$=2:1, pressures of 20 bar and 36 bar and temperatures of 650°C, 750°C and 850°C were
135 considered in the gasification tests (Table 4).

Table 4. Experimental conditions used for ex-situ small-scale gasification tests.

Test No.	Temperature (°C)	Pressure (bar)	O_2 flow rate (L/min)	H_2O flow rate (mL/min)	H_2O:O_2 molar ratio
Test 1	650	20	0.4	0.3	1:1
Test 2	650	20	0.4	0.6	2:1
Test 3	850	20	0.4	0.3	1:1
Test 4	850	20	0.4	0.6	2:1
Test 5	650	36	0.7	0.53	1:1
Test 6	650	36	0.7	1.05	2:1
Test 7	850	36	0.7	0.53	1:1
Test 8	850	36	0.7	1.05	2:1
Test 9	750	20	0.4	0.6	2:1
Test 10	750	36	0.7	1.05	2:1

Prior to each experiment, a sample was loaded in a quartz boat which was inserted into the tubular pressure reactor (Fig. 3). Upon closing the pressure reactor and connecting it to the gas pipeline, the system was isolated by closing the valves. The pressure of the system was then raised up to the designated value using O_2 by applying a flow rate of 3 l/min. Once the pressure stabilised, the flow rate was reduced to the predetermined value (see Table 4) and the valves were opened. The temperature of the system was then increased up to the predetermined value setting up a heating rate of 20 °C/min. Injection of de-ionised water at a predetermined flow rate (see Table 4), via an HPLC pump, commenced upon temperature reaching 200°C which was then evaporated to steam due to the high temperature in the system ensured by the temperature controller providing a constant heat to the reactor. Once the temperature reached the predetermined value, each experiment was run at a constant temperature for 90 minutes.

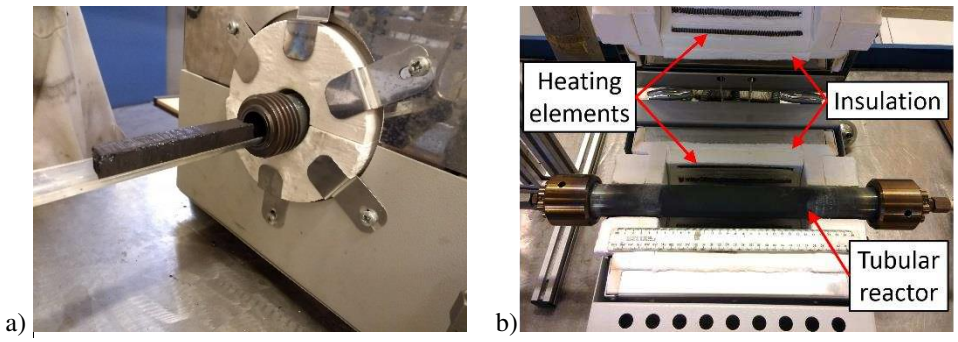


Fig. 3. Gasification rig assembly: a) Sample insertion; b) Tubular reactor with heating elements and insulation.

Hence, the gasification process was allothermal where the heat required for gasification reactions was produced outside of the reactor, via temperature controller, and then transferred inside. This allowed for an assessment of coal gasification at a range of temperatures which were controlled in a precise manner, opposite to the autothermal gasification which lacks an inside temperature control.

Eight tests (Tests 1-8) with experimental conditions described in Table 4 were conducted first. Based on the observations, which will be explained in the following section, two more tests (Test 9 and Test 10) were conducted to further analyse the impact of temperature on gas concentration with a purpose to obtain the most favourable conditions for producing a CH_4-rich syngas.

158 ## 3. Results and discussion

159 This section presents the results of gasification experiments conducted both on the “Six Feet” coal and
160 “Wesoła” coals. It is noted that the figures presented in the following sections contain absolute average
161 gas concentration values in vol.%, serving as a basis for the analysis in which positive or negative
162 changes of gas concentrations as a result of changes in the pressure, temperature, reactant supply rates
163 and coal rank are discussed.

164 ### 3.1.Product gas composition

165 The time evolutions of product gas compositions during gasification experiments conducted on the “Six
166 Feet” and “Wesoła” coals are presented in Fig. 4 and Fig. 5, respectively. For experiments where the
167 temperature was raised to 650°C, maximum CH_4 concentrations can be observed in the period when the
168 temperature had already reached 650°C. For experiments to be undertaken at 850°C, such peaks in CH_4
169 concentrations are obtained during the temperature ramping period, i.e. in the zone below 850°C. In
170 particular, the CH_4 concentration peaks were achieved and prolonged for a certain period within the
171 temperature zone of 650-780°C and 560-800°C for the “Six Feet” and “Wesoła” coals, respectively.
172 Based on those observations, it was decided that two more tests, i.e. Test 9 and Test 10, are performed
173 under the temperature condition of 750°C (using 20 bar and 36 bar pressures at H_2O:O_2=2:1 molar ratio)
174 in order to provide a verification of the results and confirm the optimal temperature to obtain a steady
175 production of CH_4-rich syngas.

176 The results obtained on “Six Feet” coal reveal that CH_4 concentration started to rapidly increase after
177 approximately 20-25 minutes from the start of each test conducted at 20 bar when the temperature
178 reached between 350-460°C (Fig. 3). For the “Wesoła” coal, it took 18-22 minutes for the CH_4
179 production to occur when the temperature reached 300-460°C, at the same pressure conditions (Fig. 4).
180 In general, CH_4 formation begins between 300°C and 550°C and as the temperature continues to rise,
181 semi-coke begins to solidify and contract followed with the yield of CH_4, H_2 and CO_2 [2, 17]. The fact
182 that CH_4 formation starts earlier for the “Wesoła” coal compared to “Six Feet” coal might be related to
183 coal pyrolysis which is influenced by the coal rank. Liu et al. [17] have shown that temperatures at

184 which CH_4 forms shift towards high temperatures with an increase in coal rank, as more active groups
185 and radicals are available in lower rank coals increasing the instantaneous formation rate of CH_4 inside
186 the coal particles.

187 It can be inferred that the increase in pressure from 20 bar to 36 bar as well as the increase in the amount
188 of steam with respect to oxygen increase the time required for the beginning of CH_4 production. This is
189 reasonable to expect as changes in the pressure can shift the chemical equilibrium of the system as well
190 as affect the heat and mass transfer, while excess steam in the system can affect the thermal efficiency
191 of the process [7, 15].

192 CO occurs earlier than H_2 both at experiments conducted at 20 bar and 36 bar, i.e. 10-16 minutes and
193 20-26 minutes earlier for the "Six Feet" coal and 6-12 minutes and 16-22 minutes earlier for the
194 "Wesoła" coal, respectively. Early breakthrough of CO is due to the partial oxidation of coal, followed
195 by endothermic reactions favoured by an increase in temperature, i.e. Boudouard reaction and steam
196 gasification producing more CO and H_2. Large volumes of H_2 will only be produced at temperatures
197 much higher than 600°C as the high temperature is required for the C-H bonds to rupture [17, 45].

198 CO_2 is the first gas produced in each test, owing to strong oxidation of coal, which shows a constant
199 increase throughout each experiment, i.e. initial rapid increase in concentration, followed by a drop in
200 CO_2 concentration which coincides with peak production of CH_4, H_2 and CO after which gradual
201 increase of CO_2 until the end of each experiment occurs. This is related to the fact that oxidising
202 reactions continue as long as there is free O_2 in the injection stream, yielding high amounts of CO and
203 CO_2 [16].

204 A summary of average gas compositions obtained for the duration of each experiment conducted on
205 both coals is given in Table 5. Based on the results for "Six Feet" coal, the highest average CH_4
206 concentration of 15.34 vol.% was observed in Test 10 (T=750°C, P=36 bar, H_2O:O_2=2:1). Under the
207 same experimental conditions, the highest average CH_4 concentration of 14.64 vol.% was obtained
208 during the gasification of "Wesoła" coal. The peak CH_4 concentrations observed for the "Six Feet" and
209 "Wesoła" coals were 44.00 vol.% and 35.55 vol.%, respectively.

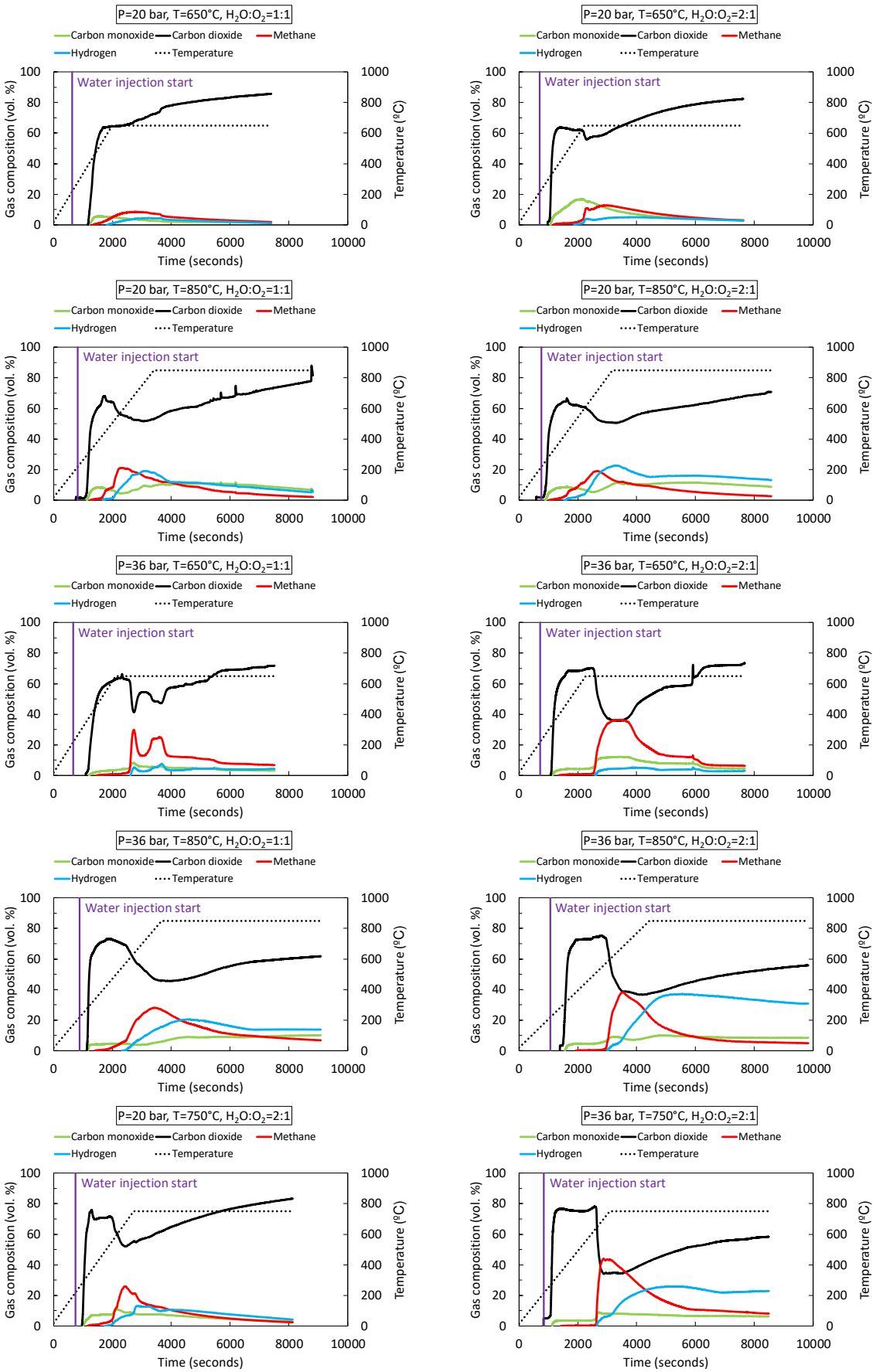
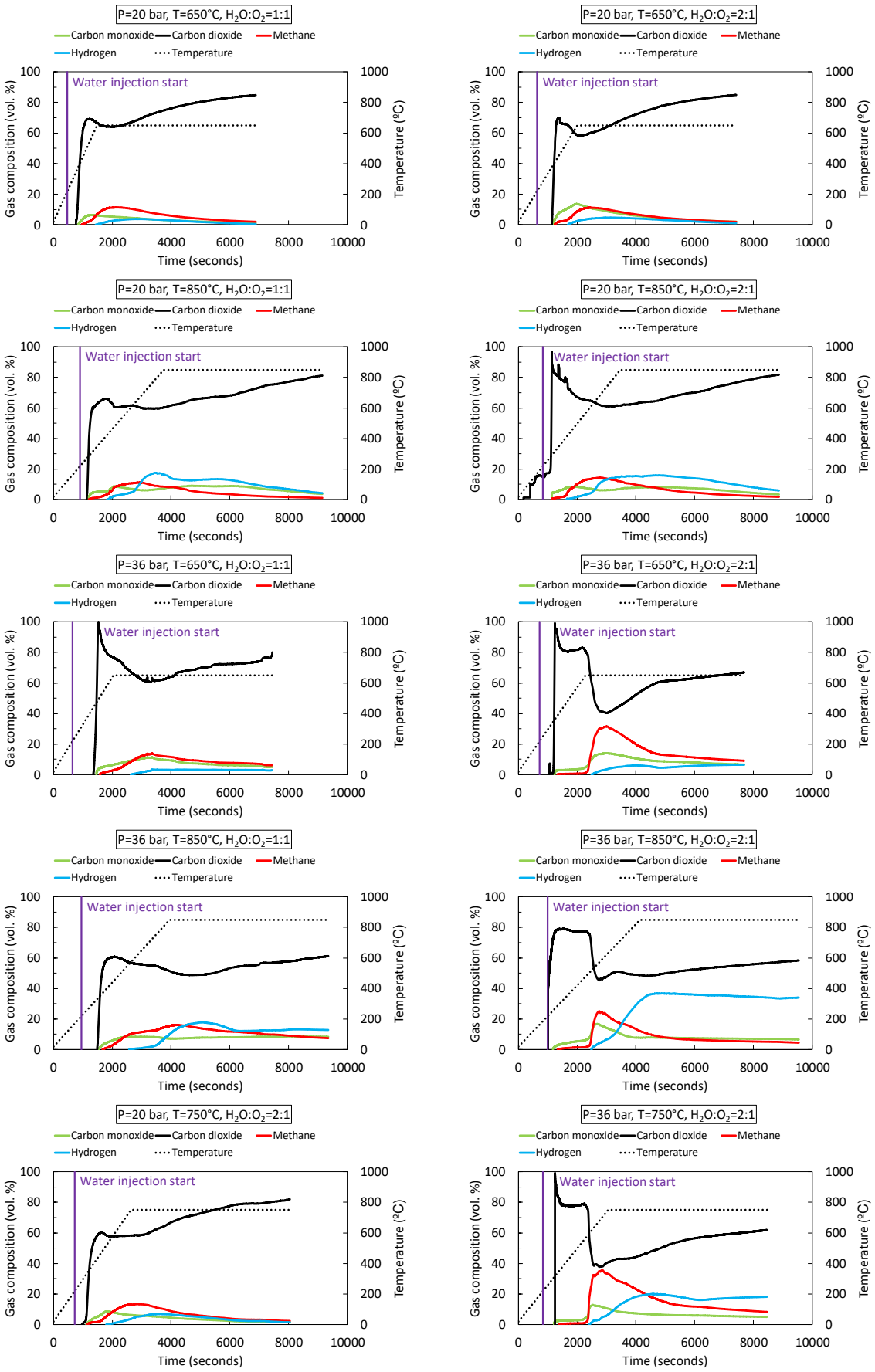


Fig. 4. Changes in gas compositions obtained during the experiments conducted on "Six Feet" coal samples at different experimental conditions.



212 **Fig. 5.** Changes in gas compositions obtained during the experiments conducted on "Wesoła" coal samples at
213 different experimental conditions.

Table 5. Average gas concentrations and calorific values obtained in tests conducted on both coals.

Test No	T (°C)	P (bar)	$H_2O:O_2$ ratio	„Six Feet" coal					„Wesoła" coal				
				Average gas concentration (vol. %)				Calorific value (MJ/Nm^3)	Average gas concentration (vol. %)				Calorific value (MJ/Nm^3)
				CH_4	H_2	CO	CO_2		CH_4	H_2	CO	CO_2	
1	650	20	1:1	4.45	2.61	2.63	74.14	2.21	5.88	2.23	3.30	73.24	2.77
2	650	20	2:1	6.36	3.86	7.40	69.16	3.63	5.52	2.94	5.99	72.22	3.06
3	850	20	1:1	7.89	9.87	8.80	60.92	5.01	4.81	9.90	7.01	67.33	3.68
4	850	20	2:1	7.36	14.56	9.54	57.83	5.42	6.53	11.06	6.61	63.97	4.37
5	650	36	1:1	9.85	4.10	4.20	59.26	4.51	8.30	2.84	7.34	69.63	4.21
6	650	36	2:1	13.70	3.74	7.20	57.94	6.23	13.56	5.16	8.30	60.60	6.47
7	850	36	1:1	12.48	14.47	7.56	56.78	7.00	10.70	11.64	7.81	54.52	6.08
8	850	36	2:1	11.16	29.87	7.99	50.29	8.24	8.10	30.14	7.78	56.58	7.14
9	750	20	2:1	7.89	7.83	5.92	69.33	4.42	6.39	3.80	3.93	67.12	3.20
10	750	36	2:1	15.34	20.94	6.31	52.01	8.56	14.64	15.65	6.27	56.32	7.73

However, Test 10 produced less H_2, and CO than Test 8 during the gasification of both coals. This proves that the most favourable conditions for the methanation reaction are at 750 °C, in which hydrogen and carbon monoxide are consumed to form methane. Owing to high methane content obtained in Test 10, average calorific values of the syngas produced in Test 10 were 4% and 8% higher than in Test 8 for the "Six Feet" and "Wesoła" coals, respectively.

Fig. 6 and Table 6 show the gasification residues and their masses, respectively. It can be observed that the gasification proceeds in one direction and the ash layer (white area) forms at the end where reactants are injected. By comparing the results presented in Table 6 and Table 2, about 2/3 of the total coal mass for both coals were consumed by chemical reactions. However, one can observe that 12% less of gasification residue were left after the gasification of "Wesoła" coal compared to "Six Feet" coal.

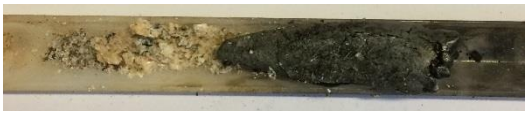
a)  b)

Fig. 6. Gasification residues: a) "Six Feet" coal; b) "Wesoła" coal.

Table 6. Mass of the gasification solid residues obtained from ex-situ small-scale gasification tests.

Test number	Mass (g)	
	"Six Feet" coal	"Wesoła" coal
Test 1	12.51	9.02
Test 2	11.13	9.33
Test 3	8.18	4.29
Test 4	7.92	5.35
Test 5	16.52	14.60
Test 6	8.16	16.78
Test 7	13.21	14.28
Test 8	13.20	11.68
Test 9	11.51	6.64
Test 10	18.18	13.63
Average	12.05	10.56

3.2.Effect of pressure

The effect of pressure on the reaction rate depends on the specific reaction involved [7]. Some gasification reactions in which the number of moles of reactants is higher than the number of moles of products, e.g. hydrogasification and methanation reactions, are favoured at high pressures [12]. Increasing the pressure of the system increases the average CH_4 concentrations in all experiments. For instance, in experiments conducted on "Six Feet" coal at 650°C, 750°C and 850°C with H_2O:O_2=2:1, a

change in pressure from 20 to 36 bar increases the CH_4 concentration by 115% and 94%, 52% respectively. Similarly, raising the pressure yields 146%, 129% and 24% increase in CH_4 concentration during gasification of "Wesoła" coal at 650°C, 750°C and 750°C with H_2O:O_2=2:1, respectively.

Although it is generally suggested in the literature that the production of CO_2 is favoured at higher pressures [12], this is not observed in this work which could be due to the complexity of the principal chemical reactions between carbon and oxygen that occur simultaneously and sequentially. As Lee et al. [7] suggested, oxidation of coal is significantly more complex than oxidation of pure carbon and the mechanistic chemistry explained purely through the equations in Table 1 may not be sufficient, as coal contains various reactive organic functional groups and some mineral ingredients which act as catalysts. One of the reasons may also be the intensification of the CO_2 methanation under the conditions of experiments conducted. During the gasification of "Six Feet" and in particular the "Wesoła" coal, a general trend is visible where increase in pressure generally has a positive impact on CO, especially at 650°C and H_2O:O_2=1:1, increasing the concentrations by 60% and 122%, respectively. This may be related to the fact that Boudouard reaction requires high pressure for significant conversion for higher reactant concentrations [7].

3.3.Effect of temperature

Increase in temperature above 650°C has a positive effect on CH_4 generation. In particular, as the temperature increases from 650°C to 850°C, CH_4 concentration increases by up to 77% for the "Six Feet" coal (at H_2O:O_2=1:1 and 20 bar) and 29% for the "Wesoła" coal (at H_2O:O_2=1:1 and 36 bar). However, for both coals under study, syngas with the highest CH_4 concentration was obtained at 750°C. Hydrogasification, methanation and volatile matter are the main sources for CH_4 generation [36]. Furthermore, hydrogasification and methanation reactions are exothermic and favoured at temperatures ≤670°C, opposite to steam and CO_2 gasification reactions [7]. Hence, as the temperature increases, they will proceed at lower rate decreasing the CH_4 production [7]. Increase in CH_4 concentration with temperature could also be related to the pyrolysis of coal during which CH_4 is mainly released within the temperature zone of 450-600°C, predominantly by the breakage of methylene bridges [46, 47].

However, although CH_4 can be formed at temperatures ≥700°C due to secondary devolatilisation, only small amounts of CH_4 are produced at such temperatures as a result of pyrolysis [17]. Increase in CH_4 concentration at temperatures higher than 700°C is predominantly due to excess H_2 in the system that participates in the hydrogasification reaction, as high hydrogen pressure significantly enhances this reaction [7, 17].

Both CO and H_2 concentrations show a strong correlation with temperature, increasing up to 235% and 699% for "Six Feet" coal and up to 112% and 484% for the "Wesoła" coal, respectively. High temperature (>680°C) benefits the Boudouard reaction enhancing the CO production, similar to the steam gasification reaction [7, 36]. The water gas shift reaction also contributes to the generation of H_2 and CO_2, but it is least dependent on temperature [7]. During pyrolysis, H_2 evolution starts at 400°C due to the condensation of aromatic structures and it progresses at a relatively high rate up to 1000°C, contributing continuously to the overall H_2 content in the syngas [45-47]. It is commonly understood that O_2 reacts completely in a very short distance from the location at which it comes in contact with coal, which is further pronounced at higher temperatures as the rates of reactions are intrinsically higher [7, 12]. Hence, as the reaction pathway is very complex involving several carbon-oxygen interactions, there is a general agreement that the ratio of CO to CO_2 increases with temperature [7, 45], as also supported through this work.

3.4.Effect of gasification reactant supply rates

Generation of CH_4 is generally favoured by doubling the number of moles of steam with respect to O_2 in the system, which is particularly visible at 650°C. For instance, at 36 bar during the gasification of "Six Feet" and "Wesoła" coals the CH_4 concentration increased by 39% and 63%, respectively. Similar can be observed for CO and H_2, as it increased by up to 181% and 106% during "Six Feet" coal gasification and up to 82% and 159% during "Wesoła" coal gasification, respectively.

The observed behaviour is driven by the steam gasification and water gas shift reactions which are favoured by an excess amount of steam. The former one is an endothermic reaction requiring heat input, while the latter one is mildly exothermic and takes places on the solid surface of the coal where it is

being further catalysed by carbon surfaces, despite all four chemical species involved in the reaction are in gaseous state [7]. Produced H_2 then primarily participates in the hydrogasification reaction resulting in an increased production of CH_4, but can also play role in the Sabatier reaction in which it reacts with CO_2 to generate CH_4 and steam [36]. Hence, high yield of CH_4 is controlled by the molar ratio of H_2 to CO or CO_2, depending on the reaction, suggesting that adjusting the H_2 content in the syngas through steam injection and temperature control can benefit CH_4 production.

3.5.Effect of coal rank

The gasification of coals of different rank yields notable differences in average concentrations of various gas species. The production of CH_4 was consistently higher during the gasification of the "Six Feet" semi-anthracitic coal compared to the "Wesoła" bituminous coal, showing up to 64% higher concentration, depending on the experimental conditions applied. Similarly, H_2 and CO concentrations were generally higher during the gasification of the "Six Feet" than "Wesoła" coal, i.e. up to 50% and 106% higher, respectively. Although the effect of coal rank does not have a pronounced effect on average concentrations of CO_2 produced, the values obtained suggest a mild tendency to decrease with an increase in coal rank.

In general, the gasification of coal is affected by its properties such as carbon content, volatile matter, ash content, pore structure, particle size and thermodynamic conditions [7, 48]. Coals of higher rank can generate more CH_4, especially during the pyrolysis process, as the loss of oxygen-functional sites during the maturation process can increases the concentration of the CH_4 precursors [17]. Furthermore, high effective carbon content during the stable gas production phase enforces the reduction of CO_2 and increases the CO content [16]. Coals of higher rank contain predominantly micropores which offer most of the surface area where the actual gasification takes place in comparison to lower rank coals which consist of macropores, mesopores and micropores [18, 49]. However, as meso- and macropores offer passage to gasification agent to reach the reactant sites in the micropores, lower rank coals are more reactive [18].

4. Conclusions

312 The influence of gaseous reactants, i.e. O_2 and steam, and their supply rates at different temperatures
313 and pressures on the gasification process of "Six Feet" semi-anthracitic coal from the South Wales
314 coalfield (UK) and "Wesoła" bituminous coal from the Silesian basin (Poland) to find the favourable
315 experimental conditions for CH_4-rich syngas production was presented in this paper. The following
316 conclusions can be made:

317 • Experiments where the temperature of the system was increased to 750°C demonstrated that it
318 is the most favourable temperature around which the highest peak was achieved and sustained
319 for a certain period of time compared to experiments conducted at 650°C and 850°C.
320 • Increasing the pressure from 20 bar to 36 bar increased the CH_4 concentration. This was the
321 most pronounced in experiments conducted at 750°C and H_2O:O_2=2:1, where CH_4
322 concentration increased by 94% and 129% for "Six Feet" coal and "Wesoła" coal,
323 respectively.
324 • Doubling the number of moles of steam with respect to O_2 in the system generally increased
325 the CH_4 concentration, by up to 43% and 63% for "Six Feet" coal and "Wesoła" coal,
326 respectively.
327 • By increasing the temperature of the system from 650°C to 850°C, CH_4 concentration
328 increased by up to 77% and 29% for "Six Feet" Coal and "Wesoła" coal, respectively.
329 However, through experiments on both coals, it was demonstrated that the optimal
330 temperature for stable and CH_4-rich syngas production is 750°C at 36 bar and H_2O:O_2=2:1.
331 • The highest peak and average CH_4 concentrations of 44.00 vol.% and 15.34 vol.% were
332 observed during the gasification of "Six Feet" coal, and concentrations of 35.55 vol.% and
333 14.64 vol.% during the gasification of "Wesoła" coal, respectively. This demonstrated that an
334 increase in coal rank favours the CH_4 generation.
335 • Overall, as the CH_4 production was favoured by an increase in pressure and an increase in the
336 amount of steam in the system, and keeping the temperature at 750°C generated syngas with
337 the highest average CH_4 content, the amount of steam injected and the dynamics of steam and

O_2 supply rates at high pressures can be the controlling factors through which the syngas with high CH_4 content is produced.

- Based on the findings of this work, generation of CH_4-rich syngas during in situ gasification could be achieved by selecting deep carbon-rich coal seams to enable gasification at high pressure conditions. In order to maintain the gasification at temperatures favourable for CH_4 production which is directly dependent on the amount of water and hydrogen amounts available within the reactor, hydrogeology of the site would need to be carefully assessed and understood so that the groundwater flowing towards the reactor would be provided at a sufficient rate to adsorb the heat within the reactor and converts to steam. This work suggests that doubling the amount of water with respect to the primary gasification agent (oxygen or air) would be beneficial and serve as a starting point, however, the optimal amount would need to be assessed and adjusted based on the quality of the product gas.

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