1 ## CO$_2$ Gasification of Charcoals Produced at Various Pressures

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8 **HIGHLIGHTS:**

9 **-** CO$_2$ gasification reactivity of charcoals is strongly influenced by carbonization pressure

10 - Larger charcoal particle size results in lower CO$_2$ gasification reactivity

11 - CO$_2$ gasification reactivity of charcoals are enhanced by their alkali content

12

13 **ABSTRACT:**

14 In this work, stem wood and branches and tops of Norwegian spruce and birch were carbonized
15 at different pressures, producing charcoals of which the CO$_2$ gasification reactivity was studied
16 by means of a thermogravimetric analyzer operated isothermally at 850 °C. The results reveal
17 that the gasification reaction rates of charcoals produced under higher pressures was lower than
18 those produced at the atmospheric pressure. Clear correlations between the CO$_2$ gasification
19 reactivity of the charcoals and their fuel and chemical properties, including the catalytic effect
20 of the inorganic matter, were observed. The semi-empirical power law kinetic model described
21 well the gasification behavior with high fit quality. The activation energy was found to be within
22 140-160 kJ/mol, whereas the reaction order varied in the range of 0.4-0.6.

23 **Keywords:** Flash carbonization, charcoals, CO$_2$ gasification, high-pressure pyrolysis, kinetic
24 modelling.

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1. INTRODUCTION

Carbon dioxide (CO_2) is the main greenhouse gas contributing to global warming. In 2014, the global CO_2 emission, arising from fossil fuel combustion and industrial processes, increased by 0.5% and amounted to 35.7 billion tons [1]. Due to the climate concerns, several different technologies and measures have been developed and employed to either decrease the CO_2 emission, capture and store it (Carbon Capture and Storage - CCS), or utilize it for other purposes such as producing biofuels and chemicals (Carbon Capture and Utilization - CCU). An appealing CCU approach is to use CO_2 as gasification agent for gasification of renewable biogenic feedstock through the Boudouard reaction wherein carbonaceous materials are gasified. This can play a crucial role in reducing CO_2 emissions [2-4], by substituting fossil based transportation fuels. The process can be integrated with other industrial processes that release intensive amounts of CO_2 such as coal power plants or cement industry. This would be a turlly green solution for CO_2 reduction.

In addition to this, CO_2 gasification of charcoal produced from woody biomass has appeared as a promising technology for bioenergy applications, as well as mitigation of air pollution. Compared to the direct biomass gasification, charcoal gasification advances considerably the performance of downstream equipment since less tar is produced. Moreover, the physical and chemical properties of charcoal are better than raw biomass regarding the high energy density on a mass basis, good grindability and relatively low ash content, resulting in reduced logistic cost and energy efficiency improvement for charcoal as briquettes or pellets. The producer gas containing mainly CO provides a potential pathway for production of hydrogen through the water-gas shift reaction and the synthesis of liquid fuel via the Fischer-Tropsch process in combination with H_2 or other chemicals [5]. However, today carbonization processes for charcoal production in idustry are inefficient, of which the charcoal yield is low and the fixed carbon yield is far from the theoretical yield [11]. For instance, a charcoal yield in the range of 21.6 to 34.2% have been obtained from Kenyan earth mouth kilns [12] whereas the traditional kilns in Madagascar and Rwanda reach only approx. 8-9 % [13]. The low efficiency of charcoal production might lead to the deforestation and finally results in global warming [12, 14, 15]. Therefore, it is necessary and possible to increase the carbonization efficiency of industrial processes, considering the predicted theoretical yield. Indeed, it has been demonstrated that elevated pressures can improve the charcoal yield as well as fixed carbon yield [16, 17].

60 On the other hand, carbonization conditions are proven as important factors affecting the
61 properties of charcoal and consequently their CO_2 gasification reactivity. Cetin et al. found that
62 the biomass charcoal reactivity increases with increasing pyrolysis heating rates and decreasing
63 pyrolysis pressure [6]. It is because at high heating rate, the fast volatile matter release creates
64 an internal overpressure in fuel particles, causing coalescence of smaller pores and enlarging
65 internal pores [7, 8]. On the other hand, a lower pyrolysis pressure allows higher reactivity due
66 to a larger surface area and a reduced graphitization in the charcoal structure [6]. This is also
67 consistent with the fact that the amount of low reactivity secondary charcoal obtained from the
68 condensation of tarry vapor is significantly reduced for pyrolysis of biomass under low pressure
69 [9]. Recently, an attempt to study non-isothermal CO_2 gasification kinetic of charcoals prepared
70 at atmospheric pressure and low heating rate carbonization of Norwegian wood and forest
71 residue was carried out by Wang et al. [10]. It was found that the CO_2 gasification activation
72 energies were nearly identical for chars produced from wood and forest residues, about 221 and
73 218 kJ/mol, respectively. However, there is still a lack of comprehensive understandings of the
74 influence of the carbonization process, particularly high pressure flash carbonization, on the
75 CO_2 gasification reactivity of charcoal, despite the fact that high pressure carbonization is of
76 great interest since it allows a high charcoal yield. High pressure carbonization also leads to
77 significant differences in the physical and chemical properties of the produced charcoals
78 compared to those generated from atmospheric pressure carbonization due to the secondary
79 charcoal formation as a result of the cracking and decomposition of tarry vapor [13]. The
80 oxygen content of charcoal produced at high pressure for instance was reported to be higher
81 than that produced at lower pressure while the carbon content experienced a reserved direction
82 [18]. However, while Takarada et al. [19] reported that the CO_2 gasification reaction rate was
83 not influenced by the presence of oxygen in the coal char, Matsumoto et al. [20] reported an
84 opposite trend. This suggests a need of further investigation in the field. The work presented in
85 this present paper was therefore carried out to address these issues, focusing on the effect of
86 carbonization pressure and charcoal particle size on the CO_2 gasification reactivity of the
87 produced charcoal. In addition, the influence of inorganic compounds as well as elemental
88 compositions on charcoal reactivity is also quantitatively evaluated.

89 **2. EXPERIMENTAL METHOD**

90 **2.1 Charcoal production and characterization**

91 Stem wood and forest residues originating from Norwegian spruce and birch forests were
92 studied in the present work. The samples were harvested from a local forest in southern Norway
93 (59°.63' N and 9°.14 ' E). After harvesting, the whole trees were further cut and sorted into stem
94 wood and forest residues containing mainly branches and tops (GROT). The sorted samples
95 were then chipped into small pieces and dried at 105 °C for 24 hours. Part of the dry stem and
96 forest residue wood chips were milled into particles smaller than 1 mm in size for further
97 characterization and charcoal preparation by means of a thermogravimetric analyzer (Mettler
98 Toledo TGA 851^e). The charcoal produced this way was used as the reference (base case) for
99 the evaluation of the charcoals produced at elevated pressures via flash carbonization. For this
100 purpose, an amount of 0.2 gram of the ground samples was loaded in an open crucible and
101 placed into the TGA furnace, which was purged with pure nitrogen with a flow rate of 100
102 mL/min, at ambient temperature for 30 minutes. After purging, the loaded crucible was heated
103 up to 500 °C, at atmospheric pressure (1 bar) and a heating rate of 10 °C/min. The charcoal
104 produced from each experiment were collected and stored for further CO_2 gasification reactivity
105 study.

106 The main part of the dry stem wood and forest residue wood chips was used for charcoal
107 production using a laboratory scale flash carbonization reactor operated at different pressures.
108 In a typical flash carbonization experiment, a measured amount (0.5-1.3 kg) of feedstock was
109 placed into a cylindrical canister that was loaded into the flash carbonization reactor [21, 22].
110 Pressurized air then purged into the flash carbonization reactor to produce the desired pressure.
111 Electrical power was delivered to a heating coil in the bottom of the reactor. Then ignition of
112 the feedstock at the bottom of the reactor took place and the heater was turned off. Following
113 the ignition, compressed air was delivered to the top of the reactor and flowed downwards
114 through the feedstock bed. At the same time, ignition caused flash fire of the feedstock and the
115 flame front moved upward and against the flow of air, trigging the conversion of the feedstock
116 into carbon. Gas was released from the bottom of the reactor to maintain the pressure (7.9 and
117 21.7 bar in the present work) within the reactor at a specified level. The peak temperature of
118 this carbonization process was about 500 °C. The airflow was halted as the sufficient amount
119 of air had been delivered to ensure carbonization of the feedstock bed, where after the reactor
120 was depressurized and cooled down. The charcoal product was then removed from the reactor
121 for further analysis. Further details about the experimental set-up can be found elsewhere [22].
122 Note that regarding the operating conditions of this flash carbonization reactor, the charcoals

123 were generated at slow heating rate due to the heat and mass transfer limitations, considering

124 the relatively large particle size of the feedstock.

125 The charcoals produced by using the TGA and flash carbonizer were ground and sieved to

126 collect the fraction of particles smaller than 60 μm in size. This relative small particle size was

127 selected to minimize heat and mass transfer limitations in further kinetic studies [23, 24].

128 Additionally, for the charcoal produced at 21.7 bar, samples with particle sizes of 1-2 mm were

129 also used to test their reactivity for comparison purpose.

130 Proximate analysis of produced charcoals was performed according to procedures described in

131 ASTM standard D1762-84, whereas the ultimate analysis was determined by employing an

132 elemental Eurovector EA 3000 CHNS-O Elemental Analyser. The concentrations of inorganic

133 elements in the produced charcoal were measured by means of an inductively coupled plasma

134 optical emission spectrometry (ICP-OES) according to the standard CEN/TS 15290:2006.

135 **2.2 Gasification Procedures**

136 For each TGA run, about 2 mg of charcoal was loaded in an alumina crucible of 150 μL in a

137 TGA (Mettler Toledo TGA/SDTA851^e). Because of the highly endothermic charcoal

138 gasification (172 kJ/mol for CO_2 gasification of carbon to CO), a small amount of sample was

139 chosen to avoid the self-cooling which can create a temperature gradient within the sample bed

140 in the crucible. The TGA with the loaded crucible was first purged with N_2 for 30 min at room

141 temperature before starting the heating program, to eliminate the presence of O_2. Then, the TGA

142 was heated up to 850 ^{o}C at a heating rate of 13 K/min. During the devolatilization process, the

143 N_2 gas flow through the TGA was maintained at a rate of 100 ml/min. After reaching the

144 temperature of 850 ^{o}C, the flow of N_2 was switched off and a CO_2 gas flow of 100 ml/min was

145 turned on, introducing a CO_2 atmosphere in the TGA furnace. The temperature of 850 ^{o}C in the

146 TGA furnace was maintained for 120 minutes to complete the gasification process. Because of

147 the small sample weight, the buoyancy effect may be significant. Therefore, it is a must to run

148 a blank curve which is then subtracted from the experimental curves.

149 **2.3 Kinetic Modelling**

150 In general, the CO_2 gasification of charcoal can be simplified as the reaction of CO_2 and carbon

151 to produce carbon monoxide:

152 $$C + CO_2 \rightleftharpoons 2\,CO \qquad \Delta H = 172 \text{ kJ/mol}$$
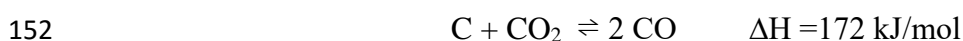
153   The rate of conversion can be expressed in the form of Eq. (1) [25]

$$\frac{d\alpha}{dt} = k(T, pCO_2) \cdot f(\alpha) \qquad (1)$$

155   In Eq. (1), k is the reaction rate constant based on the reaction temperature T, P_{CO_2} is the partial
156   pressure of CO_2. α is the conversion degree defined according to Eq. (2).

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \qquad (2)$$

158   Where m_o, m_f, and m_t are the initial mass, the final mass, and the mass at time t of the sample
159   under investigation, respectively.

160   If the partial pressure of CO_2 is assumed to be constant during the gasification process, the
161   reaction rate constant is then represented by the Arrhenius equation as below:

$$k = A \cdot e^{\frac{-E_a}{RT}} \qquad (3)$$

163   A, R and E_a stand for the pre-exponential constant (min^{-1}), universal gas constant (8.314
164   J/mol.K) and activation energy, respectively.

165   Various models have been proposed to represent the kinetic of charcoal gasification and some
166   of them are summarized in Table 1. Among these models, the three first models are the most
167   widely employed to evaluate CO_2 gasification reactivity of biomass charcoal [26]. A major
168   advantage of these models is their simplicity resulting in less computational efforts and
169   applicability for a broader range of samples compared to other models. Levenspiel (1975) also
170   argued that it might be of little use to select a complicated model describing minor reality [27].
171   However, it is worthy to remark that every model tends to be specific and its general
172   applicability is limited [28, 29]. Therefore, a screening test was made for the models presented
173   in Table 1, from which the best result was obtained for the traditional model (#4). This model
174   is actually a semi-empirical model and sometime referred to as a homogeneous model with n^{th}
175   order.

2.4 Numerical method

177   Curve development and fitting for the adopted model was carried out and optimized by applying
178   the least squares method, minimizing the objective function as given below:

$$S = \sum_{i=1}^{N} \left(\left(\frac{d\alpha}{dt}\right)_{Exp.,i} - \left(\frac{d\alpha}{dt}\right)_{Simulated,i} \right)^2 \qquad (4)$$

6

180   Where $\left(\frac{d\alpha}{dt}\right)_{Exp}$ and $\left(\frac{d\alpha}{dt}\right)_{Simulated}$ are respectively the experimental and simulated conversion

181   degree, and N is the number of experimental points. The quality of curve fitting is numerically

182   quantified by Eq. (5).

183
$$Fit\ (\%) = \left(1 - \frac{\sqrt{\frac{S}{N}}}{\left(\frac{d\alpha}{dt}_{Exp.}\right)_{max}}\right).100\%$$
     (5)

3. RESULTS AND DISCUSSION

3.1 Charcoal characteristics

186   The characteristics of the tested charcoals together with the charcoal yield obtained from flash

187   carbonization processes are summarized in Table 2. The concentrations of inorganic elements

188   in the produced charcoals are listed in Table 3. As can be seen from Table 2, the charcoals

189   produced at 21.7 bar contain higher oxygen contents than the charcoals produced at 7.9 bar,

190   whereas the carbon contents exhibit an opposite trend. In addition to this, higher volatile matter

191   and lower fixed carbon contents are consistently observed for the charcoals produced at 21.7

192   bar in comparison with those produced at 7.9 bar. The mechanism for this phenomenon can be

193   explained by the fact that secondary char forming reactions are enhanced at elevated pressures,

194   while the vapor residence time within the char matrix prolonged [30]. As a result, also the ash

195   content decreases with increasing carbonization pressures and charcoal yields except for the

196   case of birch GROT charcoal which when produced at 21.7 bar induced slightly higher ash

197   content compared to that produced at 7.9 bar.

198   On the other hand, from Table 3 one can see that the amount of Ca in all of the charcoal samples

199   is dominating compared to the others. It is because Ca is an essential macronutrient for plant

200   growth which is transported from the soil to the tree in an aqueous solution [31-33]. However,

201   other minor elements such as alkali metals, could be of high importance with respect to catalytic

202   effects. Noticeably, birch GROT and spruce GROT contain higher concentrations of these

203   elements than their corresponding stem woods. It is reasonable because the biologically active

204   tissues of the tops and branches need more indigenous mineral matter for its growth [34].

205   Fig. 1 presents scanning electron microscope (SEM) images of birch charcoals produced at

206   atmospheric pressure, 7.9 and 21.7 bar. In the present work, since the intrinsic gasification

207   reactivity was studied via a TGA, each charcoal sample was ground first in a mortar with the

208   same grinding time for reducing particle size and homogenizing purpose. As a result of this, the

charcoal samples after grinding contained mainly particles with size smaller than 60 µm. For these very fine particles, the original structures hardly remained as shown in the SEM images. However, the SEM analyses reveal that the charcoals produced under pressure in the flash carbonization reactor had better grindability and appeared as thin flakelike particles with smooth surfaces. On the other hand, the charcoals produced in the TGA retained a partially fibrous structure with openings, indicating large surface area of the TGA charcoals. This promotes higher gasification reactivity of charcoals produced at atmospheric pressure compared to those produced at elevated pressures.

3.2 Effect of Carbonization Pressure on CO_2 Gasification Reactivity of Charcoal

The gasification reactivity is normally quantified by a reactivity index, *R,* which is defined and related to the reaction rate according Eq. 6 and Eq. 7 below [35-37]:

$$R = \frac{0.5}{\tau_{0.5}} \tag{6}$$

$$R = \frac{-1}{w}\frac{dw}{dt} = \frac{1}{1-X}\frac{dX}{dt} \tag{7}$$

where $\tau_{0.5}$ is the time required to reach 50% of charcoal conversion degree; w and X is mass and conversion degree. The value of R is often calculated through the correlation between the conversion degree and time relationship. From a terminological point of view, the reactivity and reaction rate are not often distinguished from each other and are used equally. In fact, Eq. 6 indicates a linear proportional relation between the reactivity index, R, and reaction rate; thereby, they are equivalent.

Fig. 2 presents the effect of carbonization pressure on charcoal gasification reactivity towards CO_2, of which Fig. 2A is for birch charcoals and Fig. 2B for spruce charcoals. As shown in Fig. 1A, birch charcoal reactivity in CO_2 decreased with increased carbonization pressure. In addition, the decreasing trend in reactivity of the charcoal produced from birch stem wood was more pronounced than that of the charcoal from birch GROT. For the spruce charcoals the trend is overall similar to that of the birch charcoals, except for the unexpected variation at 21.7 bar in Fig. 2B. Except for the latter, the trend is in good agreement with the prior works that can be found from literature. Cetin and co-workers for example reported that charcoal produced at 20 bar had three times lower reactivity compared to the one produced at atmospheric pressure. The observed trend was explained by the fact that the higher carbonization pressure reduces the charcoal porosity and surface area [6]. Indeed, this observation was confirmed through the SEM

239   images and discussed in section 3.1. As a matter of fact, the volatile matter release slowly from

240   the charcoal particles due to high external pressures, resulting in insignificant enlargement of

241   pore structure. In addition, it should be noted that the formation of lower reactivity charcoal

242   obtained from the condensation of tarry vapors secondary reactions of tars in the vapor phase

243   is enhanced at high pressure pyrolysis [38]. To sum up, the CO_2 gasification reactivity of

244   charcoal is reduced with increasing pressures during carbonization.

245   On the other hand, the gasification reactivity of charcoals from birch GROT and spruce GROT

246   were higher than that of charcoals produced from birch and spruce stem woods at identical

247   conditions, respectively. This is probably due to the higher ash contents of the residues

248   compared to their stem woods as shown in Table 2, which to certain extent may act as catalysts

249   for promoting gasification of charcoal [39, 40]. It is widely believed that the presence of

250   inorganic metals such as alkali metals (K, Na) and Ca accelerates the CO_2 gasification of woody

251   biomass materials and charcoal derived from them [41, 42]. However, the differences in

252   gasification reactivity of studied charcoals become insignificant for the charcoals produced at

253   7.9 bar and 21.7 bar. Interestingly, the spruce GROT charcoal produced at 21.7 bar showed

254   higher reactivity than the one produced at 7.9 bar. The reason remains unclear since other

255   samples experienced an opposite trend. However, it can be suggested that at very high

256   pressures, the particles cannot rupture and completely melt because the external pressure does

257   not allow the volatile matter to escape freely [6]. It means that the porous structure is partially

258   maintained.

259   **3.3 Effect of Charcoal Particle Size and Biomass Type on the Reactivity of Charcoal**

260   The reactivity of charcoal produced at 21.7 bar was studied for two particle sizes of 1< d<2 mm

261   and d< 60 μm. Results from this investigation are presented in Fig. 3. In all cases of charcoals

262   produced from different types of stem wood and forest residues, the CO_2 gasification reactivity

263   of the charcoals increased when their particle size was decreased. This is in agreement with the

264   study results reported in literatures [43, 44]. However, the trend of this effect for biomass type

265   is not the same for the two particle sizes. While it is consistent for the particle size smaller than

266   60 μm that the stem wood charcoals consistently exhibited lower CO_2 gasification reactivity

267   than the corresponding charcoals from the GROT, this is not the case for the particle size of 1-

268   2 mm. This differentiation can be explained by the fact that relatively larger particles might be

269   subjected to three limitations resulting in slower and variable reaction rates. The first limitation

270   is due to the diffusional resistances associated with the concentration gradient between the

interior and exterior of the particle. The second limitation is associated with the inhibition effect imposed by CO. As the gasification reaction proceeds, the concentration of CO accumulated inside the charcoal pores can reach a substantial level, resulting in an inhibition effect [44, 45]. The third limitation is the heat transfer limitation, which depends on the effective conductivity of the particle, which will be species and sample dependent. The relative importance of these individual limitations and the sum of these might be different for the different samples.

3.4 Kinetic Analysis

Fig. 4 and Fig. 5 present results from a kinetic analysis of the TGA experimental data collected for CO_2 gasification of the charcoals, assuming the model number 4 in Table 3. From the analysis, gasification kinetic parameters were extracted, which are summarized in Table 4. Overall, the adopted model fit the experimental data well, with very high fit qualities being within 98.23 - 99.48%. In addition to this, the fits are getting better at higher conversion degrees, probably due to the reduced negative effect of the gas shift from N_2 to CO_2.

As shown in Table 4, the charcoal gasification activation energy varies between 140-160 kJ/mol, which is comparable with the results reported in literature [46-48]. It is commonly known that the values from open literatures for the gasification of biomass charcoals scatter widely between 99 and 318 kJ/mol [39, 49-52]. The reasons for this still remain incompletely understood; however, it is supposed that not only the activation energy but also the pre-exponential coefficient depends on fuel properties such as charcoal pore structure, ash constituents, charcoal formation conditions and carbon structure [19]. It is noticeable that the activation energy increases with increasing charcoal production pressure. For instance, these values were 145.56 kJ/mol and 159.15 kJ/mol for birch charcoal produced at atmospheric pressure and 21.7 bar, respectively. Interestingly, a dissimilar trend was observed for the previously mentioned spruce GROT charcoal for which charcoal produced at 21.7 bar had similar activation energy with the one produced at atmospheric pressure.

The reaction order of CO_2 gasification is expected to be less than unity considering an increase in charcoal reactivity along with charcoal conversion due to increased porosity. Indeed, the reaction order obtained in the present study is in good agreement with the literature [47]. Kinetic studies of non-isothermal gasification was carried out by Wang et al. [10, 53] and the results revealed reaction orders of 0.44 and 0.58 for wood char and forest residue char, respectively, and between 0.36 and 0.42 for torrefied biomass. From another work reported by Vamvuka et

al. [54], which investigated the gasification of different chars from municipal solid waste, paper sludge and sewage sludge, reaction orders between 0.4 and 0.6 were also obtained.

3.5 Correlation between Charcoal Reactivity and its Characteristics

The influence of mineral content on the efficiency of biomass gasification has been intensively investigated. It is acknowledged that the alkaline and alkaline earth metals act as catalysts during gasification reactions of biomasses and charcoals with steam and CO_2. The promoting effect of catalysts is ranked in the order of K > Na > Ca > Fe > Mg [55]. On the other hand, the presence of silicon inhibits and lowers the reactivity [56, 57]. Indeed, an investigation conducted by Dupont et al. revealed a correlation between the reaction rate and the ratio of potassium/silicon [56]. In the present study, a similar trend was found compared to the earlier results [20]. Fig. 6 shows a clearly increasing trend of gasification reactivity with increasing concentration of alkali elements for the four charcoals produced at 21.7 bar.

Takarada et al. established two empirical equations to estimate the gasification rate of coal char towards steam and CO_2 [19]. These equations show that for both steam and CO_2, the gasification reaction rate is exponentially dependent on the concentration of sum of Ca and Na in the studied chars. In addition, the molar ratio of O/C influences the reaction rate of coal char steam gasification; however, it does not for the case of CO_2 gasification. In the other study, Matsumoto and co-workers concluded that the molar ratio of O/C affects both CO_2 and steam gasification reaction rate of charcoal [20]. In fact, an increasing reaction rate with increasing O/C ratio was found. More recently, Lin et al. found that the reaction time needed to reach 80 % conversion appeared to have a positive correlation with the O/C ratio, which looks like a decreasing trend of a power function curve [58]. In the present work, the relation between the O/C ratio and charcoal reactivity is also investigated and it is graphically presented in Fig. 7. The results reveal a roughly increasing trend of charcoal reactivity with increasing oxygen to carbon ratio for the case of charcoal produced at 7.9 bar. However, for charcoal produced at 21.7 bar, the trend is unclear. A broader range of experiments is needed to draw a general conclusion regarding the effect of the O/C ratio.

4. CONCLUSIONS

The charcoal production pressure had great influence and resulted in reduced CO_2 gasification reactivity. Furthermore, the charcoal particle size was proven as a crucial factor for its reactivity and a small particle size is needed for a chemical kinetic study.

The chosen kinetic model described well the gasification with high fit quality. The activation energy was found to be between 140-160 kJ/mol whereas the reaction order varied in the range of 0.4-0.6. The charcoal produced at higher pressure had higher activation energy which was in consonance with its lower reactivity. In this work, a strong correlation between charcoal reactivity and alkali metal content was found.

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506   **Fig. 6** Correlation between the charcoal alkali content and its CO_2 gasification reactivity

507   (charcoal produced via carbonization at 21.7 bar).

508   **Fig. 7** Correlation between the charcoal reactivity and O/C molar ratio in the charcoal

509   produced at 7.9 bar and 21.7 bar.

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511

512 **Table 1** Various models for gasification kinetics

513

No	Model	Mathematical equation	Ref.
1	Volumetric reaction model	$\frac{d\alpha}{dt} = k(1-\alpha)$	Levenspiel [27]
2	Shrinking core model	$\frac{d\alpha}{dt} = k(1-\alpha)^{2/3}$	Levenspiel [27]
3	Random pore model	$\frac{d\alpha}{dt} = k(1-\alpha)\sqrt{1-\psi ln(1-\alpha)}$	Bhatia et al. [59]
4	Traditional model	$\frac{d\alpha}{dt} = A exp\left(\frac{-E}{RT}\right)P_{CO_2}^{v}f(\alpha)$ $f(\alpha) = (1-\alpha)^n$ or $f(\alpha) = normfactor(\alpha+z)^a(1-\alpha)^n$	Liliedahl et al. [29] Khalil et al. [60]. Alvarez et al. [61]

514

515 **Table 2** Proximate and ultimate analysis of charcoal samples (dry basis, wt%)

Samples	Charcoal Production Pressure, bar	Charcoal Yield	Proximate Analysis			Ultimate Analysis				
			VM	FC	Ash	C	H	N	S	O
Birch	7.9	23.9	6.6	91.4	2.0	90.49	1.93	0.47	<0,02	7.09
	21.7	40.0	20.3	78.3	1.4	73.65	4.35	0.37	<0,02	21.61
Birch GROT	7.9	32.2	12.0	83.8	4.2	81.37	2.99	1.13	<0,02	14.49
	21.7	37.0	22.3	72.7	5.0	73.67	4.31	0.87	<0,02	21.13
Spruce	7.9	24.1	18.1	80.2	1.7	77.35	3.68	0.29	<0,02	18.66
	21.7	33.5	18.8	80.1	1.1	76.36	3.50	0.47	<0,02	19.55
Spruce GROT	7.9	38.2	13.1	80.7	6.1	83.49	2.65	0.56	<0,02	13.28
	21.7	38.2	28.5	67.7	3.7	77.34	3.79	0.66	<0,02	18.19

516 (VM: volatile matter; FC: Fixed carbon)

517 **Table 3** Concentration of inorganic elements in charcoal samples (mg/kg, dry basis)

Sample	Charcoal Production Pressure, bar	Al	Ca	Fe	K	Mg	Mn	Na	S	P	Si	Zn	Ba
Birch	1	179	4865	236	2538	1099	230	43	245	414	240	230	63
	7.9	158	3837	254	2469	911	477	33	267	408	231	477	57
	21.7	72	3332	70	1508	682	344	13	210	253	221	344	55
Birch GROT	1	762	14257	317	5005	2541	963	126	333	1629	614	432	132
	7.9	777	11145	596	5295	1894	884	254	524	1285	3004	371	123
	21.7	459	5010	342	1965	741	374	109	404	498	1463	157	55
Spruce	1	78	4494	78	2352	742	458	62	245	153	111	87	113
	7.9	55	5357	145	2172	816	824	73	293	168	91	95	124
	21.7	57	8043	116	1690	759	697	27	211	138	137	67	100
Spruce GROT	1	279	17045	220	6290	2142	2982	144	372	1047	857	280	305
	7.9	159	14902	140	4779	1609	2042	86	344	610	396	252	266
	21.7	87	9968	68	3407	1153	1595	64	329	426	594	146	156

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519

520   **Table 4** Extracted kinetic data of birch, birch GROT, spruce and spruce GROT charcoal

Sample	Charcoal Production Pressure, bar	A Min^{-1}	Ea, kJ/mol	n	Fit, %
Birch	1	4.09E+05	145.56	0.41	99.33
	7.9	4.08E+05	153.61	0.32	99.37
	21.7	6.88E+05	159.15	0.34	99.34
Birch GROT	1	3.95E+05	141.16	0.45	98.58
	7.9	7.24E+05	156.14	0.44	99.12
	21.7	9.35E+05	161.26	0.45	99.06
Spruce	1	3.74E+05	143.96	0.42	98.23
	7.9	8.89E+05	155.01	0.40	99.18
	21.7	9.32E+05	160.01	0.49	99.17
Spruce GROT	1	4.07E+05	141.52	0.44	98.64
	7.9	1.00E+06	159.95	0.34	99.48
	21.7	4.09E+05	145.29	0.46	99.12

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530   (a)

531   (b)

532   (c)
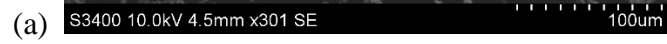
533   **Fig. 1** SEM images of birch charcoal samples: (a) TGA charcoal, (b) 7.9 bar charcoal, (c) 21.7
534   bar charcoal.

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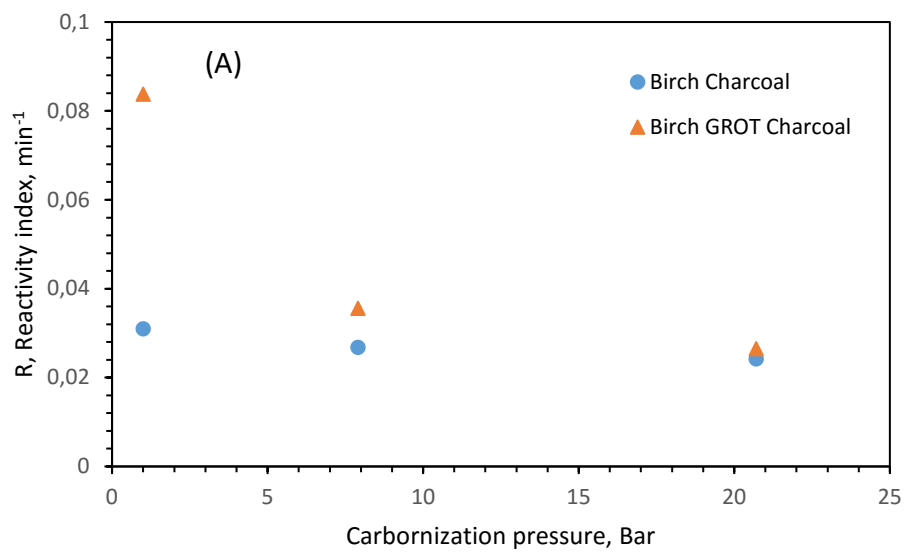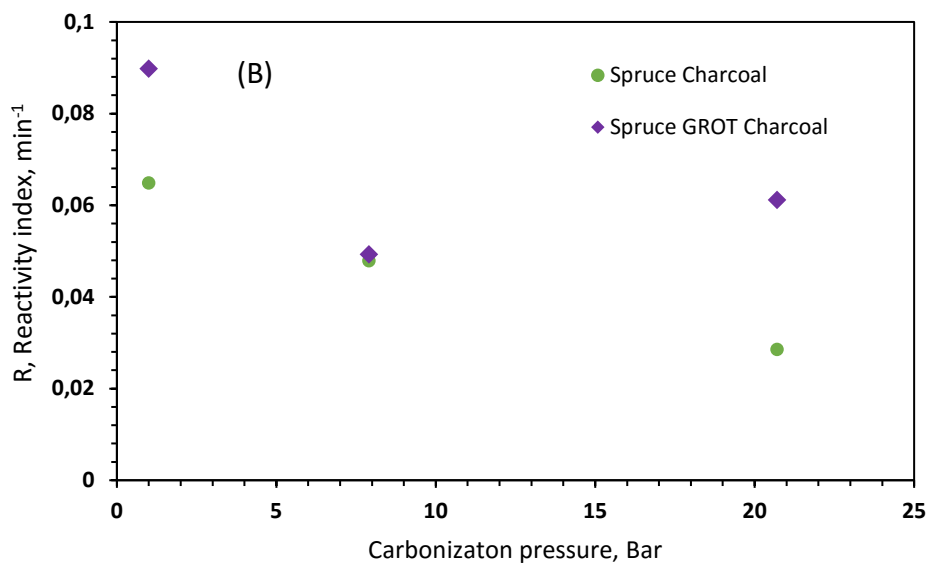
Fig. 2 Effect of carbonization pressure on charcoal reactivity; (A) birch and birch GROT, (B) spruce and spruce GROT.
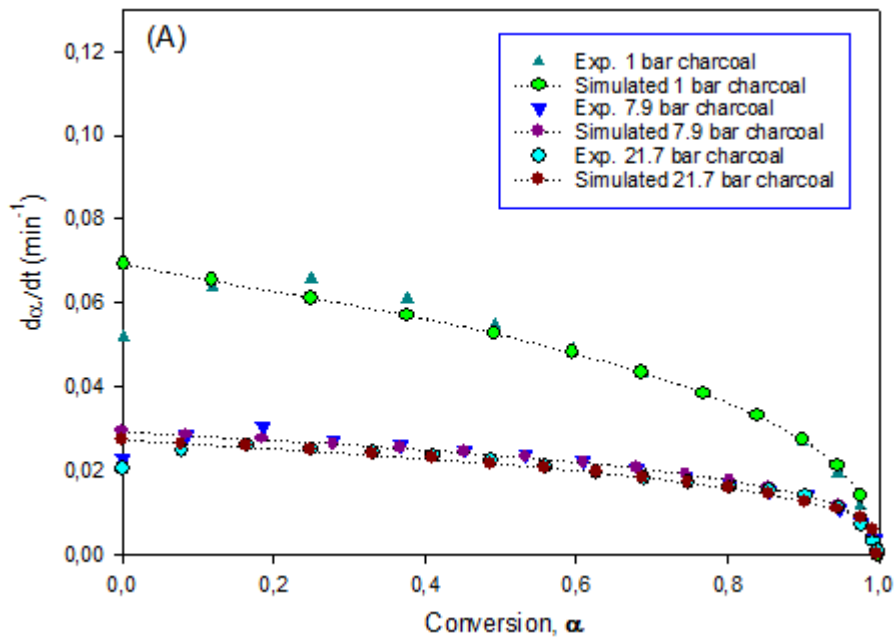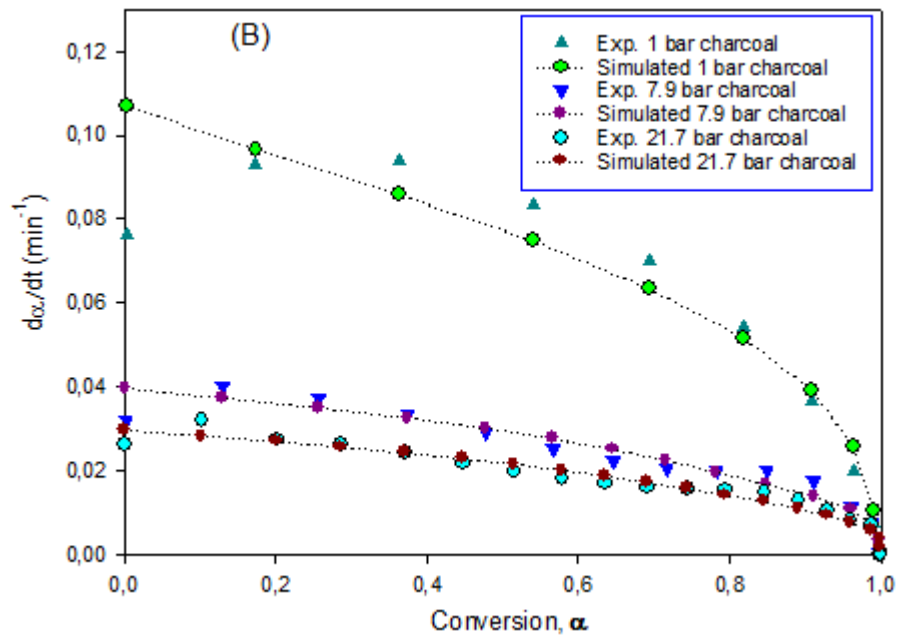
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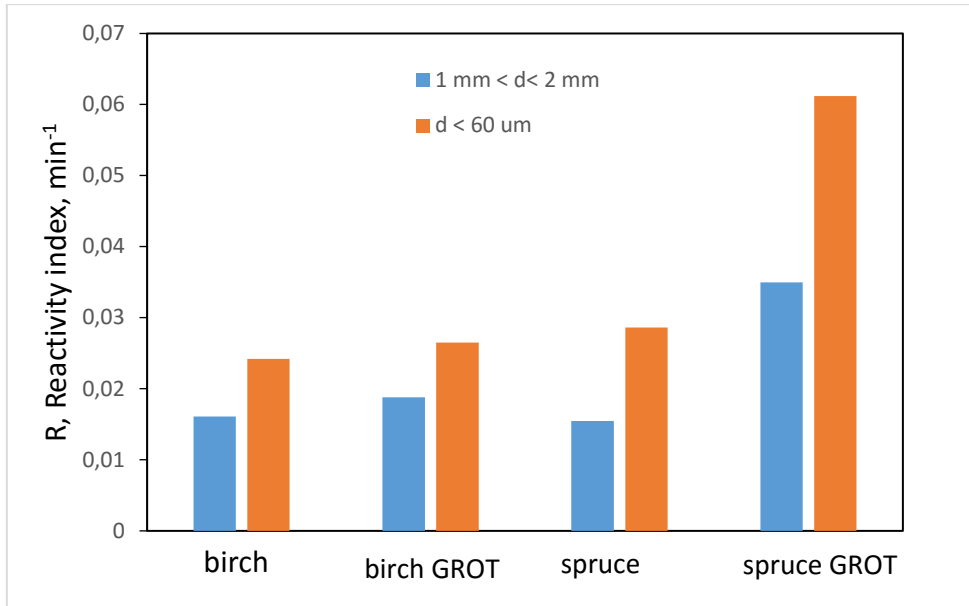
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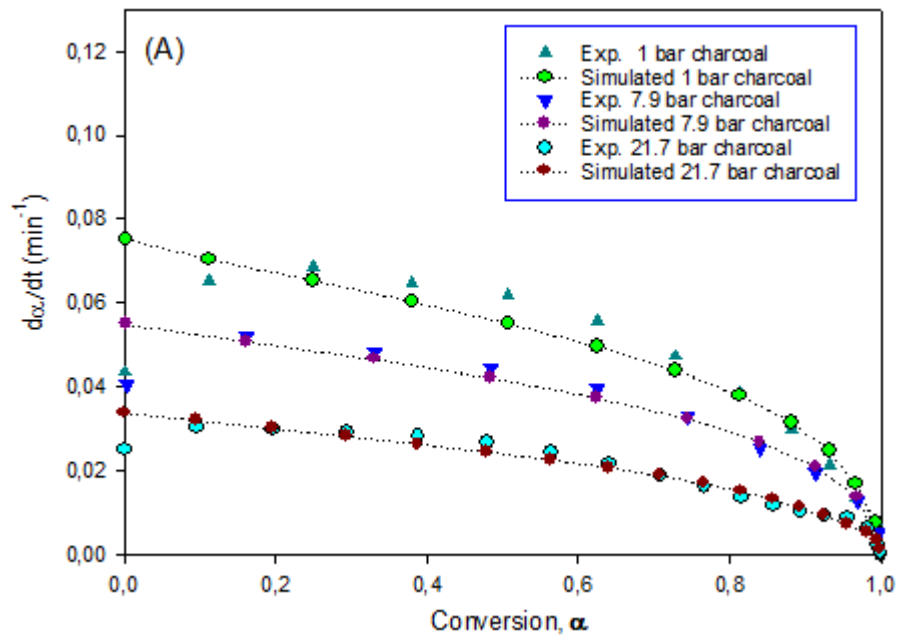544   **Fig. 3** Effect of charcoal particle size on its gasification reactivity.

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549   **Fig. 4** Simulation and curve fitting for birch (A) and birch GROT (B) charcoals.
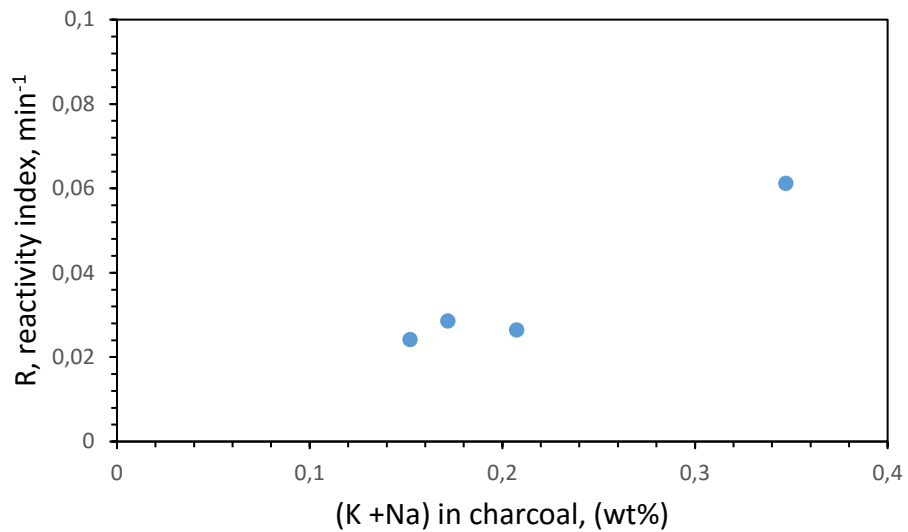

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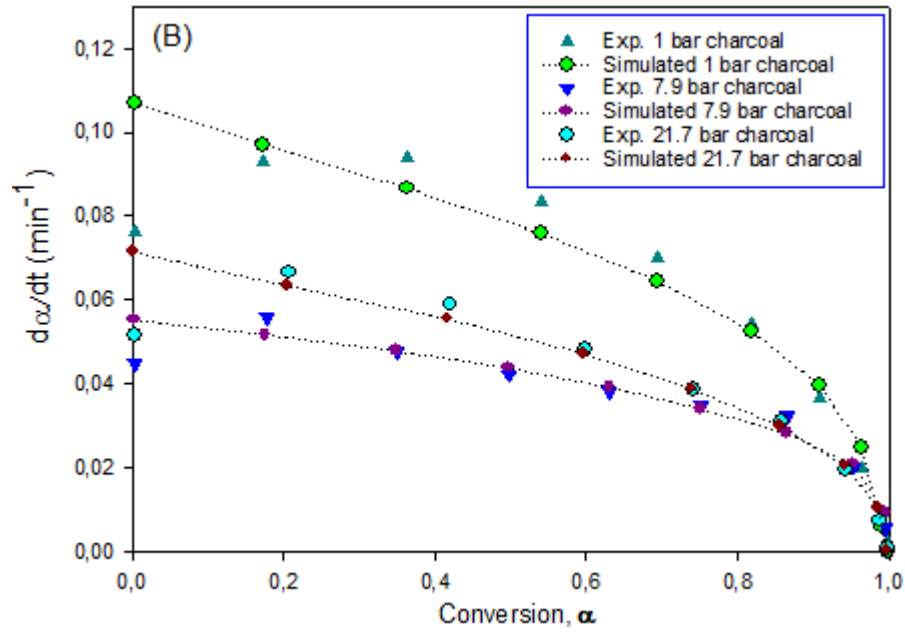
Fig. 5 Simulation and curve fitting for spruce (A) and spruce GROT (B) charcoals.

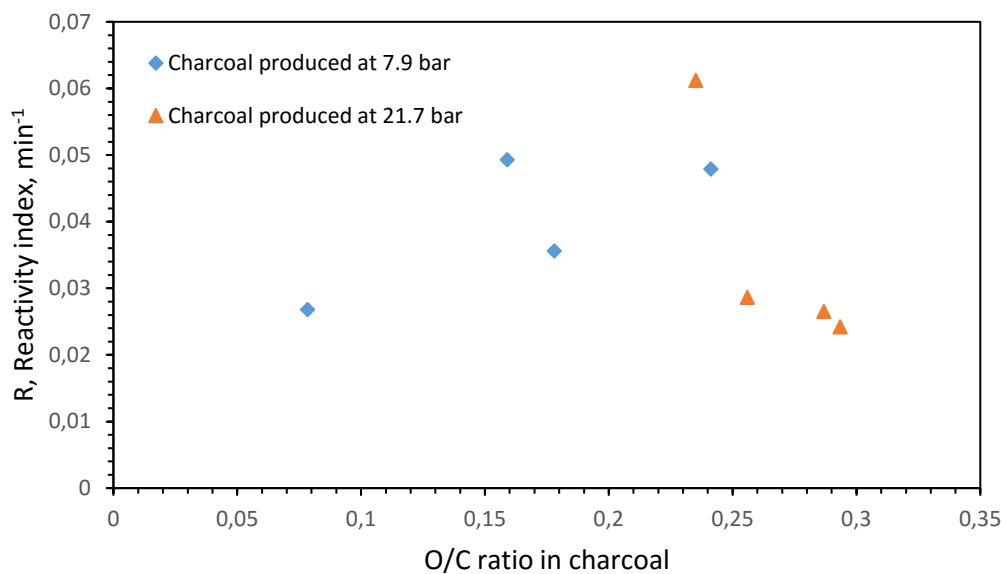**Fig. 6** Correlation between the charcoal alkali content and its CO_2 gasification reactivity (charcoal produced via flash carbonization at 21.7 bar).

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561

562 **Fig. 7** Correlation between the charcoal reactivity and O/C molar ratio in the charcoal

563 produced at 7.9 bar and 21.7 bar.