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1 **Experimental study on tar formation during underground coal gasification: Effect of**  
2 **coal rank and gasification pressure on tar yield and chemical composition**

3

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14 **Abstract**

15 The yield and composition of tar depending on coal rank and pressure during  
16 underground coal gasification (UCG) were studied. Two coals were used in a series of ex-situ  
17 UCG experiments: a Welsh semi-anthracite (Six Feet) and a Polish bituminous coal (Wesoła).  
18 Four high-pressure gasification trials under two distinct pressure regimes (20 and 40 bar)  
19 were conducted. The tar samples were collected directly from the reactor outlet. The  
20 following groups of compounds were analysed by use of gas chromatography (GC-MS): light  
21 monoaromatic hydrocarbons (BTEX – benzene, toluene, ethylbenzene and xylenes),  
22 polycyclic aromatic hydrocarbons (PAHs) and phenols. A series of gasification experiments  
23 revealed significant differences in tar yields and composition depending on the coal rank and  
24 gasification pressure. Significant decreases in tar contents were observed with the increase in  
25 gasification pressure from 20 to 40 bar for both coals. The total yields of the analysed tar  
26 components per kg of gasified coal were 2.58 g and 0.41 g for the experiments conducted on  
27 the Six Feet samples at 20 bar and 40 bar, respectively. The corresponding values for the  
28 Wesoła coal amounted to 5.48 g and 0.95 g. In all experiments, BTEX was a dominant group  
29 of tar components, constituting 69-86% of the total tar yield within the tested range of

30 compounds. The present study further proves that gasification pressure has a significant effect  
31 on the chemical composition of the produced UCG tars for both coal samples under study.

32 **Keywords:** underground coal gasification, UCG, tar, coal rank, pressure

33 **Highlights:**

- 34 • A series of four ex-situ UCG tests using large coal samples of two different ranks were  
35 carried out.
- 36 • The formation of tar compounds was studied depending on the process conditions.
- 37 • A significant effect of gasification pressure and coal rank on the yield and composition  
38 of UCG tars is demonstrated.

39

40 **1. Introduction**

41 Underground coal gasification (UCG) is a technology for converting coal into a gaseous  
42 product, often called as synthesis gas (or syngas), for the needs of chemical and energy  
43 industries [1-4]. UCG's potential to access deep, unmineable resources significantly exceeds  
44 conventional coal extraction and conversion techniques [5-8]. The exploitation and use of  
45 fossil fuels is currently perceived as highly harmful due to environmental issues, in particular  
46 the significant carbon footprint. Considering changing policies on the exploitation of fossil  
47 fuels, it should be noted that coal will remain an important source of chemical raw materials  
48 and energy on a global scale for a long time to come. Therefore, technologies related to its  
49 exploitation must be efficient, sustainable and environmentally-safe [2,9-13], and all  
50 operational aspects and products need to be properly assessed. From the point of view of the  
51 UCG process, several consecutive physical phenomena and reactions take place, of which the  
52 most important of which are: drying, combustion, pyrolysis and gasification. The product  
53 yields and composition depend on process conditions such as coal rank, temperature,  
54 pressure, as well as flow rate and composition of the gasifying agent. The most important

55 product of UCG, which is formed as a result of the reaction of coal with the gasification  
56 agent, is a gas mixture which main components are hydrogen, carbon monoxide, methane,  
57 carbon dioxide as well as minor amounts of hydrogen sulphide and ethylene. Here,  
58 wastewater (aqueous phase) and tar are the main UCG by-products. The raw UCG gas  
59 containing vapors and aerosols of water and tarous compounds is transported to the surface  
60 via the production well. After its purification, the UCG gas can be used for energy or  
61 chemical purposes. During the transport to the surface, the gas cools down, which results in  
62 the condensation of some of the heavier tar compounds and formation of tar residues in the  
63 cooler parts of the gas collection system [14-16]. As a consequence, the composition of the tar  
64 reaching the surface may differ significantly from that coming directly from the subsurface  
65 reactor, especially in terms of the content of heavier fractions.

66 The basis of this work is the analysis of the extent to which pressure and coal rank affect the  
67 formation of tar during the UCG process. Studying the influence of these two factors improve  
68 the understanding of the key mechanisms that determine the formation of tar. [17-20].

69 The formation of tar during coal gasification is the result of energy-intensive pyrolysis  
70 reactions, since a significant amount of energy is required to break the chemical bonds of the  
71 carbon. The release of tar from coal begins at about 350 °C and ends at a temperature below  
72 1000 °C [21,22]. Tar formation is a two-stage process. In the first stage, the primary tar  
73 products are released, and the second stage involves their thermal degradation. As a result of  
74 gas-phase secondary reactions, the composition of the tar changes. The degree of thermal  
75 degradation depends mainly on two factors: temperature and residence time of tar vapors in  
76 the high temperature zone. The higher the temperature and the longer the residence time, the  
77 greater the degree of decomposition. Literature data [23,24] show that at a temperature of  
78 about 1000 °C, the time of tar degradation amounts to several seconds.

79 The physical and chemical properties of UCG tar are still not understood in detail. A product  
80 similar in composition and chemical properties to UCG tar is tar from high-temperature coal  
81 gasification [20,25,26]. Tar contains large amounts of compounds from the BTEX, PAH and  
82 phenol groups. Many of these compounds, in particular those with an aromatic structure, have  
83 not been isolated and characterized so far. Individual components present in high  
84 concentrations can be a potential source of raw materials for chemical and fuel production  
85 [20]. Of particular importance are benzene and phenol, which are one of the most frequently  
86 used raw materials in organic synthesis. According to literature data [26-33], coal tar and  
87 crude benzene are still an important source for the synthesis of 2-4-ring arenes and  
88 heterocyclic compounds. Appropriate characterization and determination of the composition  
89 of UCG tar is therefore important because similar to coke oven tar, it can become a source of  
90 valuable chemical compounds.

91 Information on the effect of gasification pressure and coal rank on the properties of UCG tar  
92 is poorly documented in the available literature. The main reason for this is most likely a  
93 general problem with proper sample collection. To ensure a proper research and analytical  
94 approach, it is optimal to take samples from the point closest to the reactor outlet. However,  
95 this is impracticable during in-situ UCG operation. In practice, the only feasible option is to  
96 take tar samples from the surface section of the gas collection pipeline. Nevertheless, there are  
97 only few such studies in the available literature [28,34-38]. An alternative option to study the  
98 formation of UCG tar is numerical modeling. However, the accuracy of the obtained results  
99 strongly depends on the correctness of the assumptions made and the extent of complexity of  
100 the constructed mathematical model [39-41]. To characterize the influence of pressure and  
101 coal rank on the efficiency and composition of UCG tar, literature data on the coal coking  
102 process can be used. Tar produced in an industrial coking plant is formed during coal  
103 pyrolysis - a process that also occurs during underground coal gasification (pyrolysis zone). In

104 spite of some differences between coal coking and UCG (heat transfer, chemical atmosphere,  
105 temperature), the phenomena occurring in both processes are quite similar.

106 Pressure is an important factor affecting the course of the UCG process, and consequently the  
107 yields and composition of tar. In many review and experimental works [42-50], it was found  
108 that the increase in coal pyrolysis pressure resulted in a decrease in the quantity of tar  
109 produced. According to the authors of these works, the main reasons for this were reductions  
110 in the content of volatile substances in the produced tar [45], in the rate of diffusion of tar  
111 vapors from the coal particles [46] and in the driving force for the transport of tar products  
112 from the disintegrated coal/char particles [47]. The sum of these factors prolonged the  
113 residence time and caused an increase in the rates of secondary reactions, leading to tar  
114 decomposition [21,42,49,50]. Other authors [21,43,44,48] did not explain the reasons, but  
115 reported similar trends under elevated pressures.

116 On the basis of a literature review, it is difficult to find a correlation between gasification  
117 pressure and tar yields, since the reported values depended on many factors. Available data  
118 [51] show that, for example, a 30% reduction in the tar yield is achieved with a pressure  
119 increase from 0.1 MPa to 0.3 MPa. According to other authors [52], the increase in pyrolysis  
120 pressure from 0.8 MPa to 2.14 MPa caused a decrease in tar yield by about 20%, mainly due  
121 to a decrease in the amount of tar compounds and phenols soluble in water, while the  
122 concentration of polyaromatic compounds increased.

123 Another factor significantly influencing the quantity and composition of tar obtained in the  
124 UCG process is the coal rank. Research conducted by [42] shows that bituminous coals,  
125 characterized by higher plasticity, produce more tar than lignite or anthracite. In the case of  
126 bituminous coals, the secondary reactions occurring during the UCG process are more intense  
127 than for other coal types, resulting in a lower tar yield. Other studies [46,53] proved that with  
128 an increase in the rank of coalification, the content of elemental carbon increases, while

129 moisture content and the amount of volatile substances decrease. Tars obtained from the  
130 pyrolysis of lignite contain a large amount of oxygen compounds, while tars obtained from  
131 bituminous coals are characterized by high hydrocarbon contents. Therefore, more tar is  
132 produced during the pyrolysis of steam coal compared to more coalified anthracite. Other  
133 results were presented in [54], demonstrating that the tar yield obtained from a North Dakota  
134 lignite was significantly lower, than that produced from bituminous coals with a high content  
135 of volatiles or from semi-anthracites, characterized by a low volatiles content.

136 The literature review findings show that the influence of coal rank and pressure on the tar  
137 formation during the thermochemical processing of coal has been the subject of many  
138 previous studies, but most of them primarily focused on the pyrolysis process. There is still a  
139 lack of knowledge about the formation of tar during the underground coal gasification  
140 process.

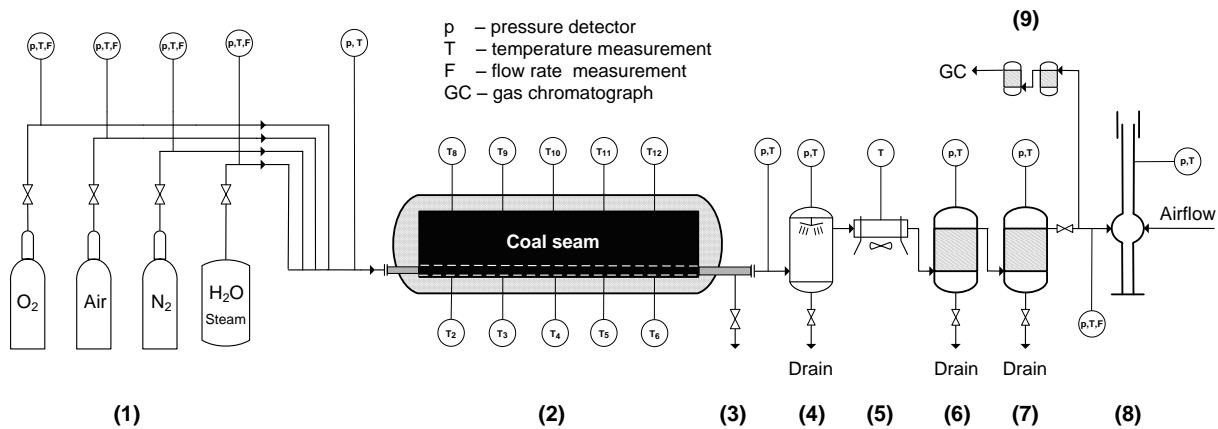
141 The results of previously conducted UCG experiments on large coal samples in a high-  
142 pressure installation under ex-situ conditions [55] were used to reduce these knowledge gaps.  
143 The main aim of these experiments was to examine the effect of pressure and coal rank on the  
144 production of a methane-rich synthesis gas. An innovative element of this work is the  
145 determination of the composition and efficiency of tar based on the analysis of samples taken  
146 directly at the reactor outlet under high pressure conditions (20 and 40 bar). Such ex-situ  
147 studies have not been described in the scientific literature so far, due to the high degree of  
148 complexity and technical challenges related to the sampling procedure. Although there are  
149 several papers documenting on tars being taken directly from the reactor or from its outlet  
150 during the simulation of an ex-situ UCG process [56-59], none of them addressed the impacts  
151 of pressure and coal rank on tar formation. The results presented in the article may therefore  
152 contribute to a deeper understanding of the impact of these parameters on the composition and

153 yield of tar in the UCG process. Furthermore, this knowledge can also come to the aid when  
 154 designing the large-scale in-situ coal gasification plants.

155 **2. Experimental**

156 **2.1. Apparatus**

157 The UCG experiments of interest here were carried out in artificially created coal seams in a  
 158 high-pressure steel reactor. The pressure installation enables simulation of the UCG process  
 159 in the pressure range of 0-50 bar at temperatures up to 1600 °C. A detailed scheme of the ex-  
 160 situ UCG installation is presented in Figure 1.



161 **Fig. 1.** Scheme of the ex-situ UCG installation [55]: (1) reagent supply system, (2) gasification reactor,  
 162 (3) connection for tar sampling, (4) water scrubber, (5) air cooler for process gas, (6,7) gas separators,  
 163 (8) thermal combustor, (9) gas purification module for GC analysis  
 164

165  
 166 The maximum length of the gasified coal seam is 3.05 m, and its quadratic cross-sectional  
 167 area amounts to 0.41 m × 0.41 m. Experiments can be carried out by applying gasification  
 168 agents such as oxygen, air, CO<sub>2</sub>, steam and its mixtures in appropriate proportions. Another  
 169 relevant gaseous medium, nitrogen, is used to establish inert process conditions and for  
 170 cooling the reactor after the gasification experiment is completed. Oxygen, nitrogen and CO<sub>2</sub>  
 171 with a technical purity of (99.5%) are provided by gas cylinders. The source of air is a  
 172 compressor, and the source of steam is a steam generator. All gaseous media are supplied to  
 173 the reactor through metal pipes equipped with temperature and pressure sensors as well as  
 174 mass flow regulators. Temperatures inside the reactor are measured by a set of ten



175 thermocouples (Pt10Rh-Pt) at intervals of 0.5 m. Five thermocouples (T2-T6) measure the  
176 temperatures in the lower part of the coal seam and the other five (T9-T13) that in the upper  
177 part. The raw and hot gas discharge from the reactor through the metal tubes is first cleaned in  
178 a water scrubber, where it also cools down, while tar is condensed and solid particles  
179 precipitated. After an air cooler stage, the gas is additionally cleaned in dry separators and  
180 directed to a thermal combustor. Some share of the purified gas flows to a sampling point for  
181 compositional analysis. For this purpose, the Agilent 3000A Micro GC gas chromatograph is  
182 used to analyze components such as O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> and H<sub>2</sub>S. Gas analysis is  
183 performed every half hour or more often if needed.

## 184 **2.2. Materials**

185 The following coal samples were used for artificial coal seam preparation: a semi-  
186 anthracite Six Feet coal sample received at an open-cast coal mine located in the South Wales  
187 Coalfield (UK) and bituminous coal sample from the Wesola mine in the Upper Silesia Basin  
188 (Poland). The Six Feet coal deposit's average thickness is 1.2 m, and the sampling site was 88  
189 m below the ground level. When it comes to the Wesola coal, the sampling point was 950 m  
190 below the ground level with an average coal seam thickness of 5 m. The classification of the  
191 coals was preceded by a comprehensive physicochemical analysis. The conducted analyses  
192 show significant differences between both coal samples, especially due to the contents of  
193 volatile matter, carbon and oxygen. The results of the proximate and ultimate coal samples  
194 analysis are shown in Table 1. Coal analysis was carried out in the certified laboratory at the  
195 Central Mining Institute GIG according to Polish Standards.

196 The results of the conducted analyses showed that both coal samples differ significantly in  
197 their properties. This is particularly evident in the contents of moisture, ash, volatiles, oxygen  
198 and sulfur. The Wesola coal sample was characterized by a much higher content of these  
199 substances (except for oxygen and carbon) compared to the Six Feet coal sample.

200

201 **Table 1.** Proximate and ultimate characteristics of coals used in the study [55]

Parameter	Unit	Coal sample		Polish Standard
		Six Feet Semi-anthracite	Wesola Bituminous	
As received				
Total moisture W	(%)	1.15	3.60	PN-G-04511:1980
Ash A	(%)	4.61	8.74	PN-G-04560:1998
Volatiles V	(%)	9.92	27.67	PN-G-04516:1998
Total sulphur S	(%)	1.55	0.31	PN-G-04584:2001
Calorific value Q	(MJ/kg)	33.416	28.798	PN-G-04513:1981
Analytical				
Moisture W	(%)	0.84	2.18	PN-G-04560:1998
Ash A	(%)	4.62	8.87	PN-G-04560:1998
Volatiles V	(%)	9.95	28.08	PN-G-04516:1998
Heat of combustion Q	(MJ/kg)	34.414	30.317	PN-G-04513:1981
Calorific value Q	(MJ/kg)	33.527	29.258	PN-G-04513:1981
Total sulphur S	(%)	1.55	0.31	PN-G-04584:2001
Carbon C	(%)	87.31	75.35	PN-G-04571:1998
Hydrogen H	(%)	3.97	4.61	PN-G-04571:1998
Nitrogen N	(%)	1.29	1.20	PN-G-04571:1998
Oxygen O	(%)	0.50	7.65	From difference to 100%
O/C ratio		0.0043	0.0782	
Specific gravity	(g/cm <sup>3</sup> )	1.35	1.40	PN-C-04307:2008

202 \*Oxygen calculated as  $(O^a) = 100 - (W^a) - (A^a) - (C^a) - (H^a) - (S_i^a) - (N^a)$  (%)

203

204 **2.3. Preparation of the coal block for testing**

205 Raw coal samples were cut with a diamond wire saw into pieces with a cross-sectional area of  
206 0.41 m × 0.41 m and a length depending on their shape. At the bottom part of each coal block,  
207 a gasification channel with a cross-sectional area of 0.1 m × 0.1 m was cut out. The coal  
208 blocks were placed in a reactor chamber to create a 3.05 m long artificial coal seam. An  
209 individually dedicated coal seam for each of the four gasification tests was prepared. The total  
210 mass of each seam was between 630 and 664 kg, depending on the type of coal used. The  
211 experimental stand for the high pressure ex-situ UCG tests is shown in Fig. 2.

212

213



(a)



(b)



(c)



(d)

214  
215 **Fig. 2.** An experimental stand for ex-situ UCG pressure tests: (a) cutting a block of coal, (b) a fire  
216 channel cut in a block of coal, (c) loaded reactor before closing, reactor ready for initiate  
217

218  
219

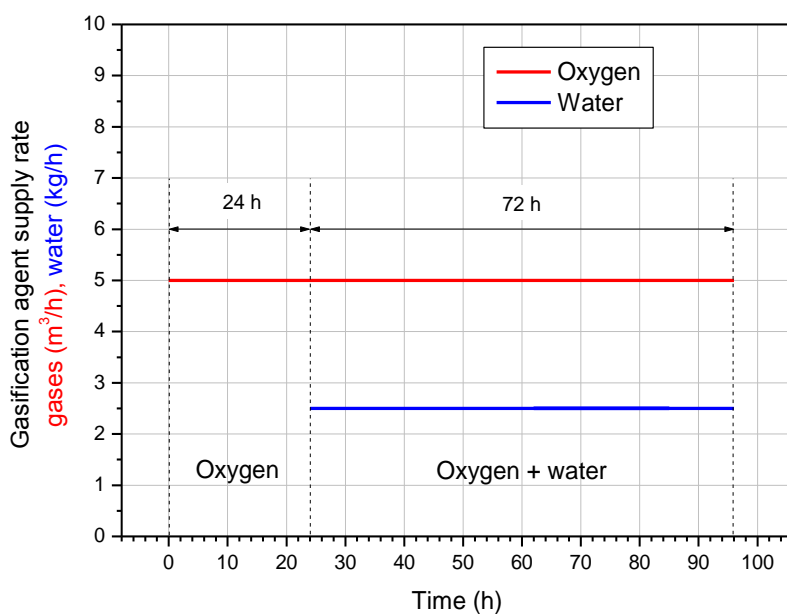
## 220 **2.4. Experimental procedure**

221 For each coal type, the gasification process was carried out at two pressure levels: 20 and 40  
222 bar, resulting in a total of four gasification experiments. The gasification time for each test  
223 amounted to 96 hours using oxygen (of technical purity) and steam as gasification agent. The  
224 oxidant supply rates during each test was  $5 \text{ m}^3 \text{ O}_2/\text{h}$  and  $2.5 \text{ kg H}_2\text{O}/\text{h}$ . The supply rate and  
225 gasification duration were determined based on data from prior tests and adapted to the  
226 geometry of the specific reactor. All relevant technical assumptions of the conducted  
227 gasification tests are presented in Table 2.

228 **Table 2.** Process assumptions for the four gasification tests conducted

Parameter	Value			
Origin of coal	Six Feet		Wesoła	
Coal rank	Semi-anthracite		Bituminous	
Pressure (bar)	20	40	20	40
Gasification time (h)	96	96	96	96
Gasification reagent	O <sub>2</sub> /H <sub>2</sub> O	O <sub>2</sub> /H <sub>2</sub> O	O <sub>2</sub> /H <sub>2</sub> O	O <sub>2</sub> /H <sub>2</sub> O
Mass of raw coal (kg)	650	630	664	661

229  
 230 Each test was started by igniting the coal bed with a pyrotechnic charge. The charge was  
 231 placed in the gasification channel, at a distance of approximately 1 m from the front face of  
 232 the coal seam. The coal was ignited at atmospheric pressure with an oxygen supply rate of 2  
 233 m<sup>3</sup>/h. After igniting the coal, the oxygen flow rate was increased to 4 m<sup>3</sup>/h. After about 2  
 234 hours from the ignition, the reactor was slowly pressurized to the target value. The time at  
 235 which the oxygen concentration in the process gas reached less than 1% was assumed as the  
 236 official start of the gasification process with a final oxygen flow rate of 5 m<sup>3</sup>/h (Fig. 3).



237  
 238 **Fig. 3.** Gasification agents flow rate [55]

239 The pure oxygen injection stage (heating) then lasted for 24 hours and after that steam was  
 240 additionally supplied at the rate of 2.5 kg/h for 72 hours. After the process was completed, the  
 241 reactor was cooled down by nitrogen at a flow rate of 2 m<sup>3</sup>/h. Then, the UCG system was  
 242 opened, cleaned and prepared for the next test.

### 243 2.5. Tar sampling

244 Collection of tar samples was one of the key steps in obtaining material for the proposed  
 245 investigations. During the gasification tests, the tar samples were taken directly from the  
 246 reactor outlet using sorption tubes at approximately 8-hour intervals. The tar sampling periods  
 247 during the gasification experiments are presented in Table 3.

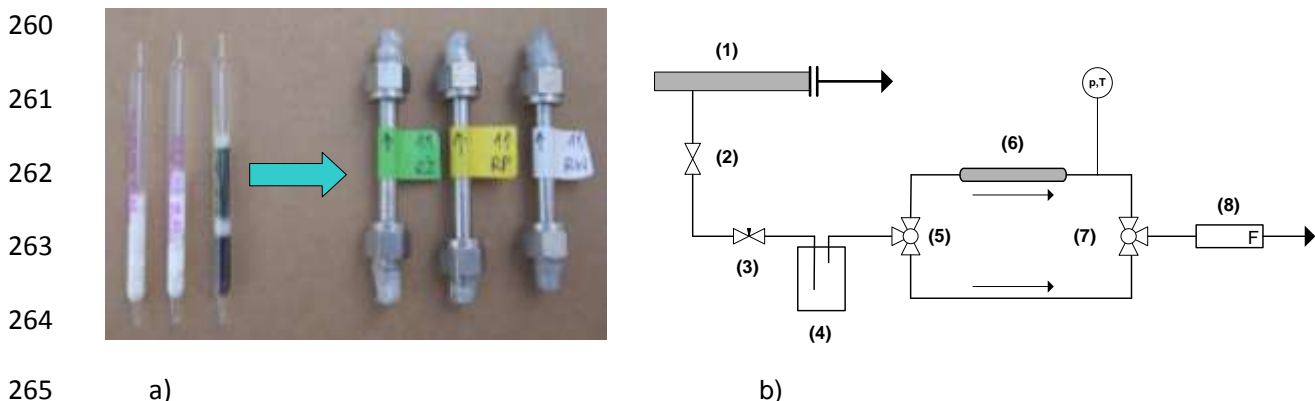
248 **Table 3.** Tar sampling times during the UCG experiments.

Sample No	Time (h)	Time interval between tar samples collection (h)
1	6	6
2	14	8
3	26	12
4	34	8
5	42	8
6	49	7
7	56	7
8	62	6
9	70	8
10	76	6
11	82	6
12	71	9

249 The sampling point was located between the reactor outlet and the gas cleaning section at a  
 250 distance of 0.6 m to the reactor outlet. This sampling setup was especially designed to ensure  
 251 optimum sampling conditions. Tar samples were collected at three different types of sorption  
 252 materials: charcoal (SKC Inc., Anasorb CSC), silica gel (SKC Inc. Silica Gel) and porous  
 253 hydrophobic organic polymer (SKC Inc., XAD-2) for BTEX, phenolic compounds and PAHs  
 254 sorption, respectively. More information on the methodology applied can be found in the  
 255 earlier paper [28].

256 Due to the overpressure occurring in the tar collection system, the sorbents from the  
 257 commercial glass tubes were transferred to pressure resistant steel tubes. Here, the dimensions

258 and packing sequence were maintained as in the original glass tubes (Fig. 4a). A scheme of  
259 the tar sampling system is presented in Fig. 4b.



265 a)  
266 b)  
267 **Fig. 4.** Tar sampling during UCG experiments: a) preparation of high pressure sorption tubes,  
268 b) high-pressure tar sampling set: (1) reactor output pipeline, (2) shut-off valve, (3) pressure reducing  
269 valve, (4) pressure compensator, (5,7) three-way valves, (6) metal sorption tube, (8) flowmeter  
270

271 The sampling procedure was as follows: after fixing the metal sorption tube (6) to the  
272 sampling system, the valves (5,7) were set to flush the system with raw process gas. Valve (2)  
273 was opened and the reducing valve (3) was gradually opened to force the process gas flow.  
274 After establishing constant gas flow conditions, the valves (5,7) were switched to sampling  
275 mode, i.e. tar sorption. Gas flow through the metal sorption tubes was maintained for about  
276 3-4 minutes with the volume recorded by a flowmeter (8) in addition to its pressure and  
277 temperature. Following the measurement completion, valves (2,3) were closed, the sorption  
278 tube was replaced with another one using a different sorbent and the procedure was repeated.

## 279 2.6. Methods of tar analysis

280 After sampling, the sorbents were quantitatively transferred from the sorption tubes into  
281 appropriate analytical solvents. Carbon disulphide, cyclohexane and acetone were used for  
282 BTEX, PAHs and phenols desorption, respectively. The concentrations of individual  
283 compounds in the solutions were determined by capillary gas chromatography using an  
284 Agilent 7890A apparatus equipped with Agilent-5MS column (length 30 m, diameter 0.25  
285 mm, film thickness 0.25 mm). A Flame Ionization Detector (FID) was used to detect BTEX

286 and phenols compounds, and mass spectrometer (Agilent 5975C MSD device) operating in  
 287 the SIM (Selected Ion Monitoring) mode was used to determine the PAHs.

### 288 3. Results

#### 289 3.1. Gas production rate, composition and calorific value

290 Table 4 summarizes the main results of the gasification tests, including the average gas  
 291 production rates, gas compositions and calorific values. The results of the mass and energy  
 292 balance of the tests conducted are presented in Table 5.

293

294 **Table 4.** Average gas production rates, compositions and calorific values [55]

Gasification test	Gas flow (m <sup>3</sup> /h)	Process gas composition (vol. %)							Calorific value (MJ/m <sup>3</sup> )
		CO <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>	CH <sub>4</sub>	CO	C <sub>2</sub> H <sub>6</sub>	H <sub>2</sub> S	
Six Feet 20 bar	9.0	36.3	0.4	19.2	15.8	27.2	0.69	0.38	11.7
Six Feet 40 bar	9.4	41.6	0.6	14.1	19.1	23.2	1.05	0.32	12.1
Wesoła 20 bar	9.3	46.3	0.7	21.6	10.9	19.5	0.64	0.37	9.2
Wesoła 40 bar	9.4	46.1	0.7	17.7	14.8	19.3	0.94	0.51	10.4

295

296 **Table 5.** Calculation of mass and energy balance [55]

Gasification test	Gas yield	Energy in process gas	Average reactor power	Mass of raw coal gasified	Rate of coal gasification	Coal conversion ratio	Energy efficiency
	(m <sup>3</sup> )	(MJ)	(kW)	(kg)	(kg/h)	(%)	(%)
Six Feet 20 bar	864	10,117.5	29.3	436.1	4.5	67.1	69.7
Six Feet 40 bar	903	10,890.2	31.5	455.5	4.7	72.3	71.6
Wesoła 20 bar	896	8243.2	23.9	504.0	5.3	75.9	56.8
Wesoła 40 bar	903	9364.1	27.1	530.2	5.6	80.2	60.8

297

298 Gasification efficiency ( $\eta$ ) was calculated by dividing the energy contained in the process gas  
 299 by the energy contained in the amount of gasified coal, according to the equation:

$$\eta = \frac{\text{Energy in process gas}}{\text{Energy in coal gasified}}$$

300 The data presented in Table 4 indicate that for both coal types used, the gas production rate  
301 increased with gasification pressure. The gas obtained at higher pressure is characterized by a  
302 higher content of methane and ethane as well as a lower content of hydrogen and carbon  
303 monoxide. The process gas produced from the coal of higher rank, i.e. Six Feet sample, was  
304 characterized by a higher content of high-calorific components (methane and hydrogen) than  
305 the gas obtained from the gasification of the lower rank Wesoła coal. As a result, the gas  
306 product from the Six Feet coal gasification test at pressures of 20 and 40 bar was  
307 characterized by relatively high calorific values, i.e. of 11.7 and 12.1 MJ/m<sup>3</sup>, respectively.  
308 These values significantly exceeded the calorific values obtained for the Wesoła coal, i.e. 9.2  
309 and 10.4 MJ/m<sup>3</sup> for 20 and 40 bar, respectively. This proves that the coal rank has a  
310 significant impact on the composition of the gaseous product, and the higher content of  
311 elemental carbon (Six Feet sample) makes it possible to obtain gas with a higher calorific  
312 value. The energy balance of the process (Table 5) indicates that under similar conditions, the  
313 total consumption of the Six Feet coal was lower than Wesoła coal. These differences are due  
314 to the lower reactivity of the Six Feet coal, which is a consequence of its higher degree of  
315 coalification. The data included in Table 5 also show that the energy efficiency of the Six Feet  
316 coal gasification at 20 and 40 bar was significantly higher than that obtained at the same  
317 pressure conditions for the Wesoła coal. For both coal types used in the experiments, the  
318 energy efficiency of the process increased with increasing pressure. These differences are  
319 mainly due to the increase in methane and hydrogen concentrations as a result of the higher  
320 gasification pressure.

## 321 **3.2. Tar analysis**

### 322 **3.2.1. Average concentrations of individual tar components and their groups**

323 For each tested tar sample, BTEX, PAHs and phenols groups were determined, consisting of  
324 5, 16 and 12 individual components, respectively (33 in total). The list of the analysed



325 individual tar compounds in the process gas and their average concentrations are presented in  
326 Table 6. The percentage share of the dominating compounds and groups is additionally  
327 presented in brackets. The total measurement error is estimated at  $\pm 20\%$  of the entire  
328 calculated value and resulted mainly from inaccuracies in measuring the time and flow rate of  
329 the sample through the sorption tubes, measurement of the process gas flow rate, eluent  
330 volume and the measurement accuracy of the analytical techniques used.

331 The data summarized in Table 6 show that in terms of concentration levels, the dominant  
332 group of tar compounds in the process gas in each gasification test is BTEX, followed by  
333 PAHs and phenols. The average concentrations of these compound groups in the gas are in  
334 the range of about 69-86%, 11-28% and 2-4%, respectively. Each of the tested groups is  
335 characterized by one compound with the highest concentration, which are benzene,  
336 naphthalene and phenol, respectively. The average concentrations of these compounds are in  
337 the range of 45-54%, 10-20% and 0.5-2%, respectively. The trends that can be observed in  
338 Table 6, indicating that gasification pressure and coal rank have a significant impact on the  
339 experimental results. Increasing the gasification pressure from 20 bar to 40 bar resulted in a  
340 significant decrease in the average concentrations of all compound groups of compounds,  
341 both for the Six Feet and Wesola coals. The concentration drop value was determined by  
342 dividing the concentration of a specific compound or compound group obtained at 20 bar by  
343 the corresponding values at 40 bar. However, depending on the type of coal used, different  
344 magnitudes of these declines were observed. For the Six Feet coal, increasing gasification  
345 pressure from 20 to 40 bar resulted in a decrease in the average concentrations of BTEX,  
346 PAHs and phenols by 7.6, 3.2 and 7.5 times, respectively. On the other hand, for the Wesola  
347 coal gasification tests, the respective decrease in the concentrations of these groups were  
348 smaller and amounted to 6.2, 3.0 and 6.5 times, respectively.

349

350 **Table 6.** Summary of analysed hydrocarbons and their average concentrations in the process gas  
 351

Compounds	Six Feet (mg/m <sup>3</sup> )		Wesola (mg/m <sup>3</sup> )	
	20 bar	40 bar	20 bar	40 bar
<b>BTEX</b>				
Benzene	657.03 (50.36%)	92.72 (45.23%)	1673.35 (54.36%)	292.65 (52.59%)
Toluene	260.97	28.66	537.11	70.67
m,p-Xylene	122.98	14.37	257.38	33.75
o-Xylene	18.54	3.35	148.11	22.86
Ethylbenzene	13.82	2.34	43.91	10.82
<b>Total BTEX</b>	<b>1073.34 (82.28%)</b>	<b>141.44 (69.00%)</b>	<b>2659.86 (86.40%)</b>	<b>430.75 (77.40%)</b>
<b>PAHs</b>				
Naphthalene	155.84 (11.95%)	40.35 (19.68%)	309.52 (10.06%)	94.12 (16.91%)
Acenaphthylene	4.93	2.23	9.87	4.57
Acenaphthene	2.87	1.48	4.56	2.51
Fluorene	4.79	2.96	6.53	3.92
Phenanthrene	3.99	2.67	5.72	3.37
Anthracene	4.31	2.72	5.24	3.23
Fluoranthene	3.79	2.21	4.38	2.41
Pyrene	3.11	2.59	0.69	0.58
Benzo(a)anthracene	< 0.01	< 0.01	< 0.01	< 0.01
Chryzene	< 0.01	< 0.01	< 0.01	< 0.01
Benzo(b)fluoranthene	< 0.01	< 0.01	< 0.01	< 0.01
Benzo(k)fluoranthene	< 0.01	< 0.01	< 0.01	< 0.01
Benzo(a)pyrene	< 0.01	< 0.01	< 0.01	< 0.01
Indenol(1,2,3-cd)pyrene	< 0.01	< 0.01	< 0.01	< 0.01
Dibenzo(a,h)anthracene	< 0.01	< 0.01	< 0.01	< 0.01
Benzo(g,h,i)perylene	< 0.01	< 0.01	< 0.01	< 0.01
<b>Total PAHs</b>	<b>183.63 (14.08%)</b>	<b>57.21 (27.91%)</b>	<b>346.51 (11.26%)</b>	<b>114.71 (20.62%)</b>
<b>Phenols</b>				
Phenol	31.02 (2.38%)	2.03 (0.99%)	35.45 (1.15%)	2.72 (0.49%)
o-cresol	2.57	0.63	7.03	2.32
m,p-cresol	2.58	0.26	8.25	1.28
2,6-dimethylophenol	1.03	0.37	1.78	0.91
(2,4),(2,5)-dimethylophenol	2.28	0.18	8.54	1.27
3,5-dimethylophenol	1.51	0.35	3.24	1.11
2,3-dimethylophenol	2.25	0.62	4.19	0.19
3,4- dimethylophenol	0.96	0.12	0.94	0.16
2,3,6-trimethylophenol	1.46	1.24	0.73	0.45
2,4,6-trimethylophenol	0.53	0.20	0.54	0.19
2,3,5-trimethylophenol	0.72	0.27	0.66	0.33
3,4,5-trimethylophenol	0.67	0.06	0.78	0.10
<b>Total Phenols</b>	<b>47.58 (3.65%)</b>	<b>6.33 (3.09%)</b>	<b>72.13 (2.34%)</b>	<b>11.03 (1.98%)</b>
<b>BTEX + PAHs + phenols</b>	<b>1304.55 (100%)</b>	<b>204.98 (100%)</b>	<b>3078.50 (100%)</b>	<b>556.49 (100%)</b>

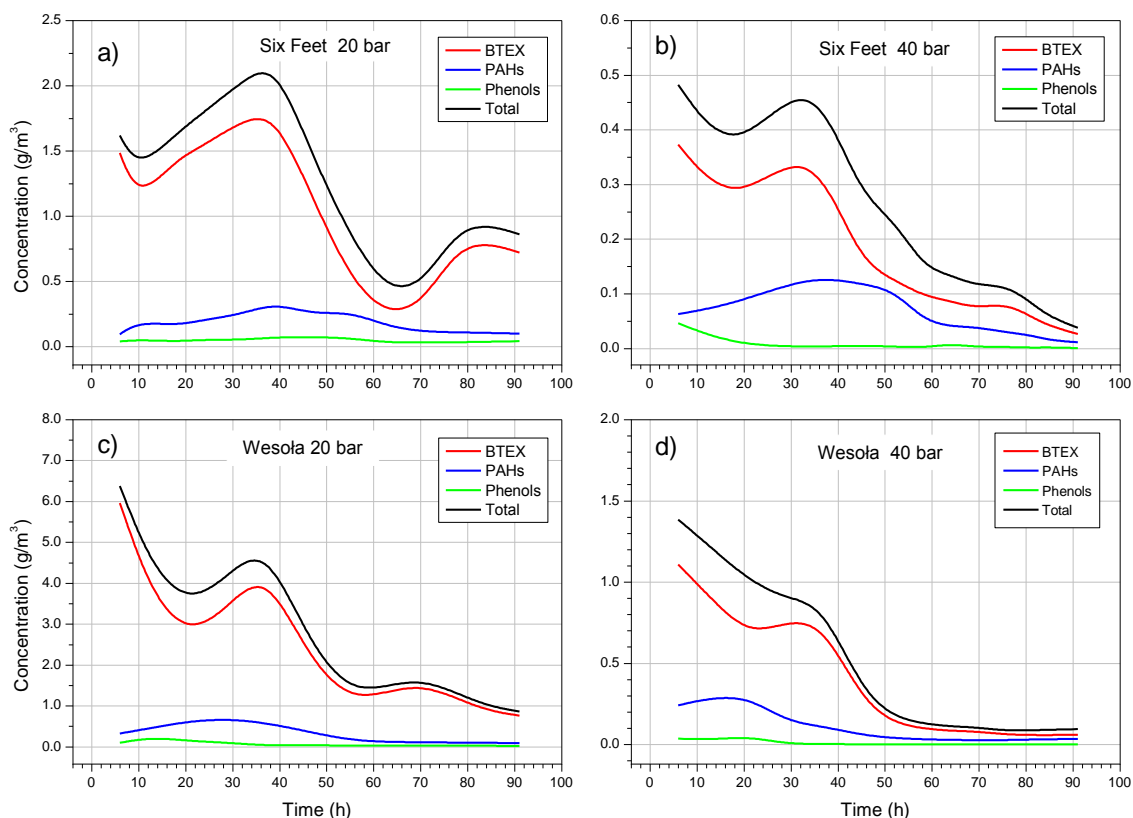
352

353

354 Changes in benzene and naphthalene concentrations were similar to the analogue changes in  
 355 the concentrations of the BTEX and PAH groups, while for phenol as an individual  
 356 component, the change in concentrations was almost twice as high as for the analogue  
 357 changes in the phenols group. It can be noticed that with increased process pressure, the  
 358 decrease in BTEX, PAHs and phenols concentrations is higher for the for Six Feet coal  
 359 compared to the Wesola one. The same dependence occurs for the changes in concentrations  
 360 of individual, dominant components of the analysed groups of tar compounds (benzene,  
 361 naphthalene and phenol).

### 362 3.2.2. Concentrations and percentage shares of BTEX, PAHs and phenols

363 Changes in the concentrations of the particular groups of tar compounds as a function of  
 364 gasification time are presented in Fig. 5.



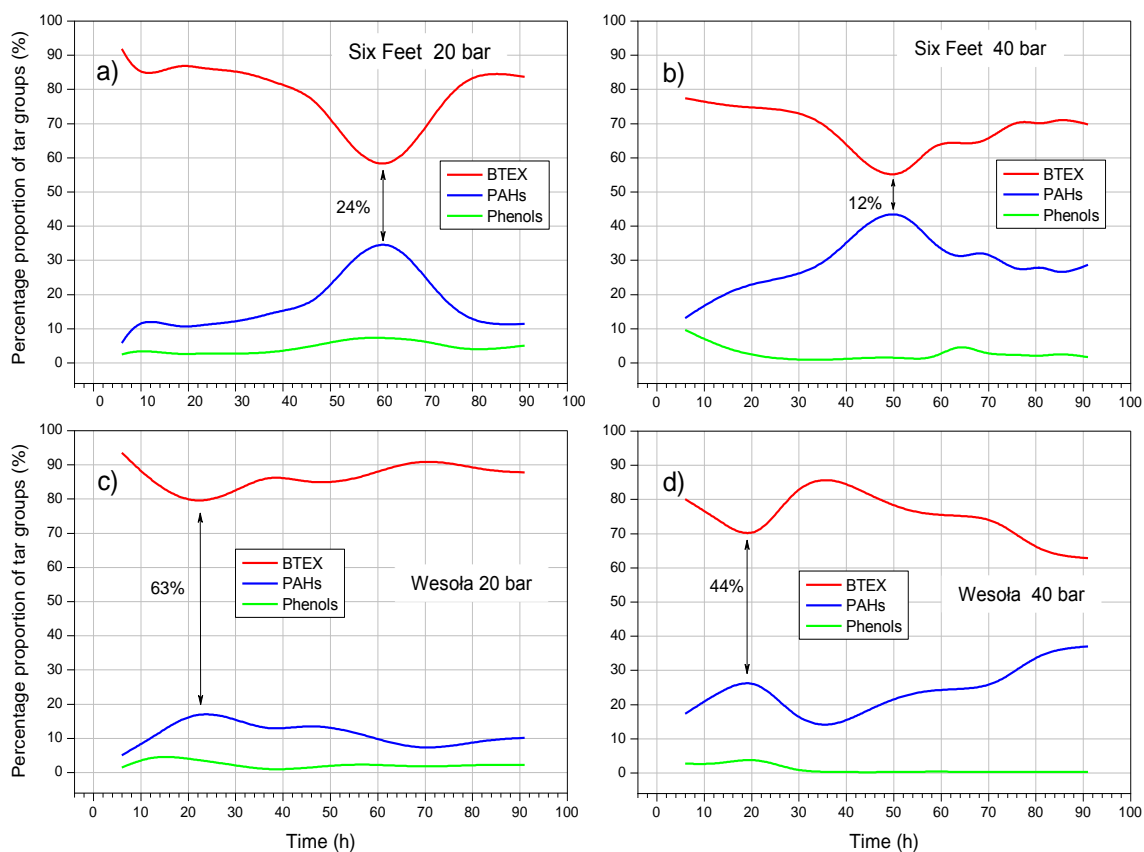
365 **Fig. 5.** Concentration of tar groups as a function of time and gasification pressure for the Six Feet and  
 366 Wesola coals at gasification pressures of a,c) 20 bar; b,d) 40 bar (all samples taken at approximately  
 367 8-hour intervals)  
 368

369 The results show that for all gasification tests, the highest concentrations of the BTEX  
370 compounds in the gas were observed between hours 30 and 40 of the experiment. After this  
371 time, the concentration of BTEX decreased rapidly. Between hours 60 and 80, another  
372 concentration peak was recorded. For both tests with the Six Feet coal, the maximum  
373 concentration of the PAH compounds occurred around hour 40 of the experiment. In the case  
374 of the Wesola coal, maximum PAHs concentrations occurred around hours 20-30 and 10-20  
375 in the 20 and 40 bar experiments, respectively. The maximum concentrations of PAHs for the  
376 Wesola coal occurred earlier than for the Six Feet coal. It was generally found that the peak  
377 concentrations of all tested groups of tar compounds appeared in the first half of the  
378 experiment. This proves that during UCG, tars are released most intensively at the beginning  
379 of the gasification process.

380 Fig. 6 presents the percentage shares of the particular group of the tar compounds under study  
381 over the course of the experiments. Regardless of the process pressure, the highest changes in  
382 the proportions appeared between hours 50-60 for the Six Feet coal, and after the 22nd hour  
383 for Wesola coal.

384 The observed differences in their occurrence times are most likely due to temperature changes  
385 in the reactor (peak temperatures), and consequently, the intensification of cracking and  
386 polymerization reactions.

387 The effect of gasification pressure on the changes in the proportions is evident. Comparing  
388 BTEX and PAHs, the proportions changed by 12% and 19%, respectively, for the Six Feet  
389 and Wesola coals, with an increase in gasification pressure by 20 bar. Figure 6cd  
390 demonstrates that the average content of BTEX compounds is much higher in the tar from the  
391 Wesola coal, whereas the PAHs content is higher in the Six Feet coal tar (Fig. 6ab). These  
392 differences are most likely due to a large difference in the content of volatile matter in the raw  
393 coals, amounting to 27.67% and 9.92% for the Wesola and Six Feet coals, respectively.



394

395 **Fig. 6.** Percentage proportion of tar groups as a function of time and gasification pressure for the Six  
 396 Feet and Wesola coals at gasification pressures of a,c) 20 bar; b,d) 40 bar

397

### 398 3.3. Total yields of the tar compounds

399 The total yields per mass of coal gasified for the individual groups of tar compounds are  
 400 presented in Table 7 and in Fig. 7. In addition, Table 7 also presents the results of calculations  
 401 demonstrating the multiplicity of decreases in the yield of individual groups of tar compounds  
 402 (quotient of yield ratio) with the increase in gasification pressure from 20 to 40 bar.

403 In terms of the amount of raw coal gasified, the total tar yield for the Six Feet coal at  
 404 pressures of 20 and 40 bar was 2.58 and 0.41 g tar/kg coal, while the yield was much higher  
 405 for the Wesola mine coal at 5.48 and 0.95 g tar/kg coal, respectively.

406

407

408

409

410 **Table 7.** Total yields of the particular groups of tar compounds

Group of tar compounds	Six Feet		Wesoła	
	20 bar	40 bar	20 bar	40 bar
Yield (g/kg coal gasified)				
BTEX	2.13	0.28	4.73	0.73
PAHs	0.36	0.11	0.62	0.20
Phenols	0.09	0.01	0.13	0.02
Total	2.58	0.41	5.48	0.95
Quotient of yield ratio at 20 bar to 40 bar				
BTEX	7.6 ↓		6.5 ↓	
PAHs	3.3 ↓		3.1 ↓	
Phenols	9.0 ↓		6.5 ↓	
Total	6.3 ↓		5.8 ↓	

411 ↓ - decrease in yield ratio

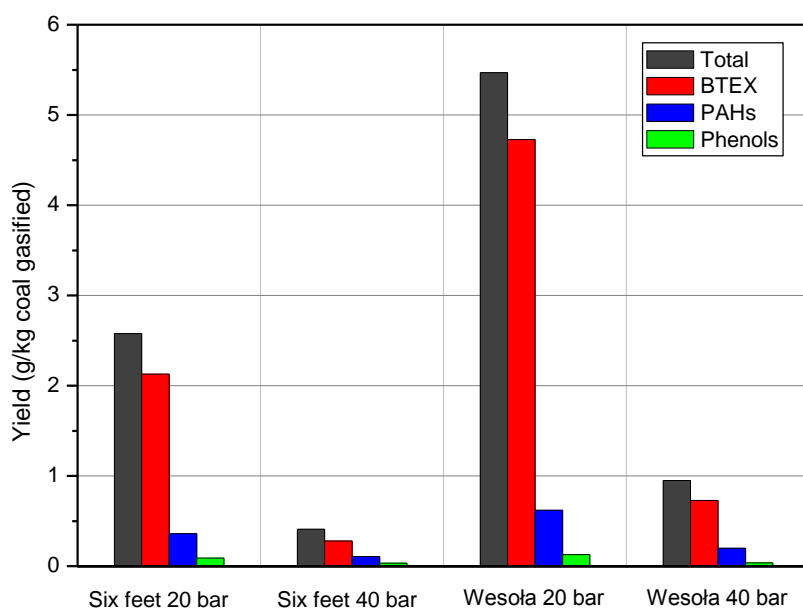
412 These data show that increasing the gasification pressure reduces the yield of tar of the Six  
 413 Feet coal by 6.3 times, and by 5.8 times for the Wesoła coal. Similar dependencies were  
 414 observed for individual groups of the tar compounds, i.e. BTEX, PAHs and phenols. For the  
 415 Six Feet coal, the decrease in the yield of these compound groups was 7.6, 3.3 and 9.0 times,  
 416 and for the Wesoła coal, it was 6.5, 3.1 and 6.5 times, respectively. It is therefore evident that  
 417 yield level reduction is greater for the Six Feet coal compared with the Wesoła one.

### 418 **3.4. Temperature distribution inside the reactor**

419 Temperature changes in the bottom and roof part of the reactor in dependence on the  
 420 gasification time are presented in Fig. 8 and Fig. 9. The data show that up to approximately 48  
 421 hours of the test (first half), the temperature inside the reactor in the case of Wesoła coal  
 422 increased faster compared to Six Feet coal. For example, the average temperature at the  
 423 pressures of 20 and 40 bar was 740 °C and 830 °C, respectively, in the experiments conducted  
 424 with the Wesoła coal at the 30th hour, whereas both pressure levels showed much lower  
 425 temperature, amounting to approximately 460 °C and 540 °C in the tests run with the Six Feet  
 426 coal. The observed effect is most likely related to the lower coalification rate of Wesoła coal  
 427 and, consequently, to its higher reactivity. The maximum gasification temperatures during all

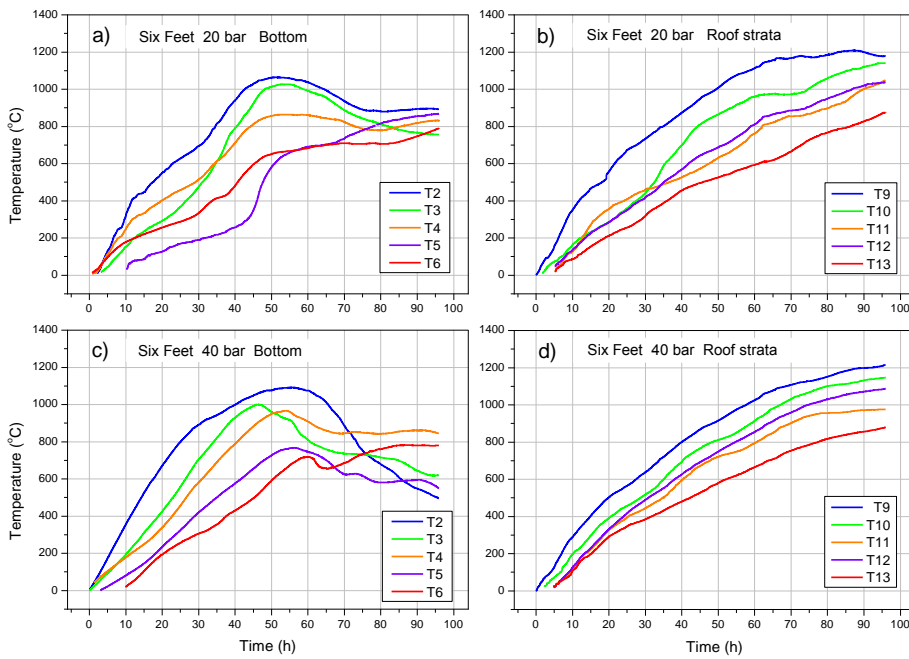
428 tests were approximately 1200 °C and were registered in the roof strata. It should be noted  
429 that the measuring parts of the thermocouples were placed in the ceramic cover of the reactor  
430 at a distance of approximately 5 cm from the reaction chamber. This means that the actual  
431 temperature in the reactor could have been about 50-100 °C higher than the registered one. It  
432 is also characteristic for each experiment that the temperatures in the roof strata were  
433 generally higher compared to the bottom strata. The reason for this is the fact that the ash and  
434 slag produced during gasification have insulating properties and limit the conduction of heat  
435 from the reaction chamber to the bottom of the reactor.

436 In order to estimate the impact of the pressure increase on the temperature in the reactor  
437 during each process, the temperature measurement results from all ten thermocouples were  
438 averaged for the entire gasification time (Fig. 8 and Fig. 9). In the case of Wesola coal, the  
439 average process temperature at a pressure of 20 and 40 bar was 735 °C and 763 °C, while for  
440 Six Feet coal it was 627 °C and 636 °C, respectively. Calculated as a temperature difference,  
441 the impact of increasing the pressure on the grow in the average gasification temperature  
442 amounted 18 °C for Wesola coal and 9 °C for Six Feet coal.



443  
444 **Fig. 7.** Yields of total measured BTEX, PAHs and phenolic compounds per kg of coal gasified

445

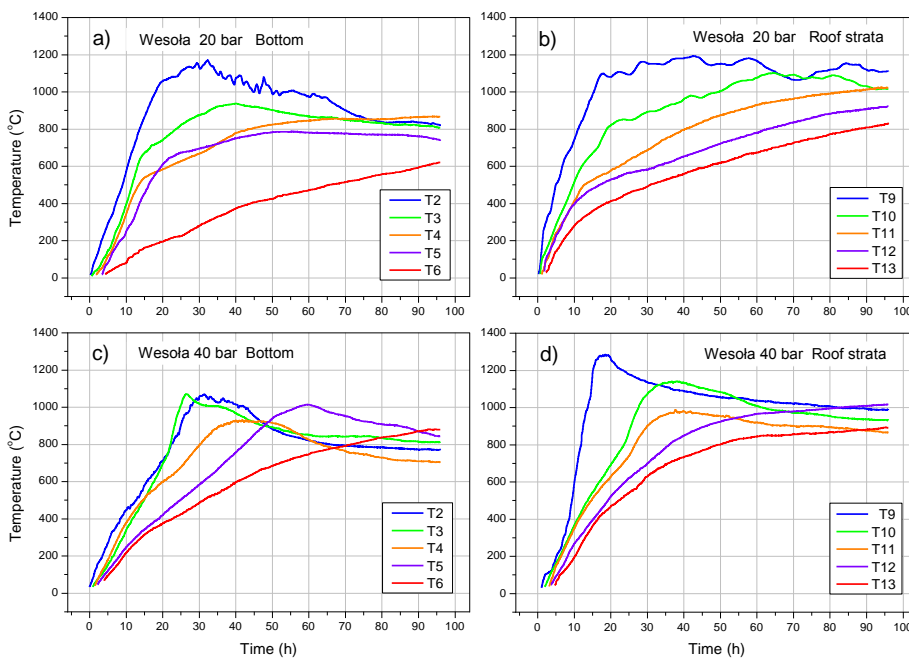


446

447 **Fig. 8.** Temperature distribution during Six Feet coal gasification at 20 and 40 bar [55]

448 a,c) bottom, b,d) roof strata

449



450

451 **Fig. 9.** Temperature distribution during Wesola coal gasification at 20 and 40 bar [55]

452 a,c) bottom, b,d) roof strata

453



#### 454 **4. Discussion**

455 A characteristic feature of each tested tar in terms of its individual composition is the  
456 dominance of benzene, naphthalene and phenol. For the tested groups of tar compounds, the  
457 highest yields were obtained for BTEX, followed by PAHs and phenols. The high content of  
458 the three individual components results from the fact that these are the final products of  
459 thermal degradation of tar and, at the same time, the most thermodynamically stable products  
460 of tar decomposition.

461 The increase in pressure during the experiment, regardless of the gasified coal type, caused a  
462 decrease in the BTEX and phenols concentration in the process gas, while the concentration  
463 of PAHs increased. The experimental results confirm the dependence of two important  
464 process parameters, which are coal rank (coalification degree) and the applied gasification  
465 pressure.

466 Considering the effect of the coalification degree on the yield of the tar products, it was  
467 found that the tar yield of the low-coalified *Wesoła* coal, regardless of the applied pressure,  
468 was higher than the that of the high-coalified *Six Feet* coal. This was due to the higher content  
469 of volatile matter in the *Wesoła* coal (27.67%) compared to the *Six Feet* one (9.92%). It has  
470 also to be noted that the increase in pressure was accompanied by a significant decrease in tar  
471 yields, which were higher for the *Six Feet* coal than for the *Wesoła* one.

472 From the collected temperature distribution data, it can be concluded that there is a positive  
473 correlation between the process pressure and temperature, i.e. an increase in gasification  
474 pressure results in an increase in temperature. Increasing the oxygen pressure accelerates the  
475 gasification reactions, which results in a faster coal conversion into a synthesis gas. A higher  
476 rate of gasification can also increase the thermal efficiency of the process as more heat is  
477 generated from exothermic reactions. This, in turn, can result in higher temperatures in the  
478 reactor. This phenomenon was particularly evident during the first half of gasification

479 wherein the mean working temperature escalated at a swifter rate for Wesola coal than for Six  
480 Feet coal. This is probably related to the specific properties of the Wesola coal: its lower  
481 coalification rank, and consequently its higher reactivity. A certain measure of coal reactivity  
482 can be the O/C ratio in the coal [44]. The higher the ratio, the more reactive it is. Elemental  
483 analysis of both raw coals showed that the O/C molar ratio of the Wesola and Six Feet coals  
484 was 0.0782 and 0.0043, respectively. This confirms the earlier assumption that coal from the  
485 Wesola mine is more reactive than Six Feet coal.

486 Temperature values in the reactor have a significant impact on the formation and  
487 decomposition of BTEX compounds, PAHs and phenols [62]. During coal pyrolysis, BTEX  
488 compounds are formed in the temperature range of 500 °C to 600 °C and begin to decompose  
489 above 700 °C. Phenols typically form between 400 °C and 700 °C and begin to decompose  
490 above 700 °C. PAHs compounds are commonly formed at higher temperatures, ranging from  
491 700 °C to 1000 °C. The minimum decomposition temperature of these compounds oscillates  
492 in the range of 900-1000 °C. The presented data show that phenols have the lowest  
493 temperature of formation and decomposition. For comparison, the respective temperatures are  
494 slightly higher for BTEX and the highest for PAHs compounds.

495 Based on an analogy with the coal pyrolysis process (see Introduction), it can be  
496 assumed that an increase in process pressure impedes the release of tar vapors from the coal  
497 matrix and prolongs its residence time in the reactor. The extended residence time of tar in the  
498 hot reaction zone induces the intensification of secondary reactions in this way that the tar  
499 obtained from coal gasification under high-pressure conditions contains fewer BTEX and  
500 phenols, and more PAH compounds, and its yield is lower.

501 It is problematic to separate the influence of the increase in temperature and pressure,  
502 because both mutually affect the formation and transformations taking place in the produced  
503 tar. The assessment of which of these two factors is decisive for tar formation can be executed

504 based on changes in the average process temperature and data on the composition and  
505 efficiency of the obtained process gas.

506 The analysis of the data presented in section 3.4 (Temperature distribution inside the reactor)  
507 proves that increasing the gasification pressure resulted in an increase in the average  
508 temperature in the reactor by 18 °C for Wesoła coal and 9 °C for Six Feet coal. The observed  
509 increase is relatively small, which may mean that the increase in pressure did not have a  
510 significant impact on the increase in the average gasification temperature. If the increase in  
511 temperature would have been of greater importance, a significant enhancement in hydrogen  
512 and/or methane-rich gases would have been observed as a result of thermal tar decomposition.  
513 However, no such changes were observed: the gas yield for both coal types of coal was  
514 almost identical at certain pressure levels.

515 The data in Table 4 show that for each type of coal, an increase in the process pressure  
516 resulted in an increase in the methane concentration with a simultaneous decrease in the  
517 hydrogen concentration in the process gases. This occurrence was caused by the  
518 intensification of methanation processes, as a result of which, at higher pressures, the amount  
519 of methane produced increases at the expense of a decrease of hydrogen production.

520 As discussed earlier, the gas composition changed, but not as a result of tar decomposition,  
521 but due to an increase in gasification pressure. Here, the main factor affecting these changes  
522 was the increase in the gasification pressure.

523 The analysed data show that both for the Six feet and Wesoła coals, the increase in the  
524 gasification pressure from 20 to 40 bar contributed to a substantial reduction in the total  
525 amount of all analysed tar compounds of about 600%. It is worth noting that this value  
526 significantly exceeds (about 30 times) the quantities which concerned the 20% decrease in tar  
527 yield obtained by increasing the pressure from 8.14 to 21.4 bar in the pyrolysis process [52].

528 Such a high difference in efficiency reduction can result from many reasons. The most

529 important is that the mentioned 20% decrease was determined on the basis of small-scale  
530 laboratory pyrolysis tests, while the actual UCG process differs from coal pyrolysis in  
531 numerous process parameters. One of the most significant differences is the method of heat  
532 supplied to the reactor. During coal pyrolysis, heat needs to be externally supplied, whereas in  
533 the UCG process a portion of the coal within the reactor is combusted, producing a certain  
534 amount of the tar [63]. In addition, the markedly higher temperatures and longer residence  
535 times of tar vapors in the reactor during UCG may significantly contribute to a change in the  
536 composition of UCG tar and the reduction in its yield compared to coal pyrolysis under  
537 comparable pressure conditions.

## 538 **5. Conclusions**

539 Based on the results of the executed experiments, the following conclusions were formulated:

- 540 1) The dominant tar compounds in all analysed samples, ranked in order of decreasing  
541 concentration are: benzene, naphthalene and phenol. As for the content of the tested  
542 compounds in the context of group concentrations, the highest levels were determined for  
543 BTEX, followed by PAHs and phenols. Their high presence in the tar results from an  
544 intensified thermal degradation of its components, occurring during coal gasification.
- 545 2) Increasing the pressure of the process leads to changes in the composition and efficiency  
546 of the tar products, causing a decrease in the concentration of BTEX and phenols, and a  
547 simultaneous increase in the concentration of PAHs.
- 548 3) The degree of coalification of the used raw coal affects the tar product yield. The low-  
549 coalified *Wesoła* coal produces more tar compared to the high-coalified *Six Feet* coal.  
550 This difference results from the higher content of volatile substances in the *Wesoła* coal,  
551 which is more susceptible to thermal decomposition, and consequently to the formation of  
552 tar.

- 553 4) Both pressure and temperature have the potential to influence the process of tar formation  
554 and conversion. Based on the research results, it is evident, that the most significant factor  
555 affecting the observed changes in tar composition and yield is a significant increase in  
556 gasification pressure. This increase most likely restricts the release of tar from the coal  
557 matrix and prolongs its residence time in the reactor. In turn, a longer residence time  
558 favors secondary thermal degradation reactions, leading to changes in the composition of  
559 the tar.
- 560 5) Compared to decrease in tar yield during coal pyrolysis under laboratory conditions (at the  
561 similar pressure rate), the decline in UCG tar yield with increasing process pressure is  
562 more noticeable. The reasons for this occurrence are partial combustion (oxidation) of  
563 coal, tar combustion, higher temperatures and probably longer residence time of tar vapors  
564 in the hot zone of the reactor.

565

#### 566 **CRedit authorship contribution statement**

567 MW – Conceptualization, Validation, Investigation, Writing-Original Draft, Writing-  
568 Review&Editing, Visualization, Formal Analysis. WB – Investigation, Visualization,  
569 Writing-Original Draft, Writing-Review&Editing, Methodology. KK – Conceptualization,  
570 Methodology, Project administration, Funding acquisition, Supervision.

571 MP-S – Investigation, Visualization. MS – Investigation.

572 HRT – Conceptualization, Validation, Writing-Review&Editing

573 RZ, SS, SM – Methodology, Validation, Writing-Review&Editing

574 TK, CO – Conceptualization, Methodology, Validation, Writing-Review&Editing

575

576 All authors have read and agreed to the published version of the manuscript.

577

578 **Declaration of Competing Interest**

579 The authors declare that they have no known competing financial interests or personal  
580 relationships that could have appeared to influence the work reported in this paper.

581

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