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

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13 Abstract:

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

32

33 Keywords:

34 Underground coal gasification; Methane; Semi-anthracite; Bituminous coal; High pressure, High
35 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.
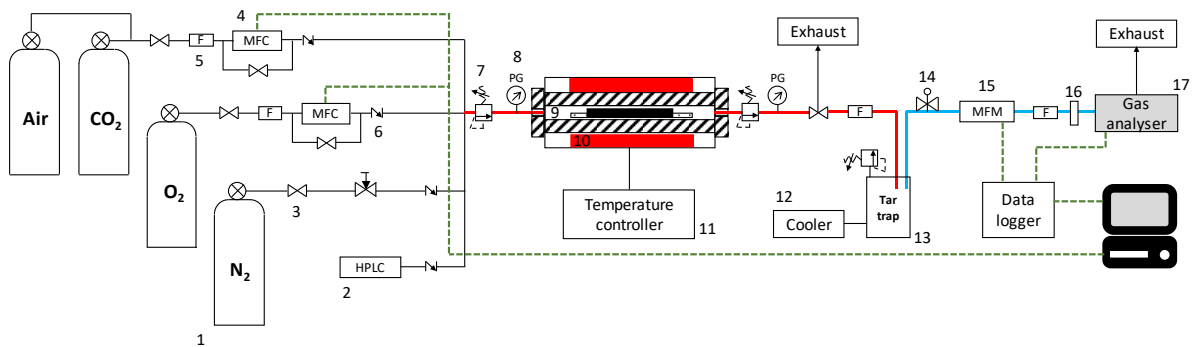

Fig. 1. Schematic of the bespoke high-pressure high-temperature ex-situ small-scale gasification rig.

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].
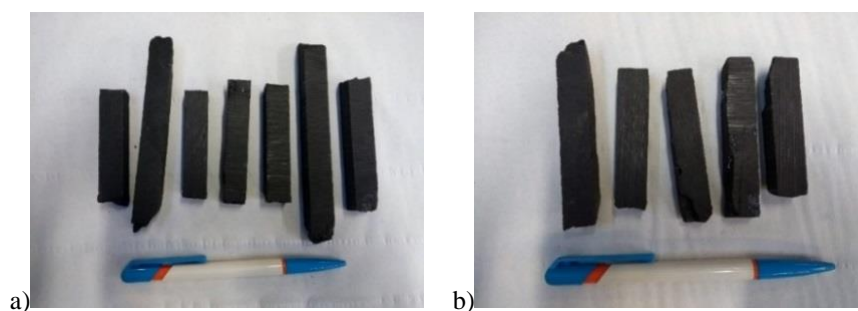

Fig. 2. Coal samples used in the gasification tests: a) "Six Feet" coal; b) "Wesoła" coal.

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).

136

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

138 Prior to each experiment, a sample was loaded in a quartz boat which was inserted into the tubular

139 pressure reactor (Fig. 3). Upon closing the pressure reactor and connecting it to the gas pipeline, the

140 system was isolated by closing the valves. The pressure of the system was then raised up to the

141 designated value using O_2 by applying a flow rate of 3 l/min. Once the pressure stabilised, the flow rate

142 was reduced to the predetermined value (see Table 4) and the valves were opened. The temperature of

143 the system was then increased up to the predetermined value setting up a heating rate of 20 °C/min.

144 Injection of de-ionised water at a predetermined flow rate (see Table 4), via an HPLC pump,

145 commenced upon temperature reaching 200°C which was then evaporated to steam due to the high

146 temperature in the system ensured by the temperature controller providing a constant heat to the reactor.

147 Once the temperature reached the predetermined value, each experiment was run at a constant

148 temperature for 90 minutes.
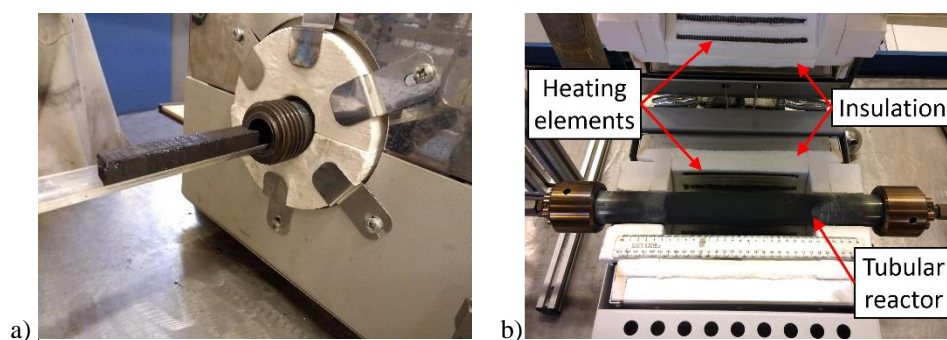
149 **Fig. 3.** Gasification rig assembly: a) Sample insertion; b) Tubular reactor with heating elements and insulation.

150   Hence, the gasification process was allothermal where the heat required for gasification reactions was

151   produced outside of the reactor, via temperature controller, and then transferred inside. This allowed

152   for an assessment of coal gasification at a range of temperatures which were controlled in a precise

153   manner, opposite to the autothermal gasification which lacks an inside temperature control.

154   Eight tests (Tests 1-8) with experimental conditions described in Table 4 were conducted first. Based

155   on the observations, which will be explained in the following section, two more tests (Test 9 and Test

156   10) were conducted to further analyse the impact of temperature on gas concentration with a purpose to

157   obtain the most favourable conditions for producing a CH_4-rich syngas.

3. Results and discussion

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

3.1. Product gas composition

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

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

9

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

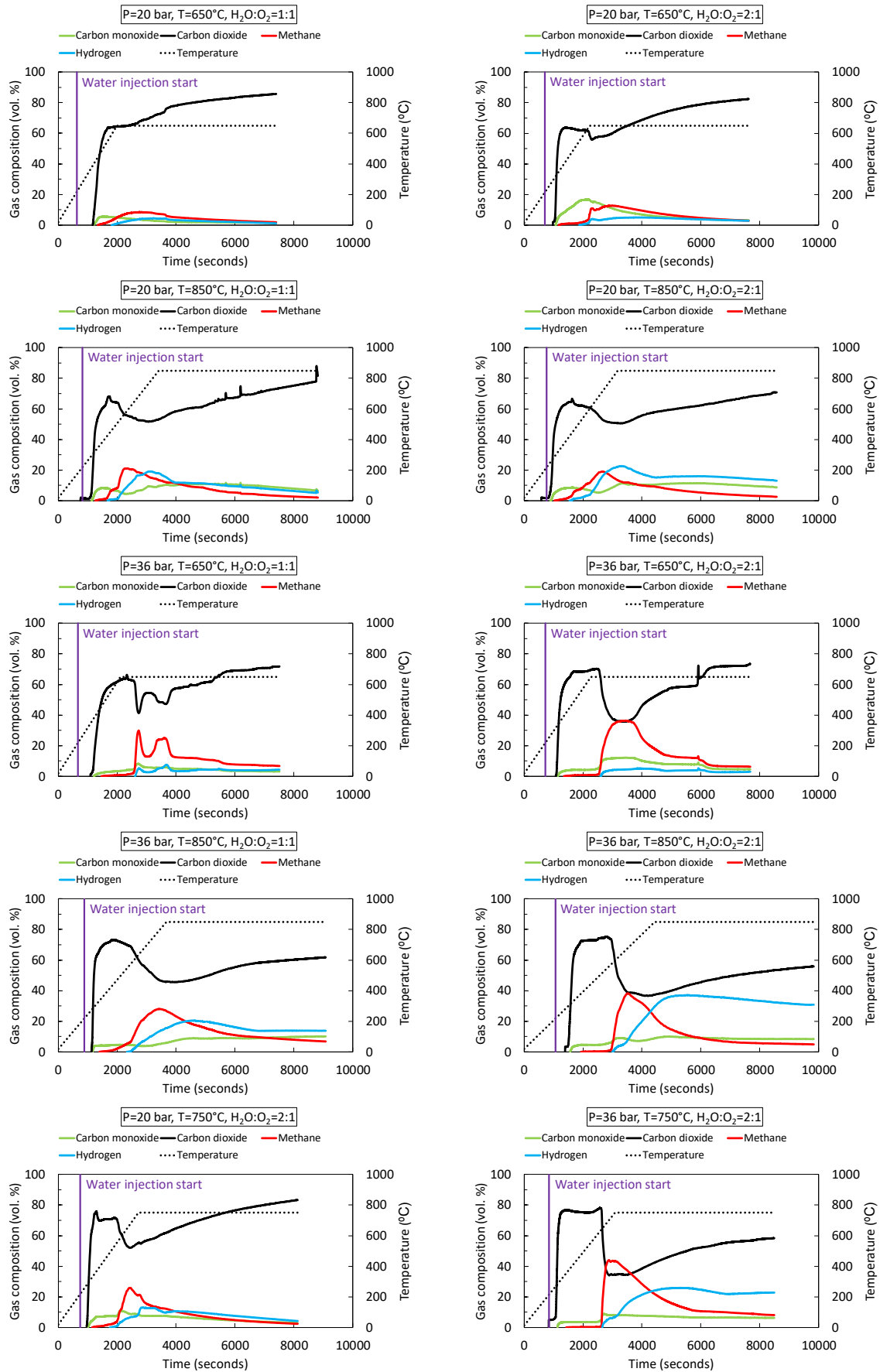209   "Wesoła" coals were 44.00 vol.% and 35.55 vol.%, respectively.

Fig. 4. Changes in gas compositions obtained during the experiments conducted on "Six Feet" coal samples at different experimental conditions.
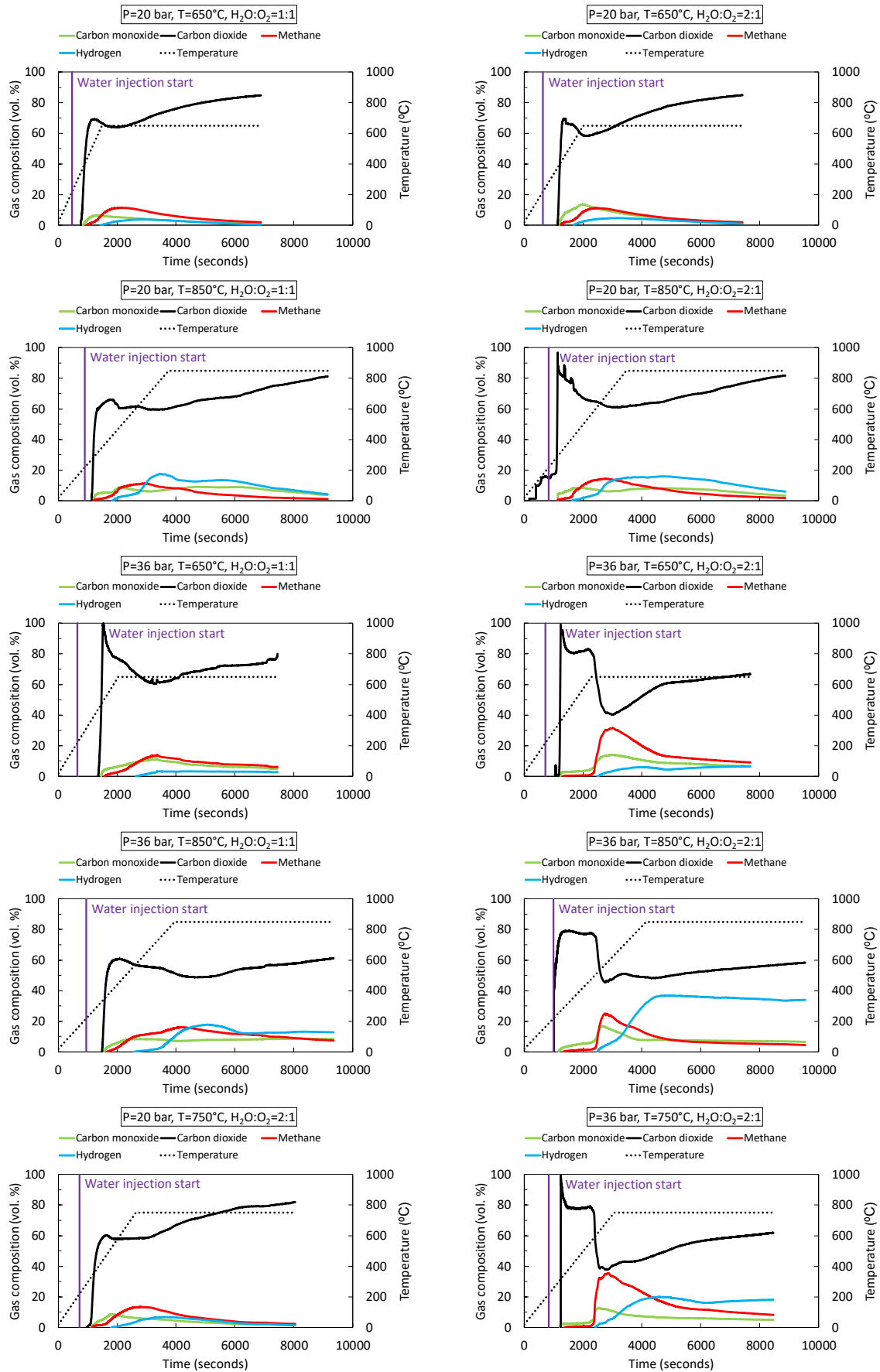
Fig. 5. Changes in gas compositions obtained during the experiments conducted on "Wesoła" coal samples at different experimental conditions.

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

Test No	T (°C)	P (bar)	H₂O:O₂ ratio	„Six Feet" coal					„Wesoła" coal				
				Average gas concentration (vol. %)				Calorific value (MJ/Nm³)	Average gas concentration (vol. %)				Calorific value (MJ/Nm³)
				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

215

14

216   However, Test 10 produced less H_2, and CO than Test 8 during the gasification of both coals. This

217   proves that the most favourable conditions for the methanation reaction are at 750 ^{o}C, in which

218   hydrogen and carbon monoxide are consumed to form methane. Owing to high methane content

219   obtained in Test 10, average calorific values of the syngas produced in Test 10 were 4% and 8% higher

220   than in Test 8 for the "Six Feet" and "Wesoła" coals, respectively.

221   Fig. 6 and Table 6 show the gasification residues and their masses, respectively. It can be observed that

222   the gasification proceeds in one direction and the ash layer (white area) forms at the end where reactants

223   are injected. By comparing the results presented in Table 6 and Table 2, about 2/3 of the total coal mass

224   for both coals were consumed by chemical reactions. However, one can observe that 12% less of

225   gasification residue were left after the gasification of "Wesoła" coal compared to "Six Feet" coal.
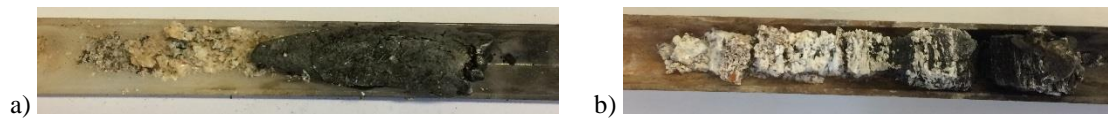

a)   b)

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

227   **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

228   3.2.Effect of pressure

229   The effect of pressure on the reaction rate depends on the specific reaction involved [7]. Some

230   gasification reactions in which the number of moles of reactants is higher than the number of moles of

231   products, e.g. hydrogasification and methanation reactions, are favoured at high pressures [12].

232   Increasing the pressure of the system increases the average CH_4 concentrations in all experiments. For

233   instance, in experiments conducted on "Six Feet" coal at 650°C, 750°C and 850°C with $H_2O:O_2=2:1$, a

234 change in pressure from 20 to 36 bar increases the CH_4 concentration by 115% and 94%, 52%

235 respectively. Similarly, raising the pressure yields 146%, 129% and 24% increase in CH_4 concentration

236 during gasification of "Wesoła" coal at 650°C, 750°C and 750°C with $H_2O:O_2$=2:1, respectively.

237 Although it is generally suggested in the literature that the production of CO_2 is favoured at higher

238 pressures [12], this is not observed in this work which could be due to the complexity of the principal

239 chemical reactions between carbon and oxygen that occur simultaneously and sequentially. As Lee et

240 al. [7] suggested, oxidation of coal is significantly more complex than oxidation of pure carbon and the

241 mechanistic chemistry explained purely through the equations in Table 1 may not be sufficient, as coal

242 contains various reactive organic functional groups and some mineral ingredients which act as catalysts.

243 One of the reasons may also be the intensification of the CO_2 methanation under the conditions of

244 experiments conducted. During the gasification of "Six Feet" and in particular the "Wesoła" coal, a

245 general trend is visible where increase in pressure generally has a positive impact on CO, especially at

246 650°C and $H_2O:O_2$=1:1, increasing the concentrations by 60% and 122%, respectively. This may be

247 related to the fact that Boudouard reaction requires high pressure for significant conversion for higher

248 reactant concentrations [7].

249   3.3.Effect of temperature

250 Increase in temperature above 650°C has a positive effect on CH_4 generation. In particular, as the

251 temperature increases from 650°C to 850°C, CH_4 concentration increases by up to 77% for the "Six

252 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).

253 However, for both coals under study, syngas with the highest CH_4 concentration was obtained at 750°C.

254 Hydrogasification, methanation and volatile matter are the main sources for CH_4 generation [36].

255 Furthermore, hydrogasification and methanation reactions are exothermic and favoured at temperatures

256 ≤670°C, opposite to steam and CO_2 gasification reactions [7]. Hence, as the temperature increases, they

257 will proceed at lower rate decreasing the CH_4 production [7]. Increase in CH_4 concentration with

258 temperature could also be related to the pyrolysis of coal during which CH_4 is mainly released within

259 the temperature zone of 450-600°C, predominantly by the breakage of methylene bridges [46, 47].

15

260   However, although CH_4 can be formed at temperatures $\geq 700°C$ due to secondary devolatilisation, only

261   small amounts of CH_4 are produced at such temperatures as a result of pyrolysis [17]. Increase in CH_4

262   concentration at temperatures higher than $700°C$ is predominantly due to excess H_2 in the system that

263   participates in the hydrogasification reaction, as high hydrogen pressure significantly enhances this

264   reaction [7, 17].

265   Both CO and H_2 concentrations show a strong correlation with temperature, increasing up to 235% and

266   699% for "Six Feet" coal and up to 112% and 484% for the "Wesoła" coal, respectively. High

267   temperature ($>680°C$) benefits the Boudouard reaction enhancing the CO production, similar to the

268   steam gasification reaction [7, 36]. The water gas shift reaction also contributes to the generation of H_2

269   and CO_2, but it is least dependent on temperature [7]. During pyrolysis, H_2 evolution starts at $400°C$

270   due to the condensation of aromatic structures and it progresses at a relatively high rate up to $1000°C$,

271   contributing continuously to the overall H_2 content in the syngas [45-47]. It is commonly understood

272   that O_2 reacts completely in a very short distance from the location at which it comes in contact with

273   coal, which is further pronounced at higher temperatures as the rates of reactions are intrinsically higher

274   [7, 12]. Hence, as the reaction pathway is very complex involving several carbon-oxygen interactions,

275   there is a general agreement that the ratio of CO to CO_2 increases with temperature [7, 45], as also

276   supported through this work.

277   3.4.Effect of gasification reactant supply rates

278   Generation of CH_4 is generally favoured by doubling the number of moles of steam with respect to O_2

279   in the system, which is particularly visible at $650°C$. For instance, at 36 bar during the gasification of

280   "Six Feet" and "Wesoła" coals the CH_4 concentration increased by 39% and 63%, respectively.

281   Similar can be observed for CO and H_2, as it increased by up to 181% and 106% during "Six Feet"

282   coal gasification and up to 82% and 159% during "Wesoła" coal gasification, respectively.

283   The observed behaviour is driven by the steam gasification and water gas shift reactions which are

284   favoured by an excess amount of steam. The former one is an endothermic reaction requiring heat input,

285   while the latter one is mildly exothermic and takes places on the solid surface of the coal where it is

286 being further catalysed by carbon surfaces, despite all four chemical species involved in the reaction

287 are in gaseous state [7]. Produced H_2 then primarily participates in the hydrogasification reaction

288 resulting in an increased production of CH_4, but can also play role in the Sabatier reaction in which it

289 reacts with CO_2 to generate CH_4 and steam [36]. Hence, high yield of CH_4 is controlled by the molar

290 ratio of H_2 to CO or CO_2, depending on the reaction, suggesting that adjusting the H_2 content in the

291 syngas through steam injection and temperature control can benefit CH_4 production.

292   3.5.Effect of coal rank

293 The gasification of coals of different rank yields notable differences in average concentrations of

294 various gas species. The production of CH_4 was consistently higher during the gasification of the "Six

295 Feet" semi-anthracitic coal compared to the "Wesoła" bituminous coal, showing up to 64% higher

296 concentration, depending on the experimental conditions applied. Similarly, H_2 and CO concentrations

297 were generally higher during the gasification of the "Six Feet" than "Wesoła" coal, i.e. up to 50% and

298 106% higher, respectively. Although the effect of coal rank does not have a pronounced effect on

299 average concentrations of CO_2 produced, the values obtained suggest a mild tendency to decrease with

300 an increase in coal rank.

301 In general, the gasification of coal is affected by its properties such as carbon content, volatile matter,

302 ash content, pore structure, particle size and thermodynamic conditions [7, 48]. Coals of higher rank

303 can generate more CH_4, especially during the pyrolysis process, as the loss of oxygen-functional sites

304 during the maturation process can increases the concentration of the CH_4 precursors [17]. Furthermore,

305 high effective carbon content during the stable gas production phase enforces the reduction of CO_2 and

306 increases the CO content [16]. Coals of higher rank contain predominantly micropores which offer most

307 of the surface area where the actual gasification takes place in comparison to lower rank coals which

308 consist of macropores, mesopores and micropores [18, 49]. However, as meso- and macropores offer

309 passage to gasification agent to reach the reactant sites in the micropores, lower rank coals are more

310 reactive [18].

311   4. Conclusions

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

- Experiments where the temperature of the system was increased to 750°C demonstrated that it is the most favourable temperature around which the highest peak was achieved and sustained for a certain period of time compared to experiments conducted at 650°C and 850°C.

- Increasing the pressure from 20 bar to 36 bar increased the CH_4 concentration. This was the most pronounced in experiments conducted at 750°C and $H_2O:O_2=2:1$, where CH_4 concentration increased by 94% and 129% for "Six Feet" coal and "Wesoła" coal, respectively.

- Doubling the number of moles of steam with respect to O_2 in the system generally increased the CH_4 concentration, by up to 43% and 63% for "Six Feet" coal and "Wesoła" coal, respectively.

- By increasing the temperature of the system from 650°C to 850°C, CH_4 concentration increased by up to 77% and 29% for "Six Feet" Coal and "Wesoła" coal, respectively. However, through experiments on both coals, it was demonstrated that the optimal temperature for stable and CH_4-rich syngas production is 750°C at 36 bar and $H_2O:O_2=2:1$.

- The highest peak and average CH_4 concentrations of 44.00 vol.% and 15.34 vol.% were observed during the gasification of "Six Feet" coal, and concentrations of 35.55 vol.% and 14.64 vol.% during the gasification of "Wesoła" coal, respectively. This demonstrated that an increase in coal rank favours the CH_4 generation.

- Overall, as the CH_4 production was favoured by an increase in pressure and an increase in the amount of steam in the system, and keeping the temperature at 750°C generated syngas with the highest average CH_4 content, the amount of steam injected and the dynamics of steam and

338 O$_2$ supply rates at high pressures can be the controlling factors through which the syngas with

339 high CH$_4$ content is produced.

340 • Based on the findings of this work, generation of CH$_4$-rich syngas during in situ gasification

341 could be achieved by selecting deep carbon-rich coal seams to enable gasification at high

342 pressure conditions. In order to maintain the gasification at temperatures favourable for CH$_4$

343 production which is directly dependent on the amount of water and hydrogen amounts

344 available within the reactor, hydrogeology of the site would need to be carefully assessed and

345 understood so that the groundwater flowing towards the reactor would be provided at a

346 sufficient rate to adsorb the heat within the reactor and converts to steam. This work suggests

347 that doubling the amount of water with respect to the primary gasification agent (oxygen or

348 air) would be beneficial and serve as a starting point, however, the optimal amount would

349 need to be assessed and adjusted based on the quality of the product gas.

Acknowledgements

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