

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

1 Impact of particle size and catalyst dispersion on 2 gasification rates measured in a thermogravimetric 3 analysis unit: Case study of carbon black catalyzed by 4 potassium or calcium

5
6 Ross A. Arnold¹, Ingrid L. Motta², and Josephine M. Hill*.

7
8 Department of Chemical & Petroleum Engineering, Schulich School of Engineering, University
9 of Calgary, 2500 University Dr, Calgary, AB, T2N 1N4, Canada.

10
11 *Corresponding author: jhill@ucalgary.ca

12
13 Abstract

14 Gasification is often studied in the laboratory using a thermogravimetric analysis (TGA) unit with
15 less than 1 g of sample in order to obtain intrinsic rates. Many studies, however, neglect to consider
16 the impact of particle size, of both the gasification feed and the catalyst, and catalyst dispersion on
17 the measured rates. The impact of these factors was demonstrated using catalytic gasification of
18 carbon black, an ash-free feed, as a case study, with K_2CO_3 or $CaCO_3$ as catalysts at 850 °C in a
19 CO_2 atmosphere. Hand-mixing and ball-milling were used to alter the initial parameters. Ball-
20 milling reduced both the particle size of both species and increased the catalyst dispersion,
21 resulting in higher interfacial areas and gasification rates than hand-mixing. The changes in
22 gasification kinetics were estimated by modeling the rates using the random pore and extended

¹ Present address: Department of Civil & Environmental Engineering, Samueli School of Engineering, University of California, Los Angeles, CA, 90095, USA

² Present address: School of Chemical Engineering, University of Campinas, Av. Albert Einstein 500, Campinas, 13083-852, Brazil

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

23 random pore models (RPM and eRPM, respectively). The impact of the interfacial contact area
24 between carbon and catalysts (varied by particle size and mixing method) was dependent on the
25 activity of the catalyst with the more active (potassium) catalyst being less affected. CaCO₃ was
26 found to sinter at 850 °C, reducing available catalytic surface area and blocking CO₂ access to the
27 carbon feed. It is recommended to consider these factors in future studies and to always report the
28 particle sizes used.

29

30 Highlights

- 31 • Gasification of carbon black mixed with K or Ca catalysts by different methods
- 32 • Dispersion more important as activity of catalyst decreases
- 33 • Catalyst size had more impact than carbon black size, confirmed by modeling
- 34 • Knowledge of phase behavior – softening and sintering temperatures – required
- 35 • eRPM describes the gasification behavior of catalyzed carbon black

36

37 Keywords

38 gasification; potassium; calcium; ball-milling; catalyst; random pore model

39

40 1. Introduction

41 Gasification is used to convert carbon-based feeds to fuels/chemical precursors, such as H₂, CO,
42 and CH₄, and can be enhanced by the presence of catalysts, such as calcium and potassium, added

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

43 to the feeds prior to gasification or intrinsically present in the feeds [1]. The limiting step in
44 gasification can either be external mass transfer of the gasification agent through the boundary
45 layer, internal mass transfer of the gasification agent through pores to reach active sites, or the
46 surface gasification carbon-oxygen reaction [2]. In the absence of mass transfer limitations, the
47 gasification rate is proportional to the surface area [3], or in the case of low catalytic loadings, the
48 number of catalytic sites [4]. At the lab scale, gasification kinetics are commonly determined using
49 a thermogravimetric analysis (TGA) instrument with sample sizes of less than 1 g (often less than
50 10 mg) to avoid mass transfer limitations [5–8]. Decreasing the particle size of the feed increases
51 the surface area and the number of available active sites for gasification [9]. The rate of catalytic
52 gasification is also increased by increased catalyst-carbon interfacial area [10,11], which is
53 improved by increasing the dispersion of the catalyst.

54
55 Both wet impregnation [12–19] and physical mixing [13,16,20] have been used to combine the
56 feed with the catalytic species. Wet impregnation results in better dispersion of water-soluble
57 catalytic species, and Kapteijn *et al.* [21] noted the importance of catalyst dispersion in their survey
58 of alkaline-earth-catalyzed gasification literature. Wet impregnation, however, is ineffective for
59 hydrophobic feeds because the catalytic species are deposited on the surface and not in the pores
60 [22]. Wet impregnation is also ineffective for sparingly soluble catalyst precursors, such as
61 $\text{Ca}(\text{OH})_2$ and CaCO_3 . Ash-free coal is an example of a hydrophobic material for which preparation
62 methods other than wet impregnation must be used [23]. Surface groups on hydrophobic materials

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

63 can enhance gasification for hydrophobic or non-porous feeds. For example, potassium addition
64 was more effective for increasing the gasification rate of raw petcoke than petcoke char because
65 pyrolysis at 975 °C removed the surface groups (including aliphatic, phenolic, aromatic, and
66 hydroxyl groups) which served as anchoring sites for potassium in the raw coke [24]. Physical
67 mixing is an alternative to wet impregnation for hydrophobic feeds and/or insoluble catalyst
68 precursors, and includes hand and mechanical mixing, such as by crushing [25], or by grinding in
69 a rotary tumbler [26] or a planetary ball-mill [27]. The effects of physical mixing techniques on
70 feed properties are rarely discussed in the literature. Hand-mixing, while simpler and less
71 expensive, is less reproducible than mechanical mixing with fixed parameters (e.g., rotation speed,
72 time). One study with raw coal (which is not hydrophobic), claimed that wet impregnation was
73 better than physical mixing for the addition of calcium catalysts $\text{Ca}(\text{OH})_2$ and CaCO_3 [28]. This
74 result is surprising given the low solubility of the calcium compounds but the method and details
75 of the physical mixing were not specified, nor were particle sizes or catalyst dispersion. Despite
76 the importance of feed properties on gasification rates, most studies still neglect to consider the
77 effectiveness of the mixing method for reducing particle size and/or increasing catalyst-carbon
78 interfacial area.

79

80 Herein, we demonstrate the impact of two physical mixing methods, hand-mixing and ball-milling,
81 to ascertain the effect of feed particle size, catalyst particle size, and catalyst dispersion on catalytic
82 gasification of carbon black, a model ash-free carbon source, with potassium and calcium. Because

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

83 calcium is less active than potassium due to its lower mobility [16,29–34], the impact of the mixing
84 method was expected to be different for these two catalytic species. Samples were prepared by
85 hand-mixing and/or low-energy ball-milling and characterized using scanning electron
86 microscopy. The samples were gasified in a TGA in a CO₂ atmosphere primarily at 850 °C. The
87 gasification kinetics were modeled using the random pore and extended random pore models.

88

89 2. Materials & Methods

90 2.1 Sample preparation and characterization

91 Carbon black (CB, Monarch 120 from Cabot Corp, Boston, MA) was used as the carbon source.
92 CaCO₃ and K₂CO₃ (>99% purity, Sigma-Aldrich, St. Louis, MI) were the calcium and potassium
93 sources, respectively. The atomic ratio between each metallic element (Ca or K) and carbon was
94 0.1 for consistency with previous publications [35,36]. The high catalyst loading ensured that the
95 number of available catalytic sites was not a limiting factor in the gasification rates. “Hand-mixed”
96 samples were combined by stirring by hand for 5 min, while “ball-milled” samples were combined
97 for 24 h in a low-energy rotary tumbler (model 33B, Lortone, Mukilteo, WA) with zirconia beads
98 5 mm in diameter unless otherwise noted. In some cases, a combination of ball-milling and hand-
99 mixing was used. For these experiments, the CB, the catalyst, or both were ball-milled
100 independently for 24 h in the rotary tumbler, and then the CB and catalyst were combined by
101 stirring by hand for 5 min.

102

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

103 CO₂ adsorption analyses were performed to determine the specific surface area of the CB samples.
104 The samples were degassed at 120 °C under vacuum for 6 h. CO₂ adsorption analyses were
105 performed using a Micromeritics Tristar II Plus unit (Norcross, GA) at 273 K, and the microporous
106 surface area was calculated using the 2D-NLDFT model.

107

108 2.2 Gasification

109 Gasification tests were performed using thermogravimetric analysis (TGA) in an SDT Q600
110 instrument (TA Instruments, New Castle, DE). For each experiment, 3.5 mg of sample was heated
111 under N₂ flow (200 mL/min) at 20 °C/min to 850 °C, then CO₂ (200 mL/min) was introduced as
112 the gasification agent. Two experiments were performed at 1000 °C for comparison. A 5 mL/min
113 flow of N₂ was maintained during gasification to limit the backflow of CO₂ to the TGA balance.
114 Weight vs. time data was smoothed to 1000 points by means of the locally estimated scatterplot
115 smoothing (LOESS) technique using SigmaPlot v14.0. In the LOESS technique, a polynomial of
116 a specified order (a third-order polynomial was used herein) is fit to a specified fraction of nearby
117 data (5% was used herein) for each data point using a weighted least squares fit, and then used to
118 determine a weighted average for each data point. Conversion, X , was calculated using Eq. 1:

$$X_t = \frac{m_0 - m_t}{m_0 - m_f} \quad (1)$$

119 where m denotes mass, and the subscripts 0 , t , and f denote the initial value, the value at time t ,
120 and the final value, respectively. The rates of reaction were calculated using numerical integration
121 (Eq. 2):

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

$$rate(t_1) = \frac{dX}{dt}(t_1) = \frac{X_{t_2} - X_{t_1}}{t_2 - t_1} \quad (2)$$

122 where the subscripts 1 and 2 denote two consecutive time points, with 50 data points collected per
123 minute. The gasification experiments were continued until the mass remained constant for 5 min.
124 The length of experiments varied between 30 min to 100% conversion (samples V to VII, Table
125 1) and 16 h to 53% conversion (sample VIII, Table 1). The TGA was only able to record 16 h of
126 data, after which experiments had to be terminated.

127

128 2.3 Scanning electron microscopy

129 Scanning electron microscopy (SEM) was used to determine particle size in the prepared mixtures,
130 and to qualitatively assess the extent of mixing. SEM images were obtained (*ex situ*, ambient
131 temperature and pressure) using a Phenom ProX electron microscope (Thermo-Fisher Scientific,
132 Waltham, MA) with energy-dispersive X-ray (EDX) spectroscopy capabilities. The particle size
133 was estimated from the SEM images using the software ImageJ. A representative SEM image with
134 approximately 100 particles was chosen for each sample, and then ImageJ was used to determine
135 the length (i.e. longest dimension) of each particle, from which a mean particle size was estimated.
136 The errors in the particle sizes are reported as a 95% confidence interval.

137

138

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

139 2.4 Kinetic Modeling

140 The results were modeled using the random pore model (RPM, Eq. 3) [37] and the extended
141 random pore model (eRPM, Eq. 4) [38]:

$$142 \quad \frac{dX}{dt} = k_j(1 - X)\sqrt{1 - \psi \ln(1 - X)} \quad (3)$$

$$143 \quad \frac{dX}{dt} = k_j(1 - X)\sqrt{1 - \psi \ln(1 - X)} (1 + c(1 - X)^p) \quad (4)$$

144

145 where k_j is a rate constant and ψ is a structural factor that represents the change in surface area
146 from the initial to the maximum value during gasification. The maximum specific surface area
147 corresponds to the maximum rate of gasification [37]. The eRPM includes two additional semi-
148 empirical parameters, c and p , to represent the shift in the maximum position when catalysts are
149 present during gasification.

150

151 Kinetic modeling and model discrimination were performed using Athena Visual Studio v14.2
152 software. In the kinetic modeling, the rate (dX/dt) versus conversion (X) data (1000 observations
153 for each sample) was fit to the models by minimization of the residual sum of squares (RSS) using
154 the nonlinear least-squares method, determining the values of k_j , ψ , c , and p . The model
155 discrimination used the Akaike information criterion (AIC) [39], defined in Eq. 5:

$$AIC = m \frac{2}{n} + \ln \left(\frac{1}{n} RSS \right) \quad (5)$$

156 where m is the number of estimated parameters, and n is the number of observations. For each
157 sample, the model with the lowest AIC value (AIC_{min}) was considered the preferred model, which

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

158 usually coincides with higher R^2 values. For further comparison, the relative likelihood L_k (Eq. 6)
159 and the Akaike probability share π_{AIC} (Eq. 7) were also determined. The relative likelihood L_k
160 compares the AIC of a model k (AIC_k) with the lowest AIC among all models (AIC_{min}), assuming
161 values between 0 and 1, while the probability share π_{AIC} compares the likelihood of a model k with
162 the likelihoods of all the other models.

$$\pi_{AIC} = \frac{L_k}{\sum_{i=1}^k L_k} \quad (6)$$

$$L_k = \exp\left(\frac{AIC_{min} - AIC_k}{2}\right) \quad (7)$$

163

164

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

165 3. Results & Discussion

166 3.1 Morphologies of raw materials

167 Micrographs of the CB, K₂CO₃, and CaCO₃, both as received and after ball-milling, are shown in
168 Fig. 1, with the corresponding particle sizes in Table 1. The CB particles as received were 5-50
169 μm sized clusters containing particles <100 nm in size. The catalyst precursors, K₂CO₃ and
170 CaCO₃, are both crystalline ionic compounds but with different morphologies. Since the
171 carbonates are hydrophilic [40], despite being sparingly soluble in water, the particles
172 agglomerated. As received, the K₂CO₃ crystals existed in agglomerates larger than 200 μm in
173 diameter and so were crushed using a mortar and pestle before use. After crushing, the largest
174 K₂CO₃ agglomerates were 60 μm in size. The particle size of K₂CO₃ (Table 1) was reported as the
175 size of the crystals, not the agglomerates, because the K₂CO₃ agglomerates dispersed into crystals
176 1.5 μm in length during the heating of the gasification experiments. CaCO₃ was present in cubic
177 crystals approximately 7.1 μm in size (Fig. 1c) and at least five times smaller than the K₂CO₃
178 agglomerates.

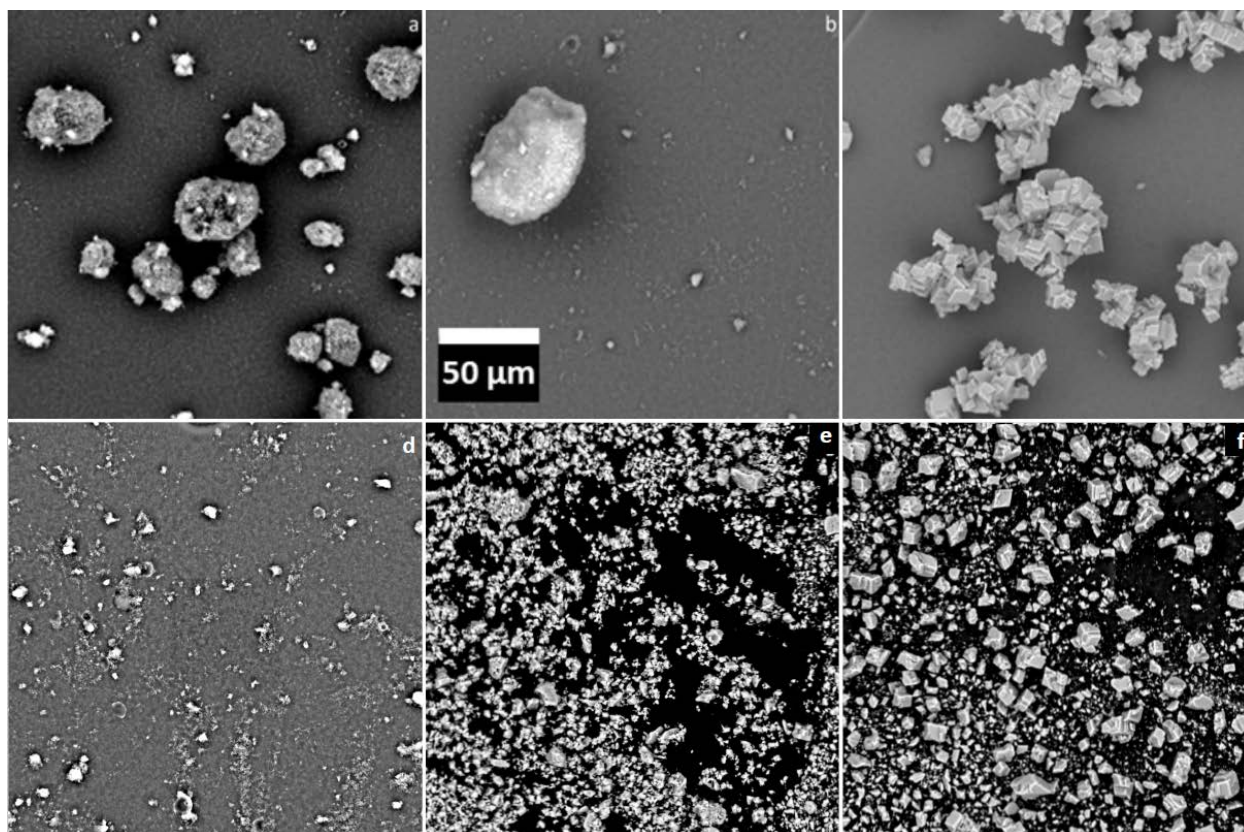
179

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

180



181

182 Fig. 1. SEM images of (a) as-received CB, (b) crushed (in mortar and pestle) K_2CO_3 , (c) as-
183 received $CaCO_3$, (d) ball-milled CB, (e) ball-milled K_2CO_3 , and (f) ball-milled $CaCO_3$. Scale bar
184 in (b) applies to all images.

185

186

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

187 Table 1. Particle sizes of pre-gasification mixtures obtained from SEM images (uncertainty
188 represents 95% confidence interval), CO₂ gasification rates at 850 °C after reaching 50%
189 conversion and the times required to reach 50% conversion. Ball-milled components are
190 underlined; mixtures with components ball-milled together are denoted with an asterisk (*).

Sample	Particle size (µm)		Rate at 50% conversion (min ⁻¹)	Time to 50% Conversion (h)
	CB	Carbonate		
CB (I)	10.6 ± 2.3	--	0.0016	7.7
<u>CB</u> (II)	3.1 ± 0.8	--	0.0022	4.8
CaCO ₃	--	7.1 ± 0.8	--	--
K ₂ CO ₃ crystals	--	1.5 ± 0.2	--	--
CB-K ₂ CO ₃ (III)	7.9 ± 1.7	1.3 ± 0.2	0.0416	0.30
<u>CB</u> -K ₂ CO ₃ (IV)	2.3 ± 0.4	1.3 ± 0.3	0.0745	0.09
CB- <u>K₂CO₃</u> (V)	9.2 ± 2.0	0.7 ± 0.2	0.2796	0.029
<u>CB</u> - <u>K₂CO₃</u> (VI)	2.4 ± 0.6	0.9 ± 0.1	0.2805	0.030
<u>CB</u> -K ₂ CO ₃ * (VII)	2.1 ± 0.5	0.5 ± 0.2	0.2751	0.032
CB-CaCO ₃ (VIII)	12.9 ± 3.7	8.0 ± 1.0	0.0006	15.0
<u>CB</u> -CaCO ₃ (IX)	3.7 ± 1.2	7.6 ± 0.9	0.0005	7.9
CB- <u>CaCO₃</u> (X)	11.8 ± 3.0	1.9 ± 0.6	0.0015	3.8
<u>CB</u> - <u>CaCO₃</u> (XI)	3.6 ± 1.0	1.6 ± 0.4	0.0011	9.2
<u>CB</u> -CaCO ₃ * (XII)	3.9 ± 1.5	2.3 ± 0.6	0.0086	1.1
<u>CB</u> -CaCO ₃ * (XIII)	0.8 ± 0.1	0.7 ± 0.1	0.0315	0.31

191

192

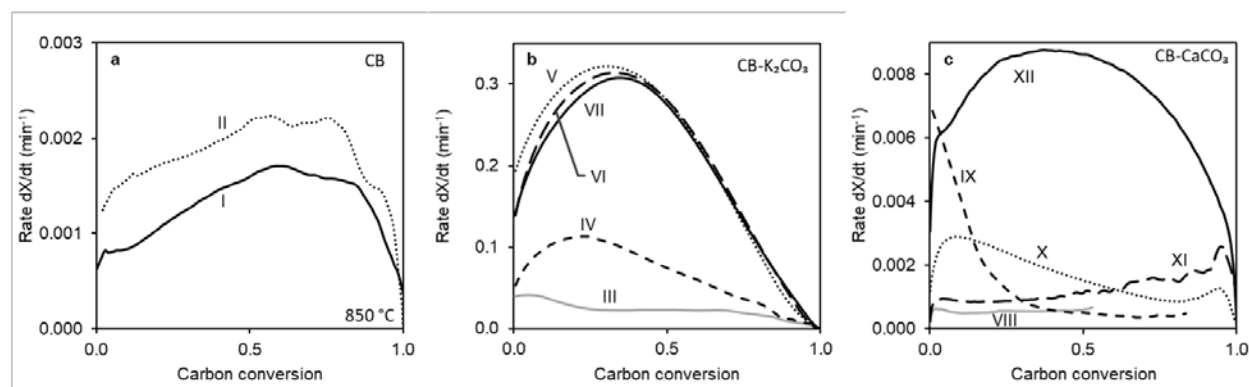
This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

193 3.2 Effect of mixing method

194 Ball-milling reduced the CB particle size and size distribution each by a factor of approximately
195 three (Table 1). The particle size reduction led to an increase in reaction rate (Fig. 2a).



196
197 Fig. 2. CO₂ gasification at 850 °C of a) CB, b) CB with K₂CO₃, and c) CB with CaCO₃. Curve
198 labels correspond to mixing methods and particle sizes in Table 1.
199

200 Assuming spherical geometry and completely dense particles, the reduction in particle size should
201 increase the surface area by a factor of 3.4. The measured surface area increased by a factor of 2.8
202 (from 18 to 50 m²/g) and the pores sizes increased (from less than 1 nm (Fig. S.1a) up to 25 nm
203 (Fig. S.1b) after ball-milling. The maximum gasification rate, however, increased by only a factor
204 of 1.4. One possible explanation for the smaller than expected increase in gasification rate may be
205 the presence of occluded pores within the carbon black that became accessible after ball milling
206 and/or once gasification began. Thus, the surface area of the as received carbon black was
207 underestimated.

208

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

209 When both CB and catalysts were present, ball-milling could result in an increased gasification
210 rate in two ways: by reducing the particle size (increasing specific surface area) and by improving
211 the initial dispersion of the catalyst (increasing interfacial area between carbon and catalyst). To
212 distinguish between these factors, the components were ball-milled separately before hand-mixing
213 (only particle size reduction) and ball-milled together (particle size reduction and catalyst
214 dispersion). Ball-milling reduced the sizes of the CaCO_3 and K_2CO_3 particles to 1.6-1.9 μm
215 (mixtures X and XI, Table 1) and 0.7-0.9 μm (mixtures V and VI, Table 1), respectively. The Mohs
216 hardness values are ~ 2.5 for a generic carbon black [41] (no specific data was available for Cabot
217 Monarch 120), ~ 3 for CaCO_3 [42], and ~ 8 for zirconia balls [43]. No data was found for K_2CO_3 ,
218 but the hardness is assumed to be lower than that of the zirconia balls. K_2CO_3 may be harder than
219 CaCO_3 as the CB particles were smaller after ball-milling with K_2CO_3 than CaCO_3 .

220
221 The gasification results for the CB- K_2CO_3 mixtures are shown in Fig. 2b. The highest rates were
222 obtained when K_2CO_3 was ball-milled – without CB being ball-milled (V), the components ball-
223 milled separately (VI), or the components ball-milled together (VII) – and the rates for these
224 mixtures (curves V, VI, and VII) were significantly higher than the rates of the other mixtures
225 (curves III and IV). The curves with the three highest rates were within experimental error above
226 40% conversion, though modeling gave different rate constant values, which is discussed further
227 in Section 3.4. The difference in the mixtures corresponding to curves III and IV was the size of
228 the CB particles (7.9 μm and 2.3 μm , respectively). As shown in Fig. 2a, reducing the size of the

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

229 CB particles increased the gasification rate but, in the presence of a catalyst, this effect was
230 enhanced. Nonetheless, ball-milling the K_2CO_3 had a larger effect than ball-milling the CB. In the
231 mixture corresponding to curve V, the average CB particle size was 9.2 μm , slightly larger than
232 that in the hand-mixed mixture (7.9 μm , curve III) and four times larger than that in the mixture
233 corresponding to curve IV (2.3 μm). The results suggest that potassium is more active when ball-
234 milled because the smaller crystals are more readily able to disperse. That is, potassium was
235 equally effective as a catalyst whether ball-milled with, or separately from, the CB because of its
236 high mobility.

237
238 Ball-milling CB and/or $CaCO_3$ led to a reduction in particle size for both the CB and the $CaCO_3$
239 (Table 1). As received, the $CaCO_3$ particles were cubic crystals (Fig. 1c). After ball-milling with
240 or without CB (Fig. 1f), the shapes of the crystals were irregular, although some cubes were still
241 visible in the SEM images. The gasification results were lower and more varied than for the CB-
242 K_2CO_3 mixtures (Fig. 2c). The gasification rate at 50% conversion varied from 0.0006 min^{-1} for
243 hand-mixed CB- $CaCO_3$ (VIII) to 0.0086 min^{-1} for CB- $CaCO_3$ ball-milled together (XII). The latter
244 rate was one third of the rate for hand-mixed CB- K_2CO_3 , while the former was less than half of
245 the value for CB as received with no added catalysts. The decrease in particle size (assuming
246 spherical particles for CB throughout and for $CaCO_3$ after ball-milling – $CaCO_3$ is cubic before
247 ball-milling) increased the surface areas by a factor of 3.3 for CB and by 1.9 for $CaCO_3$, which
248 does not account for the 14-fold increase in gasification rate.

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

249

250 The interfacial area between the catalyst and substrate was also a factor. The experiments with
251 only CB ball-milled (IX), only CaCO₃ ball-milled (X), or both components ball-milled separately
252 prior to hand-mixing (XI) had the same average rates of reaction ($\sim 0.0015 \text{ min}^{-1}$) but very different
253 reaction rate profiles as a function of conversion. This variation may be due to the heterogeneous
254 nature of hand-mixed samples. In all three cases, the rate of reaction was significantly below that
255 of CB-CaCO₃ ball-milled together (XII) from 10-99% conversion. The propensity of CaCO₃ to
256 sinter above 850 °C has been shown in previous publications [36,44]. Ball-milling the components
257 together more effectively dispersed the CaCO₃ and reduced the extent of sintering. The lower
258 mobility of Ca meant that both the particle size and the interfacial contact area between Ca and
259 CB were critical to the catalytic activity.

260

261 To further compare the behaviors of K₂CO₃ and CaCO₃ prior to gasification, EDX analysis was
262 performed on the hand-mixed mixtures after heating to 850 °C under inert N₂ flow in the TGA
263 (shown in Fig. S.2). The CB-K₂CO₃ mixture had agglomerations containing approximately 6%
264 potassium, 71% carbon, and 23% oxygen. The K₂CO₃ had dispersed on the CB surface during
265 heating to an extent perceptible in the SEM (the reactions will happen at a scale much smaller than
266 that probed by SEM). Ball-milling reduced the crystal size, further creating more potassium active
267 sites that were readily dispersed at gasification temperatures even when not ball-milled directly
268 with the CB. In contrast, there was no evidence in the SEM images that CaCO₃ had dispersed

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

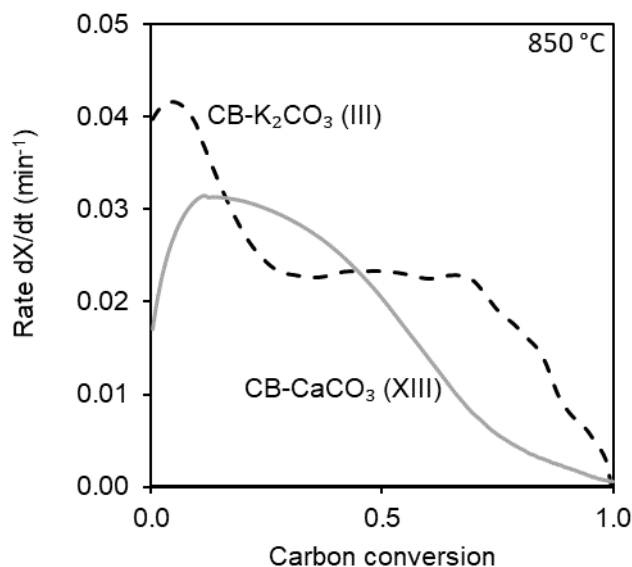
269 during heating to 850 °C, with or without ball milling, but remained in the original cubic crystalline
270 form, consistent with CaCO₃ being a less active catalyst than K₂CO₃.

271
272 In all the CB-CaCO₃ mixtures hand-mixed or ball-milled with 5 mm beads, the particle size of
273 CaCO₃ was at least 1.6 μm (curves VIII to XII, Table 1), which was larger than K₂CO₃ as received
274 (1.5 μm, Table 1). To test if further reducing the size of the CaCO₃ particles would improve the
275 activity, CB and CaCO₃ were ball-milled using 1 mm quartz glass balls (Mohs hardness of ~7 [45]
276 – SEM/EDX analysis did not detect Si or Al from these beads on the mixtures) in addition to the
277 5 mm zirconia balls, and then this CB-CaCO₃ mixture was gasified. After ball-milling with the
278 smaller balls, the CB and the CaCO₃ particles were smaller than the particle sizes in the hand-
279 mixed CB-K₂CO₃ mixture (XIII vs. III, Table 1). Reduction of the particle sizes and improved
280 catalyst dispersion increased the gasification rate (Fig. 3). Up to 50% conversion, the gasification
281 rates of CB-CaCO₃ (XIII) and CB-K₂CO₃ (III) were in a similar range, albeit the curve shapes
282 were different (Fig. 3). At higher conversions, the gasification rate with CaCO₃ was much lower
283 than that with K₂CO₃, reflecting the inhibitive sintering of CaCO₃, explored in further depth in
284 Section 3.3.

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180



285

286 Fig. 3. CO₂ gasification at 850 °C of CB with either K₂CO₃ or CaCO₃ as added catalysts.

287

288 3.3 Gasification inhibition

289 Both catalysts will inhibit gasification if they sinter and/or block access of CO₂ to the CB. To

290 further illustrate this inhibition, tests were performed with different placements of CB and K₂CO₃

291 (Fig. 4a) or CaCO₃ (Fig. 4b, note the different y-axis range than in Fig. 4a) within the crucible.

292 The total weight was always within 0.1 mg of the target weight, the catalysts were used as received

293 (particles sizes of 1.5 μm for K₂CO₃ and 7.1 μm for CaCO₃, Table 1), and the CB was ball-milled

294 (particle size of 3.1 μm, Table 1). The gasification rates were generally higher when the catalyst

295 was placed below the CB. For the samples with CB and K₂CO₃, the curves had similar shapes

296 regardless of the location of the catalyst with the gasification rates decreasing in the order of K₂CO₃

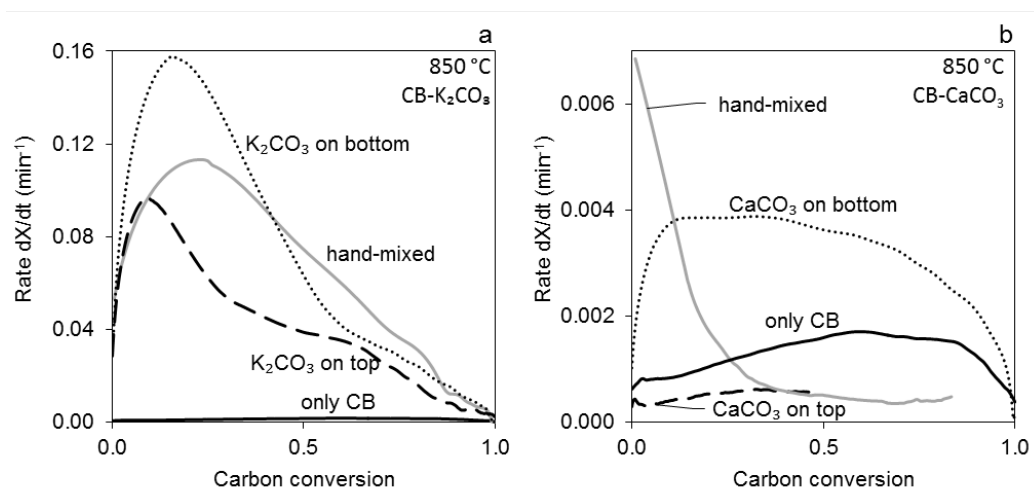
297 on bottom > hand-mixed > K₂CO₃ on top. For the samples with CB and CaCO₃, the curves had

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

298 different shapes. The gasification rate decreased exponentially for the hand-mixed sample and was
299 nearly an order of magnitude higher initially than those of the other samples for which the curve
300 shapes were concave-down and had rates decreasing in the order CaCO_3 on bottom $>$ CB $>$ CaCO_3
301 on top. That is, placing CaCO_3 on top of the CB severely inhibited the reaction.



302

303 Fig. 4. CO_2 gasification of ball-milled CB at 850 °C with different placement of a) K_2CO_3 , and b)
304 CaCO_3 relative to CB.

305

306 The Tammann softening temperature (i.e. two-thirds of the melting point) of CaCO_3 is 842 °C.

307 CaCO_3 heated to 850 °C under CO_2 then cooled to room temperature formed a fused solid in the

308 crucible. If heated under N_2 , which allowed CaCO_3 to decompose to CaO (the Tammann softening

309 temperature of CaO is 1624 °C), a loose powder remained in the crucible. The more dispersed the

310 CaCO_3 was initially (e.g., by ball-milling the mixture together, CB- CaCO_3 (XII) in Fig. 2c), the

311 higher the conversion that could be reached before the CaCO_3 formed a continuous phase through

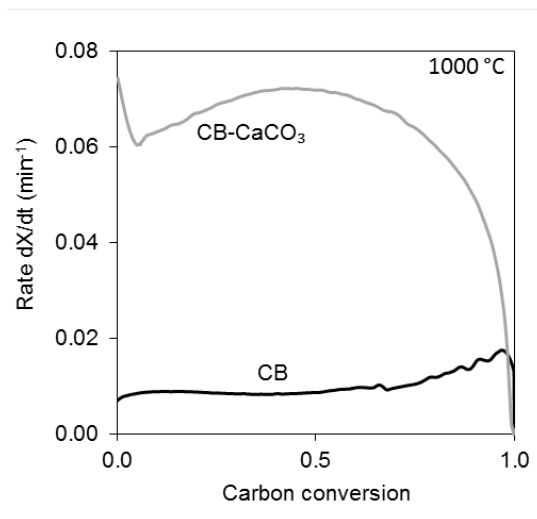
312 which CO_2 had to diffuse before reacting with the CB. Indeed, sintering is reported as the primary

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

313 mode by which calcium gasification catalysts deactivate [44]. The formation of the sintered layer
314 can be avoided by heating the mixtures in N₂ and gasifying at temperatures where CaO rather than
315 CaCO₃ is stable. The gasification of ball-milled CB by itself (CB (II)) or hand-mixed with CaCO₃
316 (CB-CaCO₃ (IX)) at 1000 °C demonstrates this idea. At this temperature, calcium remained as
317 CaO even in a ~98% CO₂ atmosphere and thus, the Ca-catalyzed gasification of CB was not
318 inhibited by sintering (Fig. 5). Thus, conditions (temperature, concentration) at which CaCO₃ will
319 sinter should be avoided where possible.



320

321 Fig. 5. Conversion versus time curves for CO₂ gasification at 1000 °C of ball-milled CB and hand-
322 mixed with CaCO₃.

323

324

325 *3.4 Kinetic modeling*

326 For quantification, the gasification results were fit to two models – RPM and eRPM. The data were

327 not well fit by the RPM, but the rate constants, k , from this fit were used as the k -values for the

328 eRPM modeling to estimate the parameters ψ , c , and p as shown in Table 2. The fits for the

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

329 gasification rates of all the CB-K₂CO₃ mixtures had R^2 values above 0.96. The values of k_j were
330 as expected, with ball-milled mixtures having higher values than hand-mixed mixtures, and K₂CO₃
331 showing values one to two orders of magnitude higher than CaCO₃. Though curves V, VI, and VII
332 (Fig. 2b) were indistinguishable above 40% conversion, the k_j values were significantly different.
333 The value was highest for ball-milled K₂CO₃ which was subsequently hand-mixed with CB as
334 received (V), suggesting that ball-milling the CB had no discernible effect on gasification rates
335 when the K₂CO₃ particle size had been reduced by ball-milling. The values of ψ for CB-K₂CO₃
336 mixtures reflected that the higher dispersions achieved through ball-milling of K₂CO₃ increased
337 pore development. The p values were much smaller for samples in which K₂CO₃ was ball-milled,
338 reflecting lower conversions for the maximum gasification rates (Fig. 1b). Ball-milling of K₂CO₃
339 increased the initial rate of porosity generation, and hence the initial gasification rate. No trend
340 was observed in the c values for CB-K₂CO₃, similar to a previous study on coal gasification [32].

341
342 In the case of the CB-CaCO₃ samples, mixtures VIII and XI had similar gasification profiles as
343 the CB samples and, therefore, the eRPM did not fit the data well. The eRPM was the best fit when
344 CB and CaCO₃ were ball-milled together, further demonstrating that calcium was most effective
345 as a gasification catalyst when reduced in particle size and well-dispersed. The structural
346 parameter, ψ , for the gasification of the CB-CaCO₃ samples in which only CB was ball-milled
347 (curve IX) or in which only CaCO₃ was ball-milled (curve X) was zero. That is, there was no
348 porosity development, consistent with calcium sintering rather than moving through the CB

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

349 particles. Ball-milling the CB and CaCO₃ together (curve XII) better dispersed the catalyst and
350 allowed porosity to develop ($\psi = 11.3$) before the catalyst sintered. Overall, the eRPM modeling
351 results reflect the importance of the mixing method: ball-milling better dispersed the catalysts
352 leading to increased porosity development and thus, higher reaction rates for both potassium and
353 calcium. Better dispersion also impeded the rate of CaCO₃ sintering.

354

355 Table 2. Rate constants (k_j), structural factors (ψ), and R^2 values for the catalytic CB samples
356 calculated by the extended random pore model (eRPM) with a 95% confidence interval.
357 Underlined components were ball-milled; mixtures with an asterisk (*) were ball-milled together.

Sample	k	ψ	c	p	R^2
CB-K ₂ CO ₃ (III)	$3.2 \cdot 10^{-2} \pm 4.5 \cdot 10^{-4}$	1.98 ± 0.11	0.45 ± 0.04	13.92 ± 1.64	0.954
<u>CB</u> -K ₂ CO ₃ (IV)	$1.1 \cdot 10^{-1} \pm 1.3 \cdot 10^{-3}$	0.92 ± 0.03	-0.63 ± 0.03	24.89 ± 2.00	0.971
CB- <u>K₂CO₃</u> (V)	$3.2 \cdot 10^{-1} \pm 4.8 \cdot 10^{-3}$	18.83 ± 1.29	-0.48 ± 0.01	-0.21 ± 0.01	0.980
<u>CB</u> - <u>K₂CO₃</u> (VI)	$2.5 \cdot 10^{-1} \pm 5.1 \cdot 10^{-3}$	66.94 ± 0.00	-0.63 ± 0.00	-0.13 ± 0.00	0.990
<u>CB</u> - <u>K₂CO₃</u> * (VII)	$2.2 \cdot 10^{-1} \pm 4.4 \cdot 10^{-3}$	58.19 ± 4.71	-0.56 ± 0.02	-0.15 ± 0.01	0.990
<u>CB</u> -CaCO ₃ (IX)	$1.6 \cdot 10^{-3} \pm 3.8 \cdot 10^{-5}$	0.00 ± 0.00	7.23 ± 0.09	8.19 ± 0.10	0.973
CB- <u>CaCO₃</u> (X)	$2.6 \cdot 10^{-3} \pm 3.9 \cdot 10^{-5}$	0.00 ± 0.00	0.13 ± 0.00	-1.06 ± 0.00	0.818
<u>CB</u> - <u>CaCO₃</u> * (XII)	$3.7 \cdot 10^{-3} \pm 1.6 \cdot 10^{-4}$	11.31 ± 0.21	0.39 ± 0.01	-5.92 ± 0.00	0.992

358

359 The maximum rates observed for ball-milled K₂CO₃ ($> 0.3 \text{ min}^{-1}$, Fig. 2b) are an order of
360 magnitude higher than those observed in the literature for feeds such as coal [47] and biomass
361 [16,48]. Rates greater than 0.1 min^{-1} have been observed in our previous studies with CB [35,36],
362 suggesting that the extremely high rates are due to the properties of the CB, including the absence
363 of ash, the highly amorphous nature, and the low porosity ($18 \text{ m}^2/\text{g}$ by CO₂ physisorption). These
364 high rates, however, are likely mass transfer limited. The high ψ -values for mixtures VI and VII
365 indicate the creation of porosity, which would be expected to lead to even higher reaction rates in

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

366 the absence of mass transfer limitations. For Ca-catalyzed gasification at 850 °C, the highest rates
367 are an order of magnitude lower than the slowest rates for K-catalyzed gasification. The sintering
368 of CaCO₃ at high conversions will introduce mass transfer limitations. The presence of mixed
369 kinetic-transport control for mixtures V-VII does not affect the overall conclusions of the paper;
370 namely, Ca is most effective as a gasification catalyst when reduced in particle size and well-
371 dispersed with the gasification feed, while K is most effective when reduced in particle size, as the
372 dispersion within the feed is less of a factor due to the high mobility of K at typical gasification
373 temperatures.

374

375 *3.5 Applications for future studies*

376 Particle sizes of the feed and catalytic species are rarely provided in literature results, but the trends
377 of particle sizes or catalyst surface area versus gasification rates have been discussed. Studies vary
378 from finding slight increases in gasification rate with a reduction in particle size [49] to finding
379 dramatic increases [50]. There is also a high variability in what is considered a reduced particle
380 size; for example, one study [8] estimated 1 mm as the particle size below which diffusion
381 limitations are insignificant, suggesting that further particle size reduction was ineffective for
382 increasing the reaction rate. Our results, however, indicate that the reaction rate increased in the
383 absence of catalysts when decreasing the CB particles from 10.6 to 3.1 μm (Fig. 2a), demonstrating
384 that diffusion limitations were still present in carbon particles much smaller than 1 mm in diameter.
385 In the aforementioned study [8], the feed was highly porous (reported surface area of 620 m²/g),

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

386 more than 30 times larger than the specific surface area of the CB in our study. For highly porous
387 feeds, reducing the particle size would have a negligible effect on the specific surface area.
388 Increasing the specific surface area would also have a negligible effect for systems in which
389 external mass transfer was the limiting factor. The properties of the feed, including particle size
390 and specific surface area, should be given in all gasification papers to allow for comparison
391 between varied feeds.

392

393 The particle size of the catalyst has a much larger effect on the overall reaction rate than the particle
394 size of the CB, and this effect increases with increasing temperature. At 700 °C, a six-fold
395 reduction in catalyst size led to an increase in the reaction rate by a factor of 2.3 [51], while at
396 900 °C, a two-fold reduction in particle size led to an increase in the reaction rate by a factor of
397 4.5 [52]. Increased calcium loading up to approximately 4 wt% led to an increase in reaction rate,
398 but higher loadings did not lead to a further increase because of the increase in sintering [53]. This
399 sintering of CaCO₃ has also been observed over time, with the rate of reaction decreasing by a
400 factor of 25 after an hour of gasification at 700 °C despite not reaching complete conversion [51].
401 The results with calcium in the current study observed sintering taking place over time (Fig. 4b).
402 No studies could be found in which the particle size of a potassium catalyst was given. For
403 meaningful comparisons between gasification studies, the particle sizes of all catalysts used should
404 be provided.

405

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

406 The rate of gasification has also been found to increase with increased calcium catalyst dispersion
407 [44,54–56]. CaO has been observed to be more effective as a catalyst when added using ion
408 exchange than wet impregnation due to the low solubility of CaO in water [52,57]. Our study
409 established that increased dispersion and reduced particle size both have a significant effect on the
410 gasification rate when CaCO₃ is used as the catalyst, while only initial particle size has a significant
411 effect when K₂CO₃ is used as the catalyst. The current study also found that CaCO₃ can inhibit the
412 gasification rate if not sufficiently dispersed, which has not been discussed in the literature. When
413 reporting sample preparation techniques in gasification papers, a phrase such as “physical mixing”
414 should not be used, since it encompasses a variety of techniques from briefly stirring with a spatula
415 to high-energy planetary ball-milling. Details of the mixing method used should be provided, and
416 the extent of pre-gasification catalyst dispersion should be at least qualitatively assessed in future
417 gasification publications.

418

419 4. Conclusions

420 The catalyst introduction technique has a significant effect on the rates observed in gasification as
421 shown in this study with CB and K₂CO₃ or CaCO₃. The less active and/or mobile the catalyst, the
422 more impact parameters such as feed particle size, catalyst particle size, and dispersion have on
423 the gasification rates. In addition, the phase behavior of the catalyst must be considered. For
424 example, when CaCO₃ was insufficiently dispersed, it sintered and surrounded the carbon, which
425 reduced access of the gasification agent, CO₂, to the CB. Conversely, the gasification rates using
426 a high-mobility catalyst such as K₂CO₃ were only dependent on catalyst particle size, with the

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

427 calculated rates and modeled rate constants being independent of carbon particle size or catalyst
428 dispersion. The eRPM modeling results identified, through the changes in the structural parameter
429 ψ , that the catalyst dispersion increased the creation of porosity during gasification. With Ca,
430 porosity formation was only observed when the carbon and catalyst were ball-milled together,
431 while with K, ball-milling greatly increased the porosity generation. These results highlight the
432 significantly different rates that can be obtained depending on the properties of the feed mixture.
433 Details of particle sizes and catalyst dispersion must always be reported to allow for appropriate
434 comparison within and between studies.

435

436 Acknowledgements

437 The authors would like to acknowledge Dr. Sathish Ponnurangam for his suggestion of testing
438 CB-CaCO₃ at 1000 °C, and Dr. Jan Kopyscinski for advice concerning the kinetic modeling. This
439 work was supported by the Natural Sciences and Engineering Research Council of Canada [grant
440 number: STPGP 380927].

441

442 References

- 443 [1] Jiang M-Q, Zhou R, Hu J, Wang F-C, Wang J. Calcium-promoted catalytic activity of
444 potassium carbonate for steam gasification of coal char: Influences of calcium species. *Fuel*
445 2012;99:64–71. <https://doi.org/10.1016/j.fuel.2012.04.007>.
446 [2] Laurendeau NM. Heterogeneous kinetics of coal char gasification and combustion. *Prog*
447 *Energy Combust Sci* 1978;4:221–70. [https://doi.org/10.1016/0360-1285\(78\)90008-4](https://doi.org/10.1016/0360-1285(78)90008-4).
448 [3] Adschiri T, Furusawa T. Relation between CO₂-reactivity of coal char and BET surface area.
449 *Fuel* 1986;65:927–31. [https://doi.org/10.1016/0016-2361\(86\)90200-0](https://doi.org/10.1016/0016-2361(86)90200-0).

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

- 450 [4] Hashimoto K, Miura K, Xu J-J, Watanabe A, Masukami H. Relation between the gasification
451 rate of carbons supporting alkali metal salts and the amount of oxygen trapped by the metal.
452 *Fuel* 1986;65:489–94. [https://doi.org/10.1016/0016-2361\(86\)90038-4](https://doi.org/10.1016/0016-2361(86)90038-4).
- 453 [5] Annamalai K, Ryan W, Dhanapalan S. Interactive processes in gasification and
454 combustion—Part III: Coal/char particle arrays, streams and clouds. *Prog Energy Combust
455 Sci* 1994;20:487–618. [https://doi.org/10.1016/0360-1285\(94\)90002-7](https://doi.org/10.1016/0360-1285(94)90002-7).
- 456 [6] Kirubakaran V, Sivaramakrishnan V, Nalini R, Sekar T, Premalatha M, Subramanian P. A
457 review on gasification of biomass. *Renew Sustain Energy Rev* 2009;13:179–86.
458 <https://doi.org/10.1016/j.rser.2007.07.001>.
- 459 [7] Hu Y, Yu H, Zhou F, Chen D. A comparison between CO₂ gasification of various biomass
460 chars and coal char. *Can J Chem Eng* 2019;97:1326–31. <https://doi.org/10.1002/cjce.23417>.
- 461 [8] Mermoud F, Golfier F, Salvador S, Van de Steene L, Dirion JL. Experimental and numerical
462 study of steam gasification of a single charcoal particle. *Combust Flame* 2006;145:59–79.
463 <https://doi.org/10.1016/j.combustflame.2005.12.004>.
- 464 [9] Malekshahian M, De Visscher A, Hill JM. A non-equimolar mass transfer model for carbon
465 dioxide gasification studies by thermogravimetric analysis. *Fuel Process Technol*
466 2014;124:1–10. <https://doi.org/10.1016/j.fuproc.2014.02.009>.
- 467 [10] Lund CRF. Staged carbon gasification with nickel catalysts. *Carbon* 1987;25:337–41.
468 [https://doi.org/10.1016/0008-6223\(87\)90004-2](https://doi.org/10.1016/0008-6223(87)90004-2).
- 469 [11] Liew SC, Hill JM. Impacts of vanadium and coke deposits on the CO₂ gasification of nickel
470 catalysts supported on activated carbon from petroleum coke. *Appl Catal Gen* 2015;504:420–
471 8. <https://doi.org/10.1016/j.apcata.2014.11.006>.
- 472 [12] Kapteijn F, Peer O, Moulijn JA. Kinetics of the alkali carbonate catalysed gasification of
473 carbon: 1. CO₂ gasification. *Fuel* 1986;65:1371–6. [https://doi.org/10.1016/0016-2361\(86\)90107-9](https://doi.org/10.1016/0016-2361(86)90107-9).
- 475 [13] Sutton D, Kelleher B, Ross JRH. Review of literature on catalysts for biomass gasification.
476 *Fuel Process Technol* 2001;73:155–73. [https://doi.org/10.1016/S0378-3820\(01\)00208-9](https://doi.org/10.1016/S0378-3820(01)00208-9).
- 477 [14] Kramb J, Gómez-Barea A, DeMartini N, Romar H, Doddapaneni TRKC, Konttinen J. The
478 effects of calcium and potassium on CO₂ gasification of birch wood in a fluidized bed. *Fuel*
479 2017;196:398–407. <https://doi.org/10.1016/j.fuel.2017.01.101>.
- 480 [15] Meijer R, Weeda M, Kapteijn F, Moulijn JA. Catalyst loss and retention during alkali-
481 catalysed carbon gasification in CO₂. *Carbon* 1991;29:929–41. [https://doi.org/10.1016/0008-6223\(91\)90171-E](https://doi.org/10.1016/0008-6223(91)90171-E).
- 483 [16] Perander M, DeMartini N, Brink A, Kramb J, Karlström O, Hemming J, et al. Catalytic effect
484 of Ca and K on CO₂ gasification of spruce wood char. *Fuel* 2015;150:464–72.
485 <https://doi.org/10.1016/j.fuel.2015.02.062>.
- 486 [17] Kapteijn F, Abbel G, Moulijn JA. CO₂ gasification of carbon catalysed by alkali metals:
487 Reactivity and mechanism. *Fuel* 1984;63:1036–42. [https://doi.org/10.1016/0016-2361\(84\)90184-4](https://doi.org/10.1016/0016-2361(84)90184-4).
- 488

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

- 489 [18] Meijer R, Kapteijn F, Moulijn JA. Kinetics of the alkali-carbonate catalysed gasification of
490 carbon: 3. H₂O gasification. *Fuel* 1994;73:723–30. <https://doi.org/10.1016/0016->
491 2361(94)90015-9.
- 492 [19] Kapteijn F, Moulijn JA. Kinetics of the potassium carbonate-catalysed CO₂ gasification of
493 activated carbon. *Fuel* 1983;62:221–5. [https://doi.org/10.1016/0016-2361\(83\)90203-X](https://doi.org/10.1016/0016-2361(83)90203-X).
- 494 [20] Tang J, Wang J. Catalytic steam gasification of coal char with alkali carbonates: A study on
495 their synergic effects with calcium hydroxide. *Fuel Process Technol* 2016;142:34–41.
496 <https://doi.org/10.1016/j.fuproc.2015.09.020>.
- 497 [21] Kapteijn F, Porre H, Moulijn JA. CO₂ gasification of activated carbon catalyzed by earth
498 alkaline elements. *AIChE J* 1986;32:691–5. <https://doi.org/10.1002/aic.690320421>.
- 499 [22] Kopyscinski J, Habibi R, Mims CA, Hill JM. K₂CO₃-Catalyzed CO₂ Gasification of Ash-
500 Free Coal: Kinetic Study. *Energy Fuels* 2013;27:4875–83.
501 <https://doi.org/10.1021/ef400552q>.
- 502 [23] Kopyscinski J, Rahman M, Gupta R, Mims CA, Hill JM. K₂CO₃ catalyzed CO₂ gasification
503 of ash-free coal. Interactions of the catalyst with carbon in N₂ and CO₂ atmosphere. *Fuel*
504 2014;117:1181–9. <https://doi.org/10.1016/j.fuel.2013.07.030>.
- 505 [24] Malekshahian M, Hill JM. Potassium catalyzed CO₂ gasification of petroleum coke at
506 elevated pressures. *Fuel Process Technol* 2013;113:34–40.
507 <https://doi.org/10.1016/j.fuproc.2013.03.017>.
- 508 [25] Luo S, Xiao B, Hu Z, Liu S, Guo X, He M. Hydrogen-rich gas from catalytic steam
509 gasification of biomass in a fixed bed reactor: Influence of temperature and steam on
510 gasification performance. *Int J Hydrog Energy* 2009;34:2191–4.
511 <https://doi.org/10.1016/j.ijhydene.2008.12.075>.
- 512 [26] Yeboah YD, Xu Y, Sheth A, Godavarty A, Agrawal PK. Catalytic gasification of coal using
513 eutectic salts: identification of eutectics. *Carbon* 2003;41:203–14.
514 [https://doi.org/10.1016/S0008-6223\(02\)00310-X](https://doi.org/10.1016/S0008-6223(02)00310-X).
- 515 [27] Zou J, Yang B, Gong K, Wu S, Zhou Z, Wang F, et al. Effect of mechanochemical treatment
516 on petroleum coke–CO₂ gasification. *Fuel* 2008;87:622–7.
517 <https://doi.org/10.1016/j.fuel.2007.07.021>.
- 518 [28] Yamashita H, Nomura M, Tomita A. Local structures of metals dispersed on coal. 4. Local
519 structure of calcium species on coal after heat treatment and carbon dioxide gasification.
520 *Energy Fuels* 1992;6:656–61. <https://doi.org/10.1021/ef00035a018>.
- 521 [29] Radovic LR, Walker PL, Jenkins RG. Catalytic coal gasification: use of calcium versus
522 potassium. *Fuel* 1984;63:1028–30. [https://doi.org/10.1016/0016-2361\(84\)90329-6](https://doi.org/10.1016/0016-2361(84)90329-6).
- 523 [30] Lang RJ, Neavel RC. Behaviour of calcium as a steam gasification catalyst. *Fuel*
524 1982;61:620–6. [https://doi.org/10.1016/0016-2361\(82\)90006-0](https://doi.org/10.1016/0016-2361(82)90006-0).
- 525 [31] Berdugo Vilches T, Maric J, Knutsson P, Rosenfeld DC, Thunman H, Seemann M. Bed
526 material as a catalyst for char gasification: The case of ash-coated olivine activated by K and
527 S addition. *Fuel* 2018;224:85–93. <https://doi.org/10.1016/j.fuel.2018.03.079>.

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

- 528 [32] Islam S, Kopyscinski J, Liew SC, Hill JM. Impact of K₂CO₃ catalyst loading on the CO₂-
529 gasification of Genesse raw coal and low-ash product. *Powder Technol* 2016;290:141–7.
530 <https://doi.org/10.1016/j.powtec.2015.12.013>.
- 531 [33] Jiang L, Hu S, Xu K, Wang Y, Syed-Hassan SSA, Su S, et al. Formation, fates and roles of
532 catalytic precursors generated from the K₂CO₃-carbon interactions in the K₂CO₃-catalyzed
533 CO₂ gasification of coal char. *J Anal Appl Pyrolysis* 2017;124:384–92.
534 <https://doi.org/10.1016/j.jaap.2016.11.006>.
- 535 [34] Arnold RA, Hill JM. Catalysts for gasification: a review. *Sustain Energy Fuels* 2019;3:656–
536 72. <https://doi.org/10.1039/C8SE00614H>.
- 537 [35] Arnold RA, Habibi R, Kopyscinski J, Hill JM. Interaction of Potassium and Calcium in the
538 Catalytic Gasification of Biosolids and Switchgrass. *Energy Fuels* 2017;31:6240–7.
539 <https://doi.org/10.1021/acs.energyfuels.7b00972>.
- 540 [36] Arnold RA, Hill JM. Effect of calcium and barium on potassium-catalyzed gasification of
541 ash-free carbon black. *Fuel* 2019;254:115647. <https://doi.org/10.1016/j.fuel.2019.115647>.
- 542 [37] Bhatia SK, Perlmutter DD. A random pore model for fluid-solid reactions: I. Isothermal,
543 kinetic control. *AIChE J* 1980;26:379–86. <https://doi.org/10.1002/aic.690260308>.
- 544 [38] Zhang Y, Ashizawa M, Kajitani S, Miura K. Proposal of a semi-empirical kinetic model to
545 reconcile with gasification reactivity profiles of biomass chars. *Fuel* 2008;87:475–81.
546 <https://doi.org/10.1016/j.fuel.2007.04.026>.
- 547 [39] Akaike H. A new look at the statistical model identification. *IEEE Trans Autom Control*
548 1974;19:716–23. <https://doi.org/10.1109/TAC.1974.1100705>.
- 549 [40] Zhang J, Guo J, Li T, Li X. Chemical Surface Modification of Calcium Carbonate Particles
550 by Maleic Anhydride Grafting Polyethylene Wax. *Int J Green Nanotechnol Phys Chem*
551 2010;1:P65–71. <https://doi.org/10.1080/19430871003684341>.
- 552 [41] Berbezier I, Martin JM, Kapsa Ph. The role of carbon in lubricated mild wear. *Tribol Int*
553 1986;19:115–22. [https://doi.org/10.1016/0301-679X\(86\)90016-2](https://doi.org/10.1016/0301-679X(86)90016-2).
- 554 [42] Rothon R. *Particulate-filled Polymer Composites*. iSmithers Rapra Publishing; 2003.
- 555 [43] Koottathape N, Takahashi H, Iwasaki N, Kanehira M, Finger WJ. Two- and three-body wear
556 of composite resins. *Dent Mater* 2012;28:1261–70.
557 <https://doi.org/10.1016/j.dental.2012.09.008>.
- 558 [44] Radovic LR, Walker PL, Jenkins RG. Importance of catalyst dispersion in the gasification of
559 lignite chars. *J Catal* 1983;82:382–94. [https://doi.org/10.1016/0021-9517\(83\)90205-1](https://doi.org/10.1016/0021-9517(83)90205-1).
- 560 [45] Zellnitz S, Redlinger-Pohn JD, Kappl M, Schroettner H, Urbanetz NA. Preparation and
561 characterization of physically modified glass beads used as model carriers in dry powder
562 inhalers. *Int J Pharm* 2013;447:132–8. <https://doi.org/10.1016/j.ijpharm.2013.02.044>.
- 563 [46] Fei H, Hu S, Xiang J, Sun L, Fu P, Chen G. Study on coal chars combustion under O₂/CO₂
564 atmosphere with fractal random pore model. *Fuel* 2011;90:441–8.
565 <https://doi.org/10.1016/j.fuel.2010.09.027>.
- 566 [47] Habibi R, Kopyscinski J, Masnadi MS, Lam J, Grace JR, Mims CA, et al. Co-gasification of
567 Biomass and Non-biomass Feedstocks: Synergistic and Inhibition Effects of Switchgrass

This is the author accepted version of the following paper:

Arnold, R. A., Motta, I. L., & Hill, J. M. (2020). Impact of particle size and catalyst dispersion on gasification rates measured in a thermogravimetric analysis unit: Case study of carbon black catalyzed by potassium or calcium. *Fuel*, 119677. <https://doi.org/10.1016/j.fuel.2020.119677>

Fuel, JFUE-D-20-02180

- 568 Mixed with Sub-bituminous Coal and Fluid Coke During CO₂ Gasification. *Energy Fuels*
569 2013;27:494–500. <https://doi.org/10.1021/ef301567h>.
- 570 [48] Edreis EMA, Li X, Luo G, Sharshir SW, Yao H. Kinetic analyses and synergistic effects of
571 CO₂ co-gasification of low sulphur petroleum coke and biomass wastes. *Bioresour Technol*
572 2018;267:54–62. <https://doi.org/10.1016/j.biortech.2018.06.089>.
- 573 [49] Takarada T, Ichinose S, Kato K. Gasification of bituminous coal with K-exchanged brown
574 coal prepared from potassium chloride. *Fuel* 1992;71:883–7. [https://doi.org/10.1016/0016-2361\(92\)90237-I](https://doi.org/10.1016/0016-2361(92)90237-I).
- 575
- 576 [50] Hernández JJ, Aranda-Almansa G, Bula A. Gasification of biomass wastes in an entrained
577 flow gasifier: Effect of the particle size and the residence time. *Fuel Process Technol*
578 2010;91:681–92. <https://doi.org/10.1016/j.fuproc.2010.01.018>.
- 579 [51] Ismail K, Yarmo MA, Taufiq-Yap YH, Ahmad A. The effect of particle size of CaO and
580 MgO as catalysts for gasification of oil palm empty fruit bunch to produce hydrogen. *Int J*
581 *Hydrog Energy* 2012;37:3639–44. <https://doi.org/10.1016/j.ijhydene.2011.05.100>.
- 582 [52] Linares-Solano A, Almela-Alarcón M, Salinas-Martínez de Lecea C. CO₂ chemisorption to
583 characterize calcium catalysts in carbon gasification reactions. *J Catal* 1990;125:401–10.
584 [https://doi.org/10.1016/0021-9517\(90\)90313-9](https://doi.org/10.1016/0021-9517(90)90313-9).
- 585 [53] de Lecea CS-M, Almela-Alarcón M, Linares-Solano A. Calcium-catalysed carbon
586 gasification in CO₂ and steam. *Fuel* 1990;69:21–7. [https://doi.org/10.1016/0016-2361\(90\)90253-M](https://doi.org/10.1016/0016-2361(90)90253-M).
- 587
- 588 [54] Radović LR, Walker PL, Jenkins RG. Importance of carbon active sites in the gasification of
589 coal chars. *Fuel* 1983;62:849–56. [https://doi.org/10.1016/0016-2361\(83\)90041-8](https://doi.org/10.1016/0016-2361(83)90041-8).
- 590 [55] Rewick RT, Wentreck PR, Wise H. Carbon gasification in the presence of metal catalysts.
591 *Fuel* 1974;53:274–9. [https://doi.org/10.1016/0016-2361\(74\)90048-9](https://doi.org/10.1016/0016-2361(74)90048-9).
- 592 [56] Ohtsuka Y, Asami K. Steam Gasification of Coals with Calcium Hydroxide. *Energy Fuels*
593 1995;9:1038–42. <https://doi.org/10.1021/ef00054a016>.
- 594 [57] Ohtsuka Y, Asami K. Highly active catalysts from inexpensive raw materials for coal
595 gasification. *Catal Today* 1997;39:111–25. [https://doi.org/10.1016/S0920-5861\(97\)00093-](https://doi.org/10.1016/S0920-5861(97)00093-X)
596 X.
597