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1 **Catalytic conversion of methylated aromatics over wood-derived chars – the role of**
2 **reforming agents and the effect of methyl groups**

3
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10
11 **Abstract**

12 Toluene steam reforming was performed over three wood-derived chars and compared with a
13 previously-reported pyrolytic conversion study. The heterogeneous mechanism of toluene
14 decomposition was not directly affected by the introduction of steam, but it caused gasification
15 of char and toluene-derived coke, which prolonged the initial high conversion efficiency.
16 Conversely, when oxygen was used as a substitute for steam, a direct ring-opening reaction of
17 toluene was observed, rather than solid carbon combustion. A comparison of benzene, toluene,
18 and *p*-xylene conversion revealed that the presence of a methyl group on the aromatic ring
19 enhanced its decomposition, regardless of the catalyst's activity. However, a second methyl
20 group did not further improve the conversion and only served to increase the intensity of
21 secondary recombination reactions.

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22 **Keywords:** biochar, tar, steam reforming

23

24 **1. Introduction**

25 Efficient tar removal is one of the most important challenges for the successful
26 commercialisation of biomass gasification technologies. Aromatic hydrocarbons released
27 during this conversion process create both a technical issue because they clog installations and
28 an economic disadvantage due to lower conversion of carbon into useful products [1–3].

29 Catalytic tar reforming is a solution to both those drawbacks, as it not only removes unwanted
30 volatiles from produced gases, but also promotes their conversion into calorific species, such
31 as CO and H₂. Compared with simple tar capture techniques, e.g., oil impingers, this more
32 refined method requires additional financial and operational efforts. Hence, substituting
33 commercial catalysts with gasification char produced *in situ*, i.e. low-cost with high availability,
34 has been recognised as a promising approach [2,4]. Significant efforts have been dedicated to
35 investigating the catalytic conversion of individual aromatic compounds. Simplifying the
36 composition of a real gasification tar, defined as all released “hydrocarbons with molecular
37 weight higher than benzene” [1,3], makes it possible to track the conversion efficiency and a
38 product distribution to provide fundamental knowledge on tar-char interactions. Small
39 molecules are often investigated, as their removal is the most challenging due to their highly
40 refractory nature [5–8].

41 Following a previous experiment on the pyrolytic conversion of toluene over three wood-
42 derived chars [9], a reactive atmosphere was introduced in this work. It is generally
43 acknowledged that the decomposition of aromatics creates a layer of solid carbon (coke) on the
44 catalyst surface, which decreases its activity by covering active sites and blocking pores [2,10].
45 Supplying an oxidising agent along with the tar compound often increases the longevity of

46 catalysts [5,10] due to the gasification of coke deposits, which ensures the availability of
47 catalytic surface sites for continuous compound conversion. When carbonaceous materials are
48 used, they also undergo oxidation, as suggested by an observed negative mass balance of
49 catalytic beds [5,11]. Thus, previously-conducted toluene conversion tests [9] were re-created
50 under an atmosphere of nitrogen containing 15.5 vol.% steam (based on [10]), while all other
51 previously-applied process parameters were maintained. The same activated chars prepared
52 from pine, alder, and beech were examined. Toluene pyrolysis and steam reforming were
53 investigated using the same facilities and uniform procedures to isolate the effect of steam on
54 the conversion process. Moreover, structural changes in the chars due to toluene pyrolysis and
55 steam reforming were assessed by characterising the physicochemical properties of spent
56 catalysts.

57 The results of the main experiment suggested that steam was solely involved in solid carbon
58 gasification, and it did not react directly with toluene. Therefore, additional tests using oxygen
59 – a more reactive agent – were conducted to investigate its role during the reforming of
60 aromatics. Understanding the differences in the behaviour of various oxidising agents could
61 allow the reforming atmosphere to be properly adjusted to achieve high and long-lasting tar
62 conversion. Thus, a comparison of steam and oxygen reforming provides an interesting
63 background for future, more detailed research that might result in a novel approach to tar
64 reforming.

65 The final aspect of this study was to examine what effect a methyl group attached to an aromatic
66 ring has on its conversion efficiency and product distribution. To investigate this, toluene was
67 replaced with either benzene or *p*-xylene because tar molecules with fewer substituents are
68 generally considered more refractory [5,10]. Tests were performed to verify this dependency
69 and to assess any differences in compound-catalyst interactions with respect to the number of
70 methyl substituents.

71

72 **2. Experimental**

73 Activated chars previously used in toluene pyrolytic conversion tests [9] were further studied
74 in this work. Three char samples were prepared, each from a single tree species. Pine was used
75 as the coniferous wood type, while alder and beech were selected as the deciduous trees with
76 different hardness values. Chars were prepared under laboratory conditions using a two-step
77 procedure with consecutive pyrolysis and steam activation, which was detailed in a previous
78 work [9].

79 Aromatics conversion was performed in a laboratory quartz tube reactor containing a tar-gas
80 mixture preparation section, a reaction zone with a bed of char as the catalyst, and a sampling
81 train to collect liquid and gaseous products. The details of the test rig can be found elsewhere
82 [9,12]. A representative tar compound and water (during steam reforming mode) were fed into
83 a separate heating zone of the test rig at 200 °C, acting as both an evaporator for liquid reagents
84 and a mixing chamber for the synthesised tar-gas blend. For steam reforming experiments, 15.5
85 vol.% H₂O in N₂ was used. Another reactive atmosphere was an O₂/N₂ mixture with the desired
86 concentration set by flow controllers. A model tar compound (toluene, benzene, or *p*-xylene)
87 was fed at a constant rate into the evaporator, where it was mixed with selected gases (N₂,
88 H₂O/N₂, or O₂/N₂). The flow rate of each tar-representing compound was set to obtain the
89 concentration of 12 g/Nm³; the test runs with 7 different feeding times were performed. The
90 reagents travelled to the reaction zone with a char bed held at 800 °C. Liquid and gaseous
91 products from tar compound conversion and from solid carbon gasification were then captured
92 at the reactor outlet in a set of impinger bottles and gas bags for post-run analysis using GC-
93 FID and GC-TCD, respectively. The setups of all experiments performed in this work are listed
94 in Table 1; the parameters applied in tests 1-3 were the same as during the previous studies on
95 toluene pyrolytic conversion [9] with the only difference being the introduction of 15.5 vol.%

96 of steam into the N₂ flow to obtain reforming conditions. Since the reactive atmosphere induced
 97 solid carbon (char/coke) gasification, blank tests with a char bed without toluene feeding (4-6)
 98 were also performed to investigate the intensity of steam-char interactions undisturbed by a tar
 99 compound. To evaluate the suitability of different oxidising agents for tar reforming, three tests
 100 containing O₂ instead of steam were also conducted (7-9). Finally, the effect of a methyl
 101 functional group during conversion of aromatics was examined by replacing toluene with either
 102 benzene or *p*-xylene (10-12).

103

104 Table 1. Summary of the performed tests: toluene catalytic steam reforming (1-3), blank tests
 105 for steam reforming (4-6), toluene reforming with O₂ (7-9), and tests with other compounds
 106 (10-12)

No	Char feedstock	Feeding time, min	Compound	Atmosphere
1	Alder	5, 10, 20, 30, 40, 50, 60	Toluene	H ₂ O (15.5 vol.%)/N ₂
2	Beech	5, 10, 20, 30, 40, 50, 60	Toluene	H ₂ O (15.5 vol.%)/N ₂
3	Pine	5, 10, 20, 30, 40, 50, 60	Toluene	H ₂ O (15.5 vol.%)/N ₂
4	Alder	60	None	H ₂ O (15.5 vol.%)/N ₂
5	Beech	60	None	H ₂ O (15.5 vol.%)/N ₂
6	Pine	60	None	H ₂ O (15.5 vol.%)/N ₂
7	No char	40	Toluene	O ₂ (3.5 vol.%)/N ₂
8	No char	40	Toluene	O ₂ (0.7 vol.%)/N ₂
9	Alder	40	Toluene	O ₂ (0.7 vol.%)/N ₂
10	Alder	30	Benzene	N ₂
11	Alder	30	Benzene	H ₂ O (15.5 vol.%)/N ₂
12	Alder	10, 20, 30, 40, 50	<i>p</i> -Xylene	N ₂

107

108 Some of the spent chars recovered after conversion tests were analysed to study the structural
109 changes occurring due to interactions with tar compounds and/or oxidising gases. Catalyst
110 examination involved assessing the surface functional groups using ATR-FTIR spectrometry
111 (Perkin Elmer Spectrum 100), as well as the total BET surface area and the area of micropores
112 calculated from the N₂ adsorption isotherms (Micromeritics TriStar II 3020), as described in
113 previous work [9].

114 The tar compound conversion (η_i) was expressed as the ratio of the amount of a converted
115 compound to the amount that was fed into the reactor, while the product yields (x_i) were
116 presented as the molar ratio relative to the amount of a converted compound [9]. Moreover, for
117 all studied chars, the ratio of the amount of each gaseous product released during steam
118 reforming of a selected compound (tests 1-3 and 11) to the amount produced during blank
119 reforming tests (4-6) was calculated as:

120
$$r_i = n_{iC}/n_{iB} \quad (1)$$

121 where n_{iC} and n_{iB} are the amounts of the i -th gas (mol) released during steam reforming of a
122 selected compound and during a blank test without compound feeding, respectively. All
123 conversion tests were performed in duplicate, and the average values with pooled standard
124 deviations were reported.

125

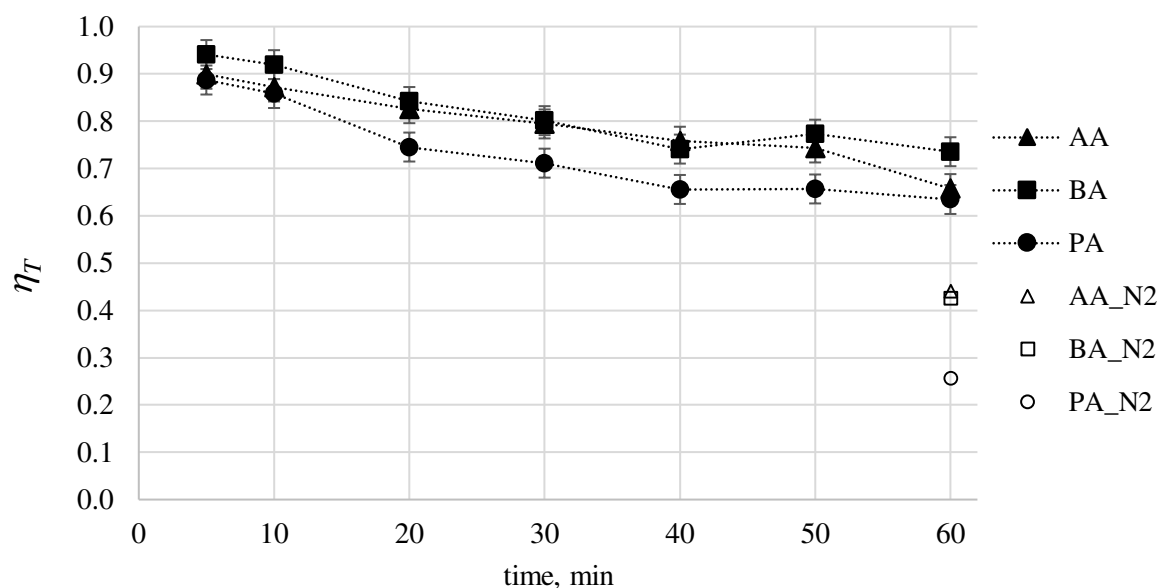
126 **3. Results and discussion**

127 **3.1. Steam reforming of toluene**

128 The catalytic conversion of toluene in the presence of 15.5 vol.% steam was carried out under
129 conditions otherwise analogous to the pyrolytic tests presented in the previous work [9]. Seven

130 steam reforming runs with different feeding times were performed with each activated char,
131 prepared from alder (AA), beech (BA), and pine (PA), and utilised as reaction catalysts. Fig. 1
132 shows the toluene conversion, η_T , expressed as the fraction of a fed compound that underwent
133 decomposition during the process. A constant decrease in the conversion efficiency was
134 observed for all applied catalysts, indicating continuous char bed deactivation due to coke
135 deposition – the main product of hydrocarbon decomposition. However, the intensity of this
136 phenomenon was lower than during pyrolytic experiments. Throughout the entire 60 min steam
137 reforming experiment, η_T remained above 0.6, while the toluene conversion under a pure N₂
138 atmosphere decreased to approximately 0.42 for AA and BA and 0.25 for PA char. The
139 prolonged catalytic activity in the presence of steam has been commonly observed in similar
140 studies [5,10], and it was attributed to the instantaneous gasification of the coke layer. Slightly
141 worse performance of pine char, compared with the other samples, was observed under
142 oxidising conditions, although this discrepancy was less pronounced compared with the
143 pyrolytic tests. During the reforming runs, char underwent gasification along with deposited
144 carbon. Since steam can widen the pores of treated materials [13,14], it likely extended the char
145 micropores in addition to removing the layer of coke. Thus, the presence of steam provided a
146 dual benefit of cleaning and widening the pores. The quicker deactivation of pine char under an
147 inert atmosphere, attributed to the higher microporosity of this material [9], was diminished
148 during tests with steam because it formed more mesopores.

149



150
 151 Fig. 1. Toluene conversion over time during steam reforming over alder (AA), beech (BA), and
 152 pine (PA) chars with the pyrolytic conversion (N₂) at 60 min used as a reference to the previous
 153 work [9]

154
 155 The same liquid by-products as those observed during previously conducted pyrolytic tests [9]
 156 were created upon steam reforming of toluene, and statistically similar benzene yields were
 157 obtained under both examined atmospheres. Analogously to the conversion under pure N₂, in
 158 the presence of steam, an increase in benzene formation was observed during the first 30 min
 159 of the reaction until it stabilised within the range of 12 – 18 % (Fig. 2). Thus, it can be expected
 160 that the two main heterogeneous conversion pathways during toluene pyrolysis were unaffected
 161 by the presence of steam during reforming tests because the same selectivity towards benzene
 162 formation was observed under both atmospheres. The formation of secondary reaction products
 163 during toluene steam reforming is presented in Fig. 3. Since the GC-FID analysis did not allow
 164 for complete analyte separation, two plausible species were assigned to two of the registered
 165 peaks. For longer feeding times, the ethylbenzene, *p*-xylene/*m*-xylene, and *o*-xylene/styrene

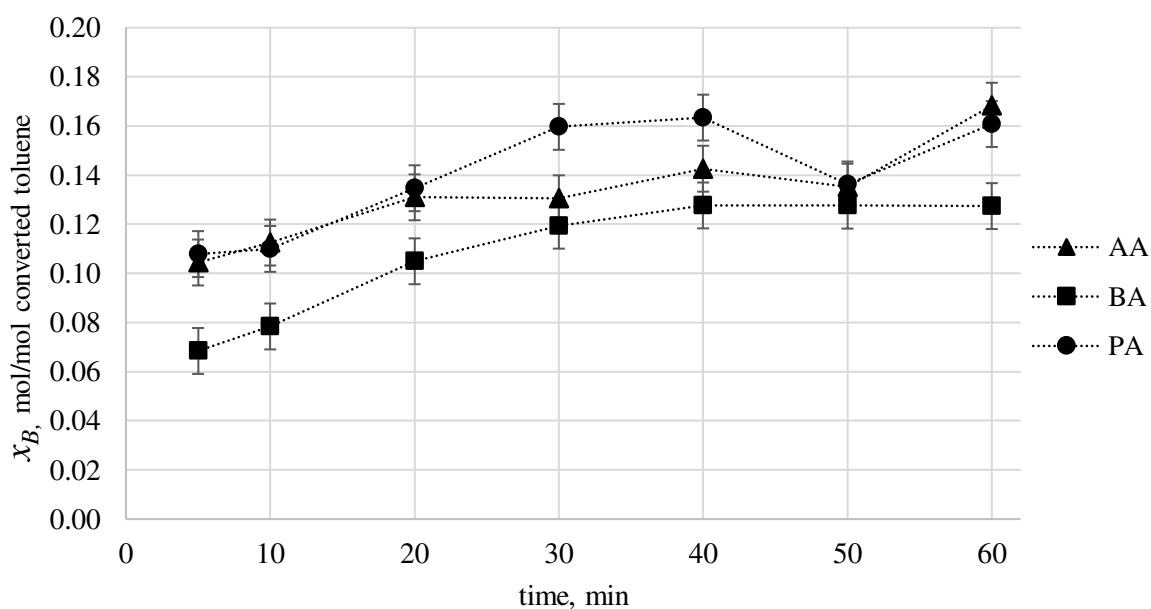
166 yields were approximately 10, 4, and 5 times lower, respectively, than the amounts detected
167 during toluene conversion under an inert atmosphere. During pyrolytic experiments, the
168 formation of secondary products was significantly increased at prolonged reaction times, i.e.
169 when the char bed was deactivated. Hence, the preservation of a catalyst surface activity during
170 reforming might have lowered the intensity of gas-phase recombination into substituted
171 benzenes, resulting in a less-pronounced increase in their yield over time.

172 Along with the liquid by-products of toluene reforming, the released gases were also analysed.
173 However, since steam interactions with char and deposited coke also formed gaseous
174 compounds, blank tests were performed to provide a point of reference. To this end, for each
175 char bed, a 60 min steam reforming run was carried out without toluene feeding, but the
176 established test procedure was otherwise maintained. For each detected species, the ratio of the
177 amounts of released gas during tests with and without toluene feeding, r_i , are presented in Fig.
178 4. In addition to methane and hydrogen detected during pyrolytic conversion, steam reforming
179 produced CO and CO₂. In the case of deciduous tree chars, the ratios $r_{CO} \ll 1$ and $r_{CO_2} \ll 1$
180 revealed that the formation of those species decreased when toluene was fed into the reactor.
181 Therefore, these gases likely originated from the steam gasification of solid carbon, and this
182 reaction was inhibited when it occurred concurrently with toluene conversion. The inhibition
183 of steam gasification of char by dissociative chemisorption of hydrogen released from
184 decomposing tar is commonly observed [15,16]. Fushimi et al. [16] reported that the decrease
185 in the char gasification rate due to the presence of gas-phase levoglucosan was greater than the
186 observed inhibition caused by hydrogen in a concentration corresponding to the amount
187 released from levoglucosan decomposition. Thus, it was concluded that both tar-derived
188 hydrogen and also vapour-phase levoglucosan and its pyrolysates inhibited char gasification. It
189 is therefore plausible that, in addition to the inhibition due to hydrogen released during toluene
190 decomposition, the tar compound and steam competed for some of the char active sites, which

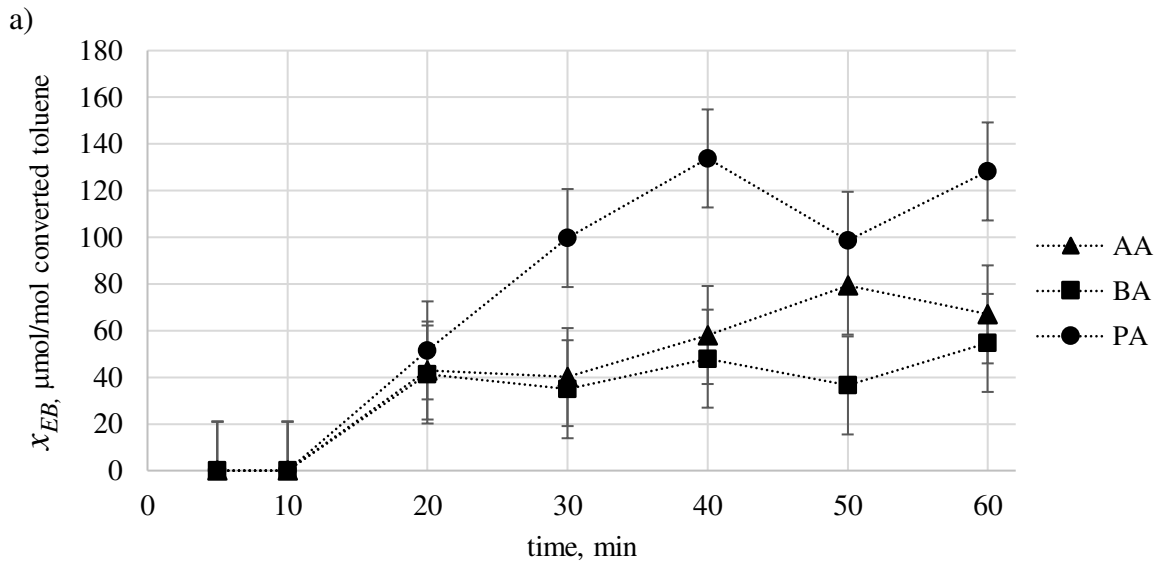
191 also impaired the solid carbon conversion. Another explanation for the inhibition of steam
192 gasification during toluene reforming lies in the plausibly less reactive nature of the toluene-
193 derived coke, compared with the char that is rich in active sites. During tests with toluene
194 feeding, the catalyst bed comprised a substantial amount of coke, which lowered the overall
195 reactivity of the solid carbon that underwent gasification, decreasing the rate of this reaction. A
196 general conclusion can be drawn that steam gasification of char during reforming tests helped
197 regenerate its surface, yet the char gasification itself was hindered because of the toluene
198 feeding. High r_{CH_4} values reaffirmed that most of the created methane was derived from toluene
199 demethylation into benzene, rather than from solid carbon hydrogasification. Pine char
200 gasification during a blank run without toluene feeding resulted in lower carbon oxide yields
201 due to the lower reactivity of this char, as observed in the TGA tests reported in a previous work
202 [9]. Therefore, it is plausible that the inhibitory effect of toluene on the char gasification rate
203 was less pronounced when this catalyst was used. Moreover, toluene-derived coke, which was
204 deposited on the char during reforming tests and concurrently gasified with steam, contributed
205 to the formation of CO and H₂ by providing another carbon source. It is plausible that the
206 inherently less-reactive pine char would benefit more from this additional carbon source than
207 the deciduous tree chars because the latter possessed more active sites, and thus the deposit with
208 a lower reactivity would have a more pronounced inhibitory effect on the char gasification rate.
209 Hence, the lower reactivity of pine char might be responsible for the positive values of r_{CO} and
210 r_{H_2} obtained for this material.

211 These findings suggest that toluene decomposition during steam reforming tests yielded the
212 same products as the ones detected during pyrolytic experiments. Similar selectivity towards
213 benzene formation was observed under both examined atmospheres; amongst the gaseous
214 products detected during steam reforming tests, only H₂ and CH₄, were attributed to the direct
215 toluene decomposition reactions, while CO and CO₂ originated from char/coke gasification.

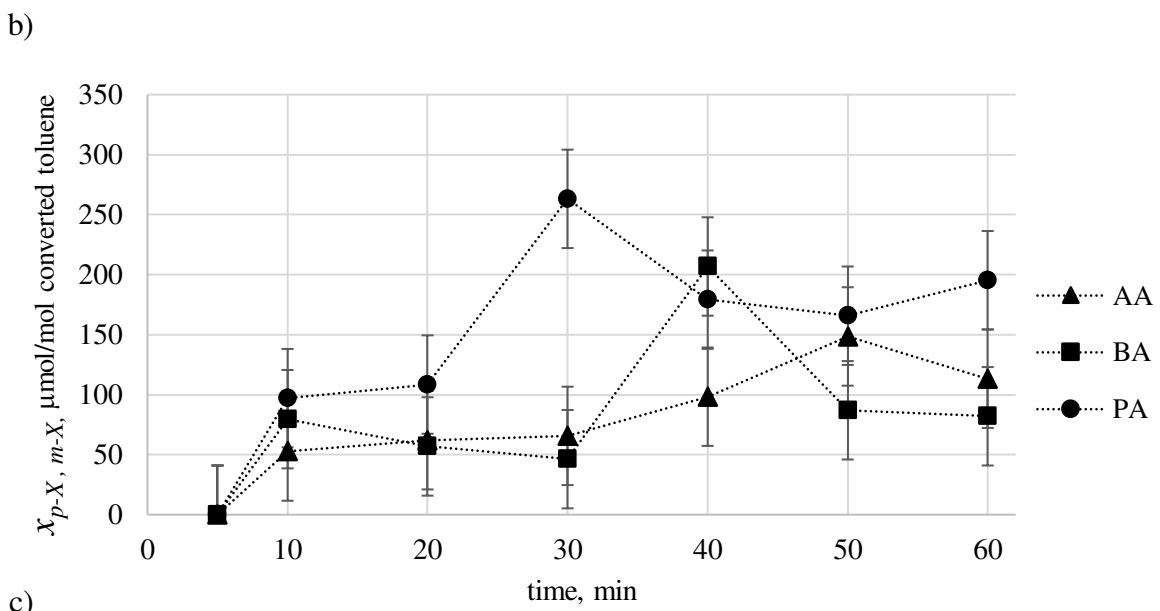
216 Therefore, it can be concluded that the principles of toluene decomposition during steam
217 reforming were the same as those during pyrolytic conversion. Two heterogeneous reactions
218 occurred on the char surface producing mainly coke and some benzene. No evidence of direct
219 toluene-steam interactions was observed – the conversion during preliminary tests without a
220 char bed was negligible, and carbon oxides formation during steam reforming could be
221 attributed to char gasification. The only noticeable role of steam was the gasification of solid
222 carbon, which prolonged the char activity by removing deposited coke and widening char pores.
223



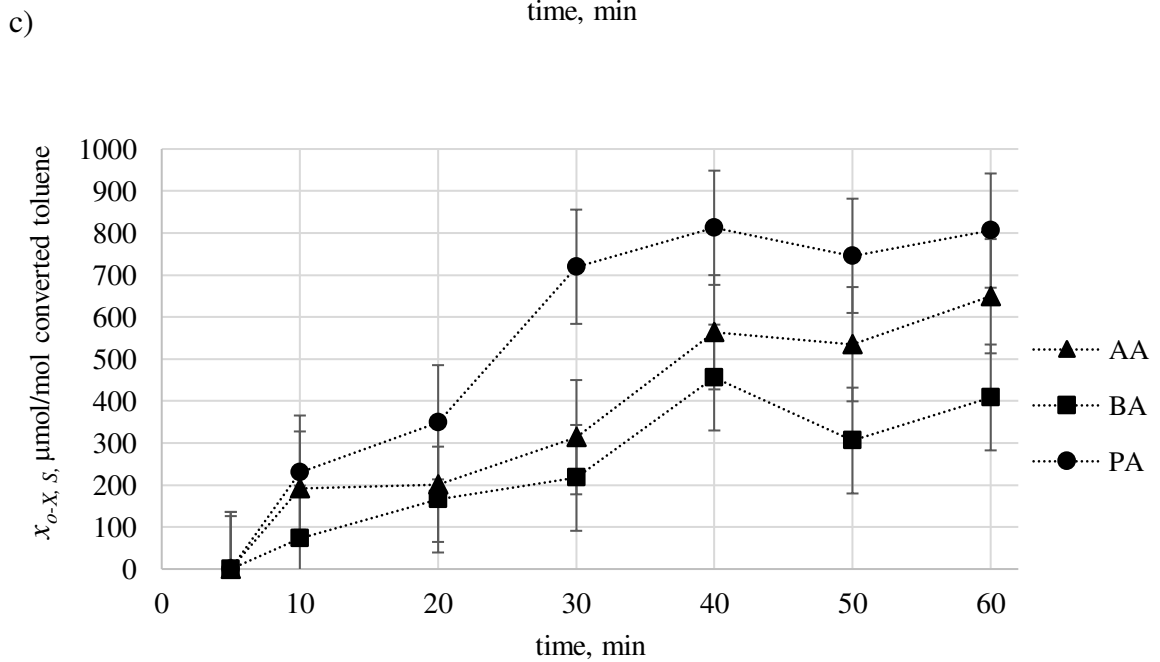
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225 Fig. 2. Relative molecular yield of benzene (converted toluene base) detected during the
226 experiments on toluene steam reforming over activated alder (AA), beech (BA), and pine (PA)
227 chars



228

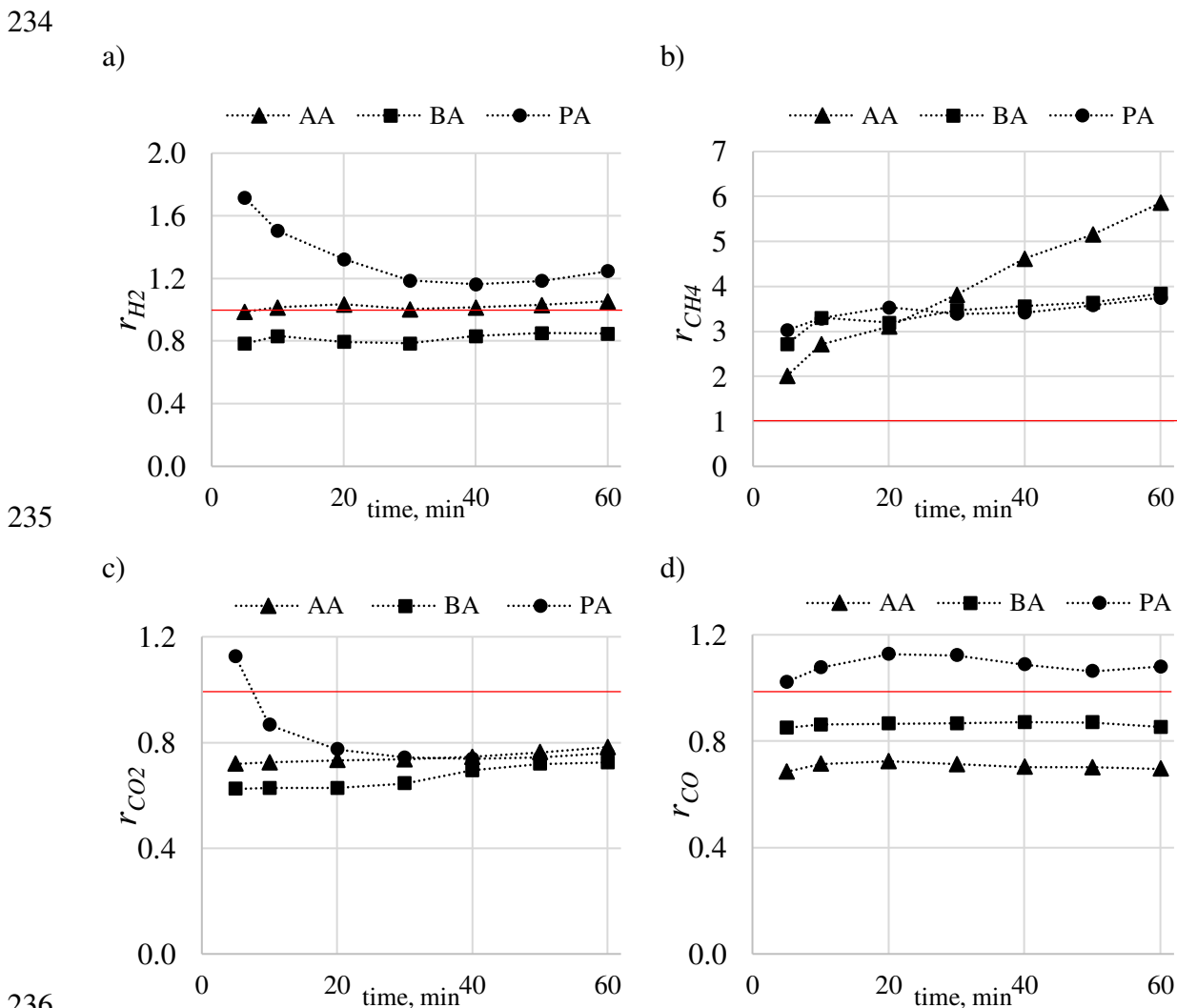


229



230

231 Fig. 3. Relative molecular yields of substituted benzenes (converted toluene base) a)
 232 ethylbenzene, b) *p*-xylene and/or *m*-xylene, c) *o*-xylene and/or styrene created during toluene
 233 steam reforming over alder (AA), beech (BA), and pine (PA) chars



237 Fig. 4. Ratio of the amount of a gas species released during toluene steam reforming to the
 238 amount released during a blank run for alder (AA), beech (BA), and pine (PA) char (Eq. 1)

239

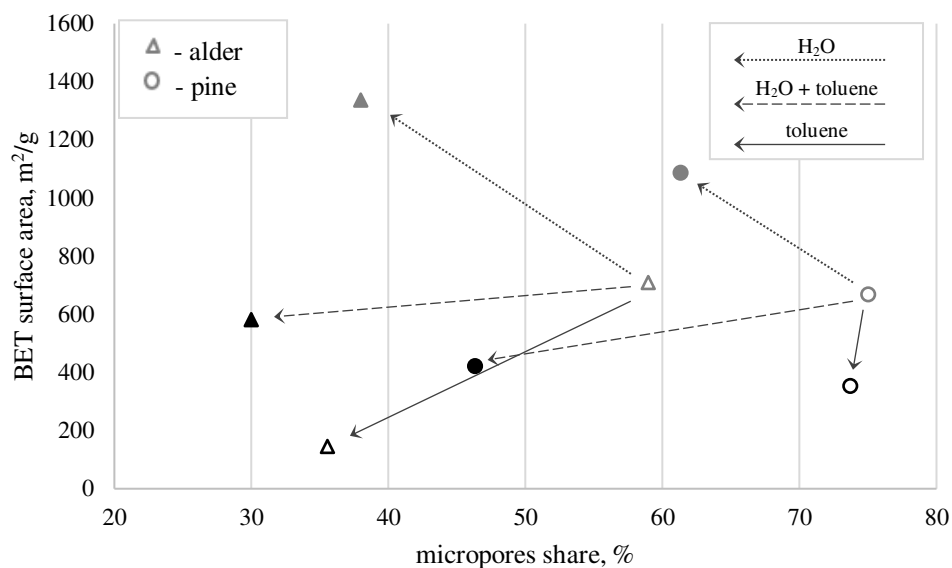
240 3.2. Spent char analysis

241 Toluene pyrolysis and steam reforming resulted in some structural changes in the examined
 242 chars. Although produced at 800 °C, and thus thermally stable in the reaction zone, the catalytic

243 bed was deactivated due to the deposition of a coke layer. Moreover, in addition to serving as
244 catalysts, carbonaceous materials are susceptible to oxidation when exposed to reactive gases
245 in a reforming atmosphere or gasification syngas. The progressive consumption of char
246 inevitably changed its surface area as well as its pore size, shape, and distribution. Hence, a
247 post-run examination of the spent catalytic material provided insight into the transformations it
248 underwent during tar conversion. Changes in the fresh alder and pine char structures after 60
249 min of toluene pyrolysis, toluene steam reforming, and blank steam reforming are presented in
250 Fig. 5. Initially, both materials had a relatively similar surface area, although pine char had a
251 significantly higher microporosity. Toluene decomposition involved significant coke formation
252 on the char surface, which decreased the surface area and microporosity, most likely due to
253 pore filling and entrance blocking. The mass of deposited coke, calculated from the carbon
254 balance, reached 69 mg and 117 mg for a 60 min pyrolytic tests with pine and alder, respectively
255 [9]. Despite the same toluene selectivity towards coke formation (80 wt.%), the overall amount
256 of solid product was lower for pine char, which explains the lower overall toluene conversion
257 over this material. More microporous structures, such as pine char, are expected to be more
258 prone to pore blocking [6]. However, a smaller deterioration in the share of micropores in pine
259 char compared with alder char suggests that the micropores in the pine char might have been
260 too narrow for the toluene to enter. Thus, a substantial share of the relatively high surface area
261 of this material did not participate in toluene-char reactions, which resulted in a lower
262 conversion efficiency, a lower amount of coke deposit, and well-preserved micropores of pine
263 char. Steam gasification of carbonaceous materials is also known to decrease their
264 microporosity, although it is due to carbon consumption and pore widening, rather than
265 blocking [14,17]. The additional activation of fresh chars, which occurred during blank tests of
266 steam reforming without tar compound feeding, produced a higher BET surface area and a more
267 mesoporous structure due to a carbon gasification. During concurrent char gasification and coke

268 deposition occurring during toluene steam reforming tests, the micropore-decreasing effects of
 269 both reactions combined to substantially diminish the share of micropores. During toluene
 270 steam reforming, the total surface area was reduced, suggesting a lower steam gasification rate
 271 than coking rate, since these reactions have an antagonistic effect on surface development. This
 272 observation was correlated with a continuous decrease in the toluene conversion over time,
 273 despite the introduction of steam. Thus, it can be concluded that coke deposition tended to
 274 decrease the microporosity and BET surface area, while steam activation also diminished the
 275 number of micropores, but it increased the total surface of char.

276



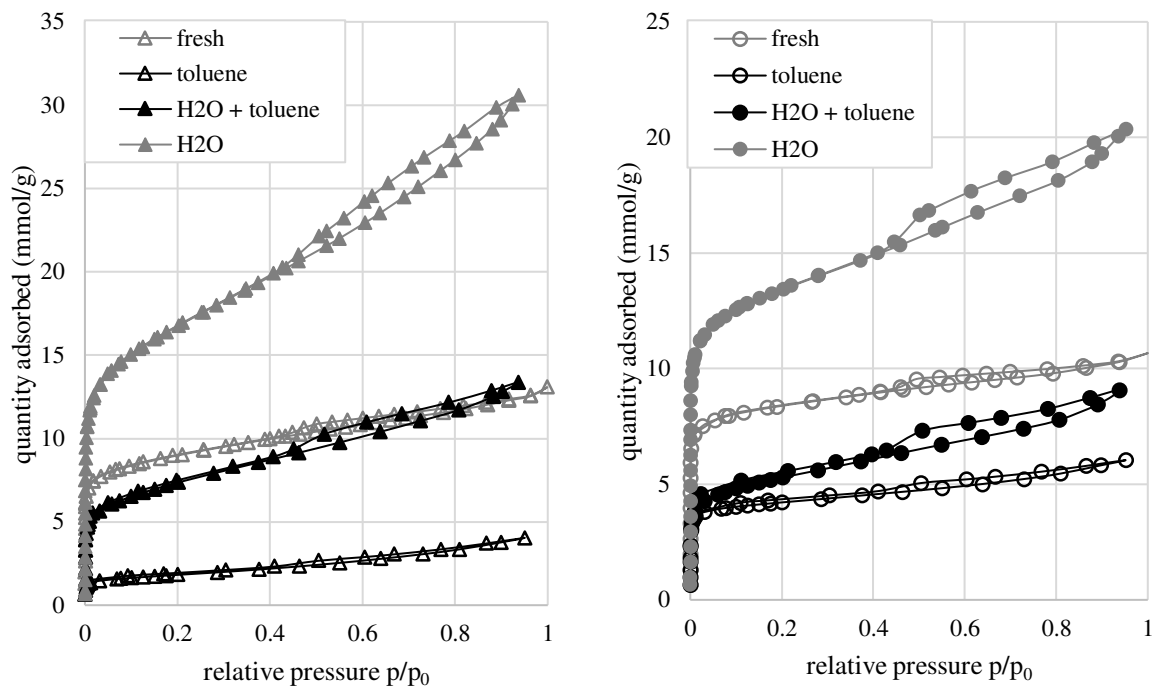
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278 Fig. 5. Change in the total surface area and a percentage of micropores in alder and pine chars
 279 after 60 min treatment with: only H₂O (blank test – tests 4 and 6 in Table 1), H₂O and toluene
 280 (steam reforming – tests 1 and 3 in Table 1), and only toluene (pyrolysis – tests presented in
 281 [9])

282

283 The nitrogen adsorption-desorption isotherms of spent chars are presented in Fig. 6. They are
 284 the composites of types I and II with an H4 hysteresis, which is the typical shape for micro-
 285 mesoporous carbon [18,19]. H4 hysteresis, commonly attributed to the presence of slit-shaped
 286 pores, was particularly pronounced in the plots of chars exposed to steam. The high-pressure
 287 parts of the isotherms of these samples were also steeper, which corresponded to a more
 288 mesoporous structure. Conversely, the plots obtained from the analysis of the fresh and
 289 pyrolysis-spent chars bore a closer resemblance to a flat type I isotherm, which is characteristic
 290 of microporous structures.

291



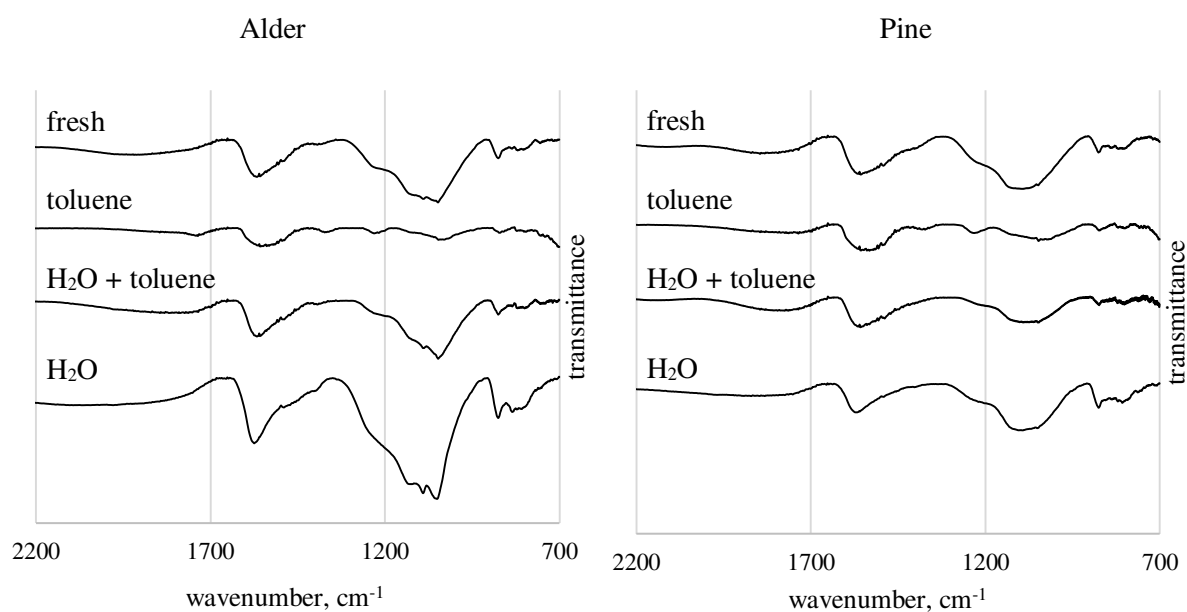
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293 Fig. 6. N₂ adsorption/desorption isotherms at 77 K for alder (triangles) and pine (circles) chars
 294 – fresh and after 60 min treatment with: only H₂O (blank test), H₂O and toluene (steam
 295 reforming), and only toluene (pyrolysis)

296

297 The chemistry of the char surfaces was evaluated using ATR-FTIR spectroscopy, and the
298 spectra are presented in Fig. 7. While the spectra of the fresh catalysts suggested a significant
299 amount of O-containing functional groups (increased absorption at $1630 - 1420\text{ cm}^{-1}$ and 1300
300 $- 900\text{ cm}^{-1}$), they were destroyed or covered by coke during a toluene pyrolytic conversion. The
301 introduction of steam during toluene decomposition preserved some of the surface functional
302 groups. The blank reforming with steam, i.e. prolonged char activation, allowed for gasification
303 undisturbed by decomposing toluene, producing a char with a well-developed spectrum. The
304 increased intensity of the absorption of the characteristic C–O vibration region ($1300 - 900\text{ cm}^{-1}$)
305 ¹⁾ was especially pronounced in alder char. As the spectrum of an initial, fresh char from this
306 wood already had better-defined bands, it is plausible that alder char was more susceptible to
307 steam activation during both char synthesis as well as its steam reforming. A higher content of
308 AAEM species and/or a higher mesoporosity (i.e., smaller diffusional limitations) of alder char
309 compared to the pine samples, were likely responsible for its higher reactivity (as revealed by
310 a lower activation energy reported in a previous work [9]), and thus its higher gasification rate.

311



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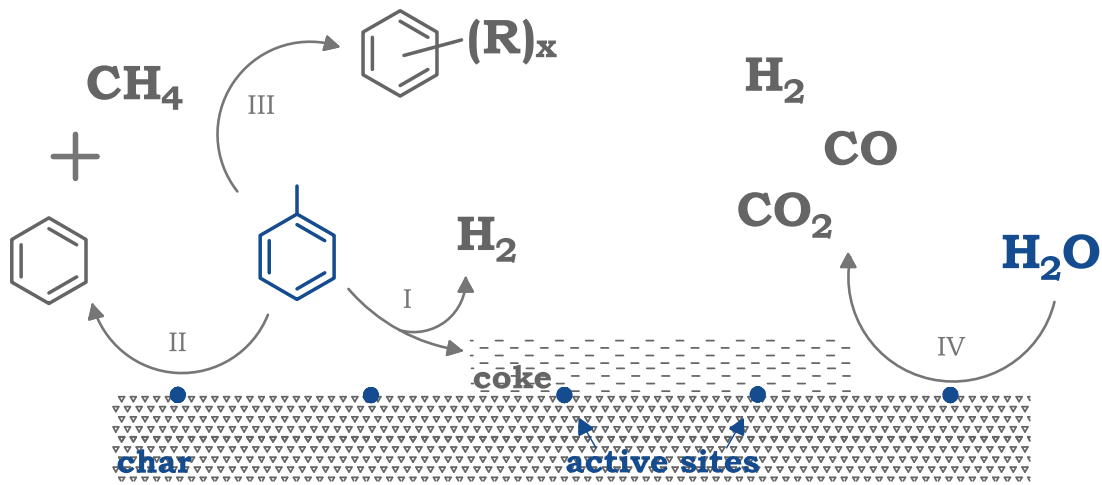
313 Fig. 7. ATR-FTIR spectra of alder and pine chars – fresh and spent after 60 min treatment with:
314 only toluene (pyrolysis), H₂O and toluene (steam reforming), and only H₂O (blank test)

315

316 **3.3. Toluene catalytic conversion mechanism**

317 Structural changes in the chars and the distribution of toluene conversion products investigated
318 during pyrolytic [9] and steam reforming conditions allowed proposing the mechanism of the
319 toluene catalytic decomposition, as depicted in Fig. 8. The results suggested that, regardless of
320 the presence of steam, coking/dehydrogenation (I) on the char surface was the main reaction
321 that led to the formation of solid carbon deposit that covered the active sites and blocked pores,
322 and thus caused catalyst deactivation. Another, competing heterogeneous reaction led to the
323 formation of benzene and methane. The toluene selectivity towards demethylation (II) increased
324 with char saturation with coke and reached ~15 %. Secondary reactions (III) between released
325 methane and freshly supplied toluene molecules occurred in the gas phase, creating trace
326 amounts of xylenes, ethylbenzene, and styrene. When steam was introduced to the reaction
327 zone, additional solid carbon (char and coke) gasification (IV) occurred, depleting the coke
328 layer, recovering active sites, increasing surface area, and widening the micropores of the char
329 bed. The similar distribution of the main products during pyrolysis and reforming and the lack
330 of homogenous conversion with steam in the empty reactor suggested that toluene reactions (I-
331 III) were not directly affected by gasification (IV). Steam most likely interacted only with the
332 toluene decomposition product (coke) and the carbonaceous catalyst (char). Thus, the beneficial
333 effect of added steam was limited to prolonging the char activity, and it did not directly increase
334 the toluene conversion rate. Moreover, competition between steam and toluene for char active
335 sites was surmised, based on the observed inhibition of steam gasification during toluene
336 reforming, as compared to the reference blank tests without tar compound feeding.

337



338

339 Fig. 8. Proposed mechanism of toluene conversion during pyrolytic (I-III) and steam reforming
340 (I-IV) experiments: I – coking, II – demethylation, III – secondary reactions, IV – steam
341 gasification of char/coke

342

343 3.4. Toluene reforming with oxygen

344 The heterogeneous nature of hydrocarbon conversion over a char bed, irrespective of the
345 presence of steam, was also reported by Hosokai et al. [10]. To further investigate the role of
346 an oxidising agent during toluene reforming, additional tests were performed where steam was
347 replaced with a more reactive compound – oxygen. 40 min of steam reforming over an activated
348 alder char bed was used as a reference (test No 1 in Table 1); a relatively long run time was
349 selected to capture the effect of char regeneration by gasification. During three additional tests
350 (No 7-9 in Table 1), the effect of two O_2 concentrations and the presence/lack of a catalytic bed
351 was examined. Toluene conversions and benzene yields during the O_2 and reference runs are
352 presented in Table 2. The first test (No 7) was conducted in an empty reactor to determine if O
353 radicals induced any homogenous toluene decomposition. Preliminary tests of steam reforming
354 without a char bed revealed that, at 15.5 vol.% H_2O , no direct toluene oxidation occurred. The

355 same experiment recreated with 3.5 vol.% of oxygen (stoichiometric ratio of 1.3) resulted in
356 almost complete toluene decomposition. 14 % of the converted toluene underwent
357 demethylation to benzene. Several heavier by-products were also detected, including all species
358 formed during catalytic toluene conversion, as well as some other compounds, e.g. O-
359 containing species. Among the latter, benzaldehyde was identified, and its yield is presented in
360 Fig. 9, along with the previously detected species. Oxygen substitution on toluene molecules,
361 yielding phenol and benzaldehyde, has been previously observed during oxygenation
362 experiments, even under O-rich atmospheres [20]. A majority of the toluene, however,
363 decomposed via gas-phase ring-opening reactions with O radicals, yielding CO₂ and CO. Due
364 to a drastic difference between the non-catalytic toluene conversion in an excess of steam and
365 oxygen, a lower concentration of oxygen was used in the following tests. The second of the
366 additional tests (No 8) was carried out at 0.7 vol.% O₂ (stoichiometric ratio of 0.25) in an empty
367 reactor. Even under the oxygen-depleted atmosphere, 16 % of toluene underwent homogenous
368 decomposition. These conditions favoured the formation of incomplete combustion products –
369 benzene (Table 2) as well as heavier hydrocarbons (Fig. 9). However, aromatic ring
370 decomposition to carbon oxides was also observed, as confirmed by analysing the released
371 gases (Fig. 10). The last O₂ test (No 9) was aimed at comparing catalytic toluene reforming;
372 hence, an activated alder char bed was applied during this run. The presence of the catalyst
373 increased the toluene conversion from 16 % to 78 %. Demethylation and secondary reactions
374 were less intense or their products were immediately decomposed on the char surface. The
375 heavier species observed during toluene-oxygen interactions in empty reactor tests were no
376 longer detected. Oxygenation in the presence of a char bed yielded only the compounds created
377 during the previous pyrolysis and steam reforming catalytic experiments. It is impossible to
378 determine if toluene oxidation that led to the formation of heavier hydrocarbons, including
379 species with O heteroatoms, ceased upon catalyst introduction, or if the products underwent

380 complete removal over the char bed. However, a comparison between toluene reforming in the
381 presence of steam and oxygen suggested that a direct, homogenous decomposition pathway –
382 observed during non-catalytic oxygen tests – remained part of the catalytic conversion
383 mechanism under an oxygen atmosphere.

384 Carbon oxides were produced during toluene conversion under both investigated atmospheres
385 (Fig. 10); however, the CO/CO₂ ratios indicated that different mechanisms were involved
386 during toluene conversion under O₂ and steam atmospheres. The ratio was similar for both
387 catalytic and non-catalytic tests with oxygen, amounting to 1.4 and 1.3, respectively. Therefore,
388 it is plausible that the formation of carbon oxides during the oxygen run with char (test No 9)
389 occurred due to ring-opening reactions, i.e. the same homogenous conversion mechanism that
390 was observed during non-catalytic reforming. In contrast, during steam reforming (test No 1),
391 the CO/CO₂ ratio was 0.3. Since toluene conversion in the presence of steam was exclusively
392 heterogeneous, the inverse proportion of carbon oxides yield was attributed to the steam
393 gasification of solid carbon, i.e. char and coke. This assumption is supported by the average
394 CO/CO₂ ratio of 0.32, calculated for the reference tests of steam reforming without toluene
395 feeding when carbon oxides were formed exclusively due to char gasification. The difference
396 in the product distribution may have also been due to the different solid gasification
397 mechanisms with steam and O₂. However, this is a less plausible scenario, since char
398 combustion would favour CO₂ formation, and thus a lower CO/CO₂ ratio, while steam
399 gasification would produce more CO due to a water-gas reaction. It is therefore expected that
400 carbon oxides created during the test No 9 originated from gas-phase toluene oxygenation,
401 while during the test No 1 (with steam) they were produced during solid carbon gasification.
402 Due to the higher amount of reactants, steam gasification was likely a more intense reaction
403 than toluene combustion, thus a higher overall gas yield during the test No 1 was observed.
404 Significant hydrogen formation during this test was attributed to a water-gas reaction.

405 The experiment suggested that, under applied conditions, oxygen was reactive enough to induce
406 direct toluene oxidation and that this homogeneous reaction occurred also during the
407 decomposition in the presence of a catalyst.

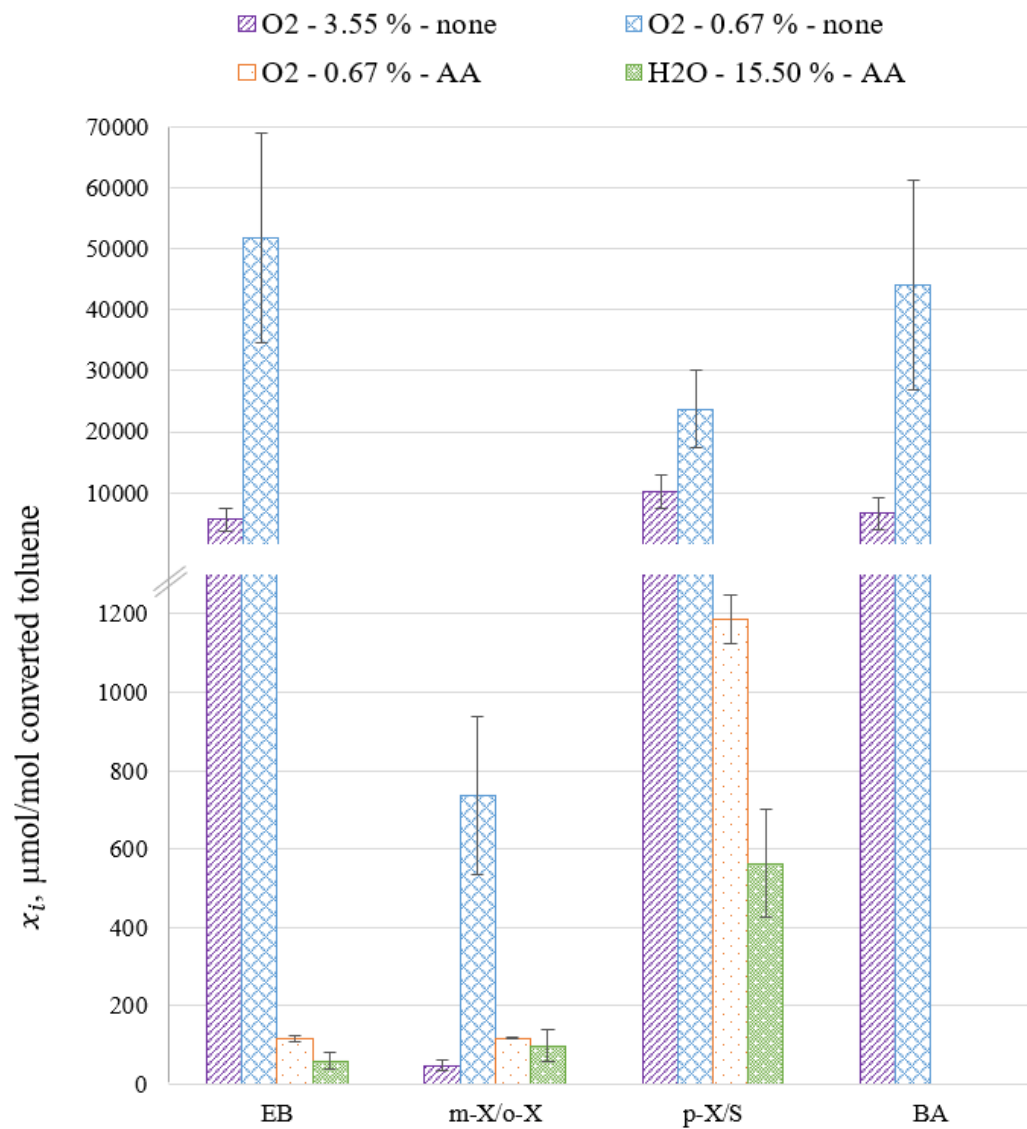
408

409 Table 2. Toluene conversion η_T and benzene molecular yield x_B (converted toluene base)
410 during 40 min reforming tests

Test number in Table 1	7	8	9	1
Oxidising agent	O ₂	O ₂	O ₂	H ₂ O
Oxidising agent concentration (vol.%)	3.5	0.7	0.7	15.5
Char bed	none	none	activated alder	activated alder
η_T	0.93 ±0.07	0.16 ±0.04	0.78 ±0.01	0.76 ±0.03
x_B	0.14 ±0.04	0.27 ±0.08	0.08 ±0.01	0.14 ±0.01

411

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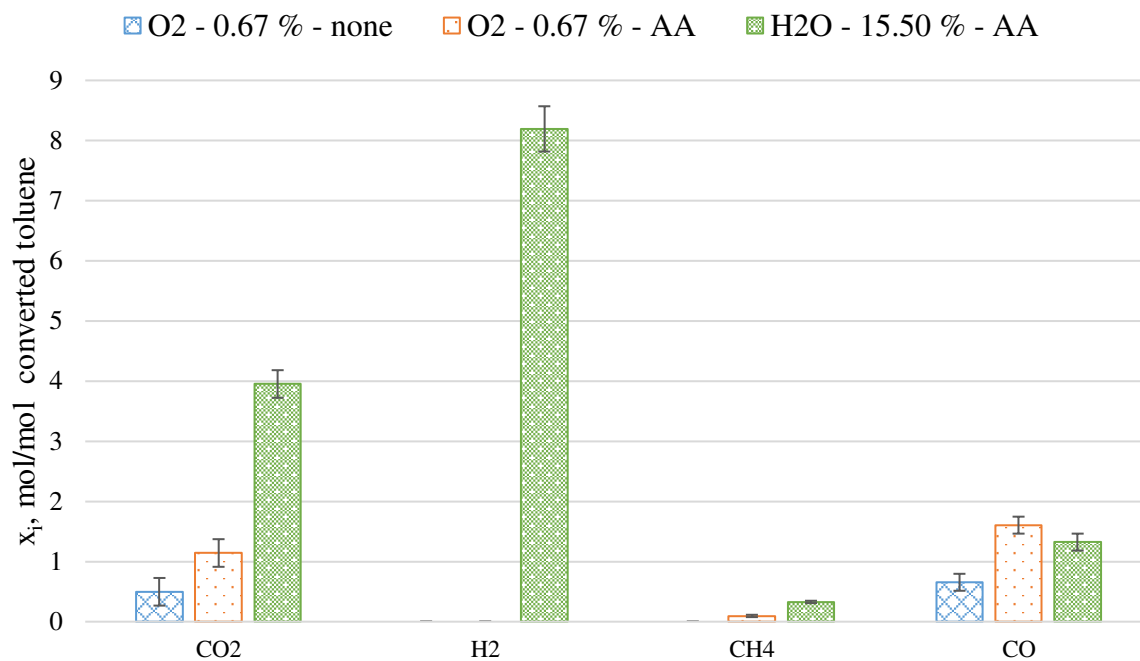
414 Fig. 9. Relative molecular yields x_i (converted toluene base) of secondary reaction products:

415 EB – ethylbenzene; *p*-X, *m*-X, and *o*-X – *p*-, *m*-, *o*-xylene, respectively; S – styrene; and BA –

416 benzaldehyde (test description form “oxidising agent – concentration – catalyst”, where AA –

417 activated alder char)

418



420
 421 Fig. 10. Relative molecular yields (converted toluene base) of gases released halfway through
 422 a 40 min reforming test (denoted as “oxidising agent – its concentration – catalyst”, where AA
 423 – activated alder char)

424

425 3.4.1. Char interaction with steam and oxygen

426 The finding on catalytic reforming of toluene suggested that, contrary to the tests with steam,
 427 during the conversion in the presence of oxygen, some of the tar compound underwent
 428 homogeneous decomposition in direct reactions with O radicals. The investigation into the
 429 different roles of steam and oxygen during the experiments was extended by analysing char
 430 interactions with these oxidising agents. To this end, the analysis of spent chars was conducted
 431 to assess the changes that occurred due to the potential gasification of catalyst bed.

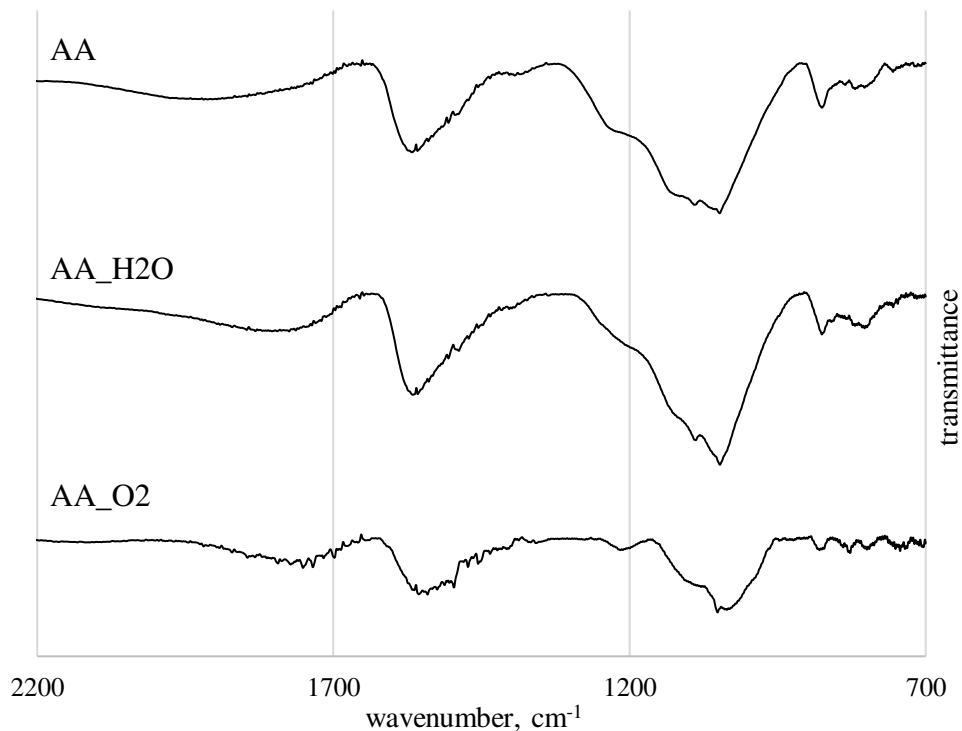
432 Although the gas analysis revealed that O₂ was consumed during reforming, the examination
 433 of the spent char surface suggested that none of the solid carbon was oxidised. The ATR-FTIR

434 spectra of fresh and spent chars (Fig. 11) revealed that the surface functionalities of the char
435 exposed to steam were preserved, while a decreased absorption of the bed recovered after
436 oxygen tests suggested its deactivation. Moreover, a decrease of the initial BET surface area of
437 alder char under a steam atmosphere was almost 3 times lower compared with the test with O₂
438 (Table 3). Thus, it can be expected that the coke layer was not removed in the latter case. An
439 intense reduction in char microporosity, commonly observed during steam
440 activation/gasification, occurred during steam reforming experiments. On the other hand, under
441 an O₂ atmosphere, the microporous structure of the char was better preserved, despite more
442 pronounced blocking by coke deposit. The total amount of oxygen introduced into the reactor
443 during the reforming test No 9 was sufficient to combust a significant part (approx. 7 %) of the
444 char bed. However, no visible effects of char oxidation/gasification and complete oxygen
445 consumption were observed. These findings correlate with the carbon oxides analysis, which
446 suggested that, in contrast to steam, O₂ was consumed during direct, homogeneous toluene
447 decomposition at the expense of char gasification.

448

449

450



451
 452 Fig. 11. ATR-FTIR spectra of fresh activated alder char (AA – from [9]) and spent char after
 453 40 min toluene reforming during the third (AA_O2) and fourth (AA_H2O) tests

454
 455 Table 3. Total (BET) surface area and micropore surface area as well as the contribution of
 456 micropores to the overall porosity of fresh activated alder char (AA – from [9]) and spent char
 457 after the third (AA_O2) and fourth (AA_H2O) tests

	BET area, m ² /g	Micropore area, m ² /g	Micropores share
AA	709 ±6	421 ±8	59 %
AA_H2O	557 ±2	208 ±2	37 %
AA_O2	282 ±1	132 ±1	47 %

458
 459 **3.4.2. The role of steam and oxygen during catalytic reforming of toluene**

460 Toluene conversion was similar during both steam and oxygen reforming tests – 0.76 and 0.78,
461 respectively. However, following the discussion of spent chars and gaseous product
462 distribution, it is expected that during steam reforming, toluene decomposed solely via
463 heterogeneous reactions on char active sites. In contrast, in the presence of oxygen, a fraction
464 of the fed compound was consumed during homogeneous gas-phase reactions while the
465 remaining part decomposed on the char surface. Since all oxygen was consumed during toluene
466 oxidation, and no char was regenerated, the efficiency of the heterogeneous conversion should
467 correspond to that registered during toluene pyrolysis. Assuming a gas-phase conversion of the
468 non-catalytic test No 8, i.e. 0.16, the remaining 0.62 of a total 0.78 fraction of toluene removed
469 in the test No 9 originated from surface reactions. This value is in agreement with the toluene
470 conversion registered during the 40 min pyrolytic run, i.e. 0.61 [9].

471 The faster char surface deactivation during the test No 9 was also responsible for higher yields
472 of xylenes, ethylbenzene, and styrene (Fig. 9), compared with the test No 1. It was previously
473 observed that the formation of these compounds was enhanced upon char saturation with coke.

474 These findings suggest different roles of steam and oxygen during toluene catalytic conversion.
475 During the steam reforming tests, toluene decomposed heterogeneously on the char surface
476 while steam gasified the catalyst bed. Contrarily, in the oxygen tests, toluene decomposed
477 partially on the char surface and partially in homogenous reactions with oxygen; the latter was
478 consumed in gas-phase reactions and thus no char gasification occurred.

479

480 **3.5. Effect of the methyl group on a conversion of aromatics**

481 **3.5.1. Benzene conversion tests**

482 Steam was observed to play a beneficial role during toluene catalytic conversion, and this was
483 further investigated using a less-reactive compound, benzene. 30 min benzene conversion tests

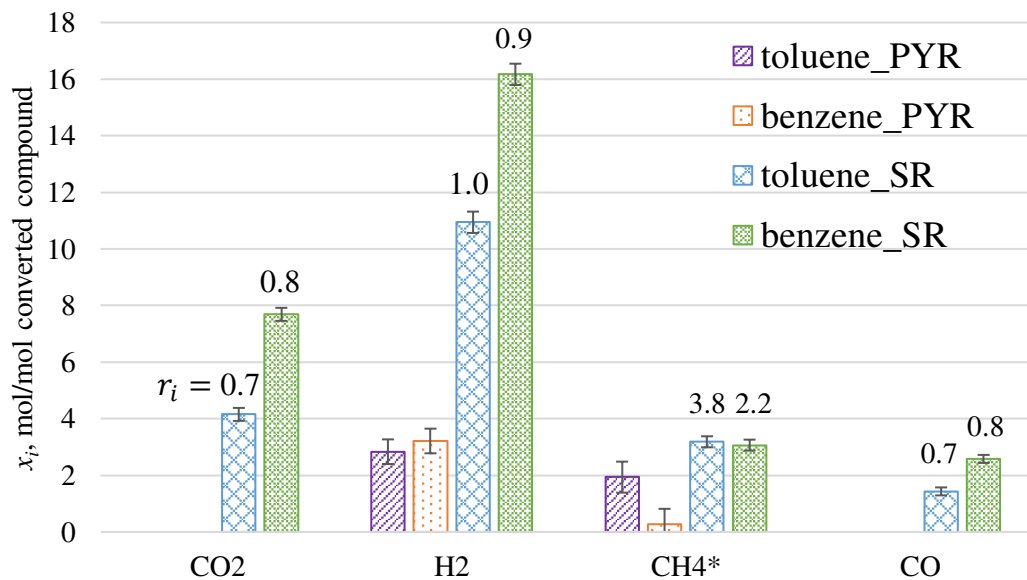
484 were performed analogously to the toluene experiments, in either pure N₂ (test No 10 in Table
485 1) or in 15.5 vol.% steam (No 11). A comparison with the findings of toluene reforming (No 1
486 in Table 1) and pyrolysis (reported in the previous work [9]) is presented in Table 4. Aromatic
487 compounds without substituents are considered more refractory [5], therefore, a lower benzene
488 conversion during pyrolysis was expected. The lack of a methyl group limited the number of
489 conversion pathways, and no by-products were detected during tests with benzene, except for
490 a trace amount of toluene.

491 Similar trends in gaseous compounds formation were observed during the decomposition of
492 both compounds, as presented in Fig. 12. No carbon oxides were formed during benzene
493 pyrolysis, suggesting a lack of homogeneous, ring-opening reactions. The lower methane yield
494 was expected due to the absence of a methyl group in benzene. An increase in gaseous product
495 formation upon introducing steam was also common to both tested species. Although the
496 released gases originated mostly from gasification reactions, the relative yields (Fig. 12) were
497 referred to the amount of a converted tar compound, which explains their higher values during
498 the less-efficient benzene conversion. Therefore, to assess the dynamics between char
499 gasification and compound conversion, the released gas ratios (r_i) were calculated (Eq. 1) for
500 steam reforming tests. The inhibition of the gasification process, previously observed when
501 compound conversion occurred concurrently with a solid reaction with steam, was less
502 pronounced during benzene reforming, as indicated by the slightly higher r_{CO} and r_{CO_2} values.
503 A less-intense heterogeneous conversion of this aromatic decreased the competition between
504 compounds and steam molecules for active sites on the char surface. Positive value of the r_{CH_4}
505 ratio indicates that methane formation was intensified during steam reforming of a compound,
506 compared with the blank tests where only char gasification occurred. The r_{CH_4} value obtained
507 from toluene reforming was higher than from benzene test suggesting that no significant
508 amounts of methane originated from benzene conversion.

509 The absence of demethylation or secondary reactions could not, however, be the sole reason for
 510 a two-times lower benzene conversion compared with toluene. Interestingly, steam
 511 introduction, which increased the toluene conversion by 13 percentage points, did not notably
 512 improve benzene decomposition. Thus, it is plausible that the worse efficiency of benzene
 513 removal was related to its inherently lower reactivity, which made it less dependent on the
 514 catalyst quality. Consequently, the regeneration of a char surface during steam gasification did
 515 not enhance benzene conversion, as observed in this study.

516 The comparison of benzene and toluene conversion confirmed the lower efficiency of catalytic
 517 decomposition of non-substituted aromatics; moreover, it suggested that more refractory
 518 compounds (like benzene) are less dependent on the activity of the catalyst, therefore their
 519 conversion is not significantly improved by the presence of steam.

520



521

522 Fig. 12. Relative molecular yield (converted compound based) of gases released during toluene
 523 (from [9]) and benzene pyrolytic conversion (PYR) and steam reforming (SR); values of r_i (Eq.
 524 1) provided for SR runs (*scaled – $x_{CH_4} \times 10^1$ is presented due to low yields)

525

526 **3.5.2. Char activity during benzene conversion**

527 Further investigation into the refractory nature of benzene was carried out by the comparison
528 of spent chars. Analyses were performed on the material recovered after benzene conversion
529 (tests No 10 and 11 in Table 1) and toluene steam reforming (test No 1 in Table 1) as well the
530 char after pyrolytic toluene conversion tests, reported in the previous work [9]. The changes in
531 catalytic properties of the chars after the pyrolytic and steam reforming tests were examined to
532 assess the importance of the activity of char during benzene and toluene conversion.

533 The analysis of spent chars (Table 4) revealed a drastic decrease in the initial surface area (709
534 m²/g) after exposure to toluene in pure nitrogen. During steam reforming, the char structure
535 deteriorated as well, although to a lower extent. Since the conversion of benzene was lower, it
536 had a smaller deactivating effect under inert conditions, and during steam reforming the char
537 surface was even increased. The initial microporosity of the activated alder char (59 %)
538 decreased due to pore blocking by coke. The additional effect of pore widening upon steam
539 activation resulted in an even greater loss of the microstructure during reforming runs. Changes
540 in the pore size distribution were observed for both compounds, suggesting that the same
541 heterogeneous conversion mechanism via coking and catalyst re-activation by steam
542 gasification also occurred during benzene decomposition, only at a lower magnitude.

543 Contrary to the area and distribution of pores, the surface functional groups of the chars
544 underwent the same extent of destruction during pyrolytic tests and showed a similar
545 development during steam reforming (Fig. 13). The similarities in char spectra might suggest a
546 similar consumption of oxygen functional groups by both compounds, despite the lower amount
547 of coke created during benzene conversion. It is possible, especially since the low frequencies
548 of the spectra suggest differently-substituted aromatic rings on the spent chars surfaces, that the
549 toluene-derived coke had a different structure than the benzene-derived one. In the case of

550 phenol adsorption, π - π^* stacking is expected, as reported by Shen [2]; it is possible that the
 551 methyl group of toluene may also allow some molecules to stack, which resulted in the
 552 formation of more developed structures on the char surface. This would explain the enhanced
 553 conversion and increased pore filling with the toluene-derived coke, and the unaffected uptake
 554 of surface functionalities. It could also explain benzene's higher resilience to decomposition,
 555 even though the activity of the char was better preserved.

556 The analysis of spent chars suggested that a lack of methyl group in a model tar compound led
 557 to a different structure of the created coke, which resulted in a lower yield of coke, and thus
 558 lower conversion of benzene, compared with toluene.

559

560 Table 4. Toluene and benzene conversion during the 30 min pyrolytic (PYR) and steam
 561 reforming (SR) tests and total (BET) and micropore surface areas, as well as the micropore
 562 contribution in the spent char bed

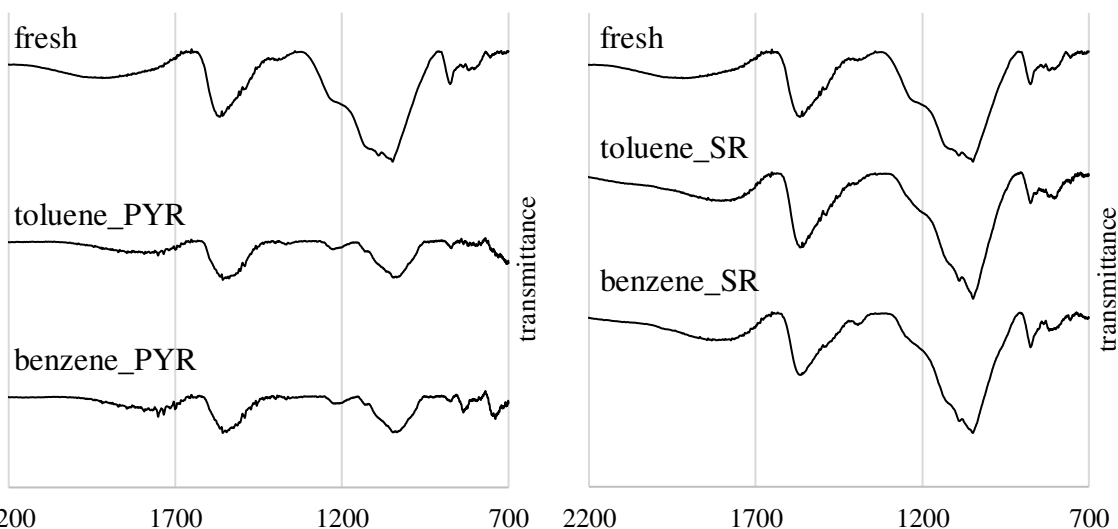
	Toluene PYR	Benzene PYR	Toluene SR	Benzene SR
η_T	0.66 \pm 0.05**	0.39 \pm 0.01	0.79 \pm 0.03	0.41 \pm 0.01
BET area, m ² /g	272 \pm 1 (0.38)*	401 \pm 2 (0.57)*	617 \pm 2 (0.87)*	749 \pm 3 (1.06)*
Micropore area, m ² /g	134 \pm 1 (0.32)*	215 \pm 3 (0.51)*	239 \pm 3 (0.57)*	343 \pm 4 (0.81)*
Micropores share	49% (0.83)*	54% (0.92)*	39% (0.66)*	46% (0.78)*

*change relative to the value for the fresh activated alder char

**value reported from previous work [9]

563

564



565
 566 Fig. 13. ATR-FTIR spectra of fresh activated alder char (from [9]) and spent chars recovered
 567 after pyrolytic conversion (PYR) and steam reforming (SR) of toluene and benzene

568
 569 **3.5.3. *p*-Xylene conversion test**

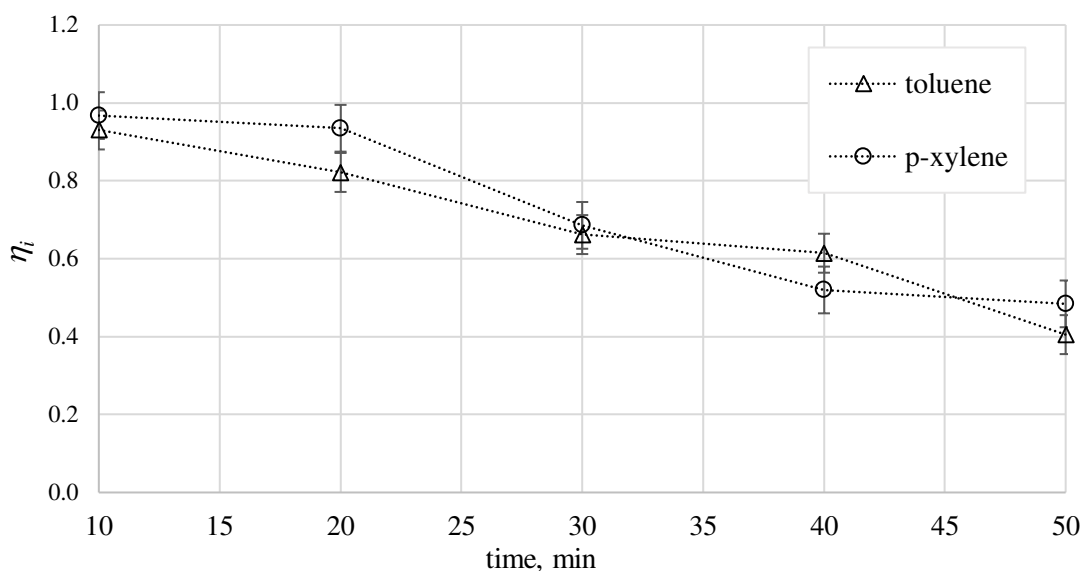
570 The significant difference between the affinity of benzene and toluene towards heterogeneous
 571 reactions with the char surface, and thus to their conversion efficiency, was attributed to the
 572 methyl group. Therefore, another experiment was conducted in which tar was represented by
 573 xylene (test No 12 in Table 1). The *p*-xylene was selected as its two methyl groups were
 574 positioned the furthest apart, thus limiting any possible interactions between them which may
 575 hinder their reactivity towards the catalyst's active sites. Moreover, *p*-xylene has the same
 576 kinetic diameter as benzene and toluene (5.85 Å) [21], ensuring their similar spatial
 577 constrictions for its molecular motion within the char pores.

578 The pyrolytic conversion of *p*-xylene and toluene are compared in Fig. 14, which shows
 579 statistically similar datasets. This experiment suggested that, while the lack of a methyl group
 580 significantly decreased the reactivity of the aromatic compound, a second substituent did not
 581 further improve the decomposition efficiency. At the same time, the more complex structure of

582 *p*-xylene resulted in a more versatile range of conversion by-products. All species recovered in
583 the impingers were identified, and their yields are presented in Fig. 15. Unfortunately, since the
584 FID peaks of *meta* and *para* xylenes overlapped, it was impossible to determine the yield of *m*-
585 xylene.

586 The findings suggested that the presence of a methyl group on an aromatic ring increased the
587 efficiency of the conversion of the compound by increasing its ability towards coke formation
588 on the char surface. However, further increase in the number of substituents was irrelevant to
589 the conversion efficiency; it only increased the yield of secondary reaction products.

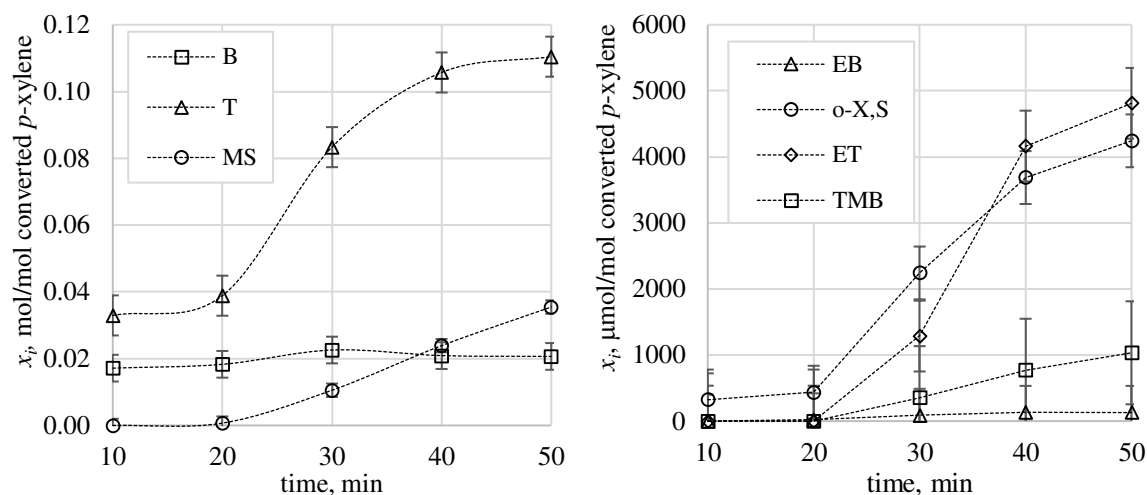
590



591

592 Fig. 14. The conversion of toluene (from the previous work [9]) and *p*-xylene over time during
593 pyrolysis over activated alder char

594



595
 596 Fig. 15. Relative molecular yields (x_i) of liquid by-products (converted *p*-xylene base) where *i*:
 597 B – benzene; T – toluene; MS – *p*-methylstyrene; EB – ethylbenzene; o-X,S – *o*-xylene/styrene;
 598 ET – *p*-ethyltoluene, TMB – 1,2,4-trimethylbenzene

599
 600
 601 **3.5.4. Secondary reactions of methylated aromatics**
 602 The demethylation of *p*-xylene occurred in two steps. In the first step, one of the methyl groups
 603 was released; during the following step, part of thus created toluene underwent further
 604 demethylation to benzene. During the 50 min run, 11 % of the total amount of decomposed *p*-
 605 xylene was converted to toluene and another 2 % yielded benzene. Thus, 0.11 and 0.04 mol of
 606 methyl groups per mol of converted *p*-xylene was released due to toluene and benzene
 607 formation, respectively. The total yield of released methyl radicals was therefore similar to that
 608 created during experiments with toluene, where its decomposition to benzene was ~15 %, i.e.
 609 where 0.15 mol of methyl groups per 1 mol of converted toluene was created. This suggests
 610 similar intensity of demethylation reaction during toluene and *p*-xylene conversion. However,
 611 during *p*-xylene conversion the intensity of the secondary reactions increased, in addition to
 612 being more diverse, compared with toluene decomposition. This shows that a larger number of

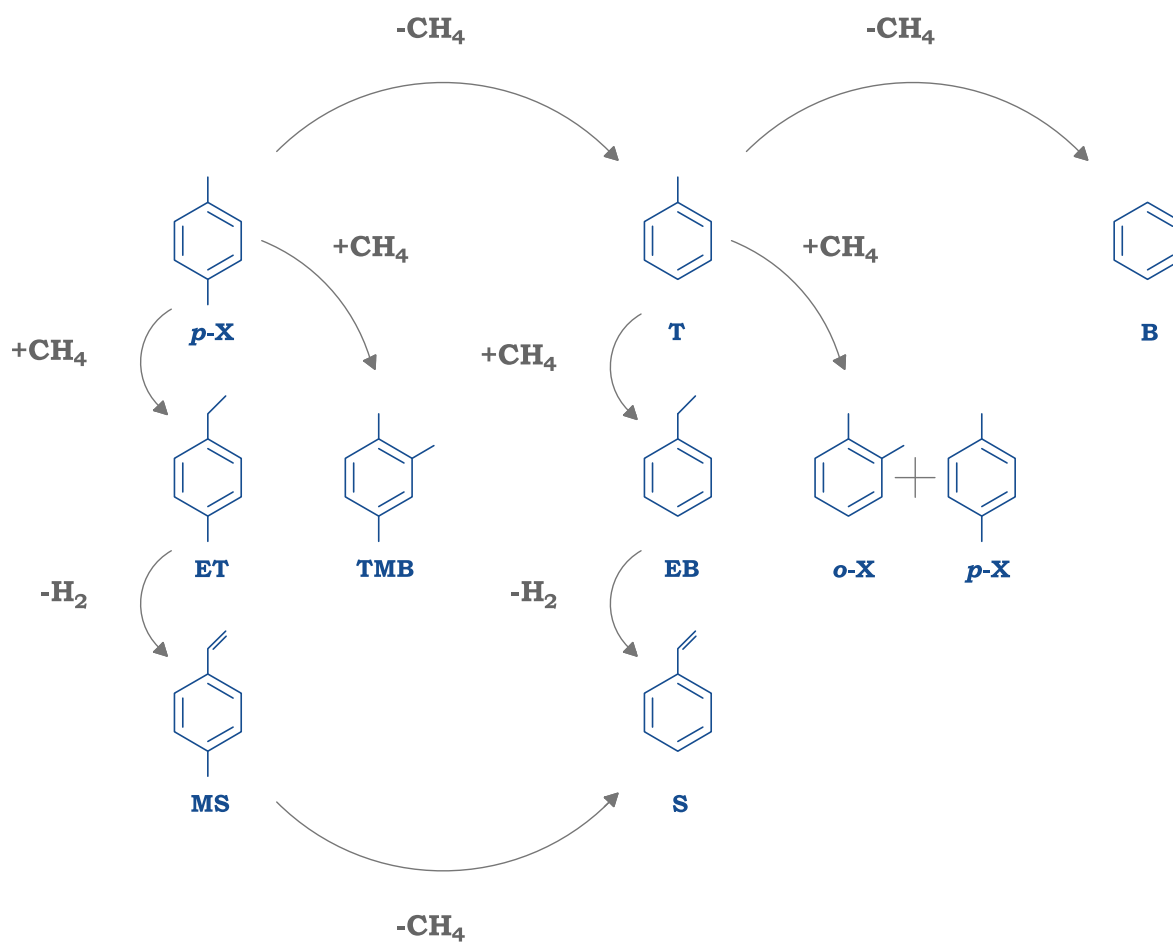
613 methyl substituents on an aromatic ring enhanced the gas-phase recombination reactions.
614 Examining the range of the toluene and *p*-xylene liquid products allowed the formulation of a
615 scenario of secondary reactions occurring during the catalytic conversion of methylated
616 aromatics (Fig. 16). Methane (or a methyl radical) released during the heterogeneous
617 demethylation of a compound underwent substitution with a freshly supplied molecule and
618 attached either directly to an aromatic ring or an existing methyl group. The yield of *p*-
619 ethyltoluene was up to 5 times higher than that of 1,2,4-trimethylbenzene. This observation is
620 in accordance with a lower C–H bond dissociation energy of the methyl group (92 kcal/mol)
621 than an aromatic ring (104 kcal/mol) [22]. Surprisingly high yields of *p*-methylstyrene and
622 styrene were observed amongst the pyrolysis by-products of *p*-xylene and toluene [9]. Thus, an
623 intense dehydrogenation of the ethyl group was expected, which was also observed during
624 toluene steam reforming, despite a mildly oxidising atmosphere. Due to a GC-FID peak overlap,
625 only the combined yield of styrene and *o*-xylene could be determined. However, a rough
626 estimate of the formed styrene was calculated by subtracting the *m*-xylene/*p*-xylene yield from
627 the *o*-xylene/styrene one, assuming similar amounts of those isomers were formed. This
628 procedure allowed the styrene-to-ethylbenzene ratio for toluene pyrolysis and steam reforming
629 experiments to be assessed. Counterintuitively, the ratios, which represented the intensity of the
630 ethyl group dehydrogenation, increased when steam was applied (from 4.2 to 7.0, 3.9 to 5.7,
631 and 1.9 to 5.1 for activated alder, beech, and pine char, respectively). The dehydrogenation was
632 likely catalysed by the char surface, and as its active sites were regenerated during gasification,
633 steam reforming enhanced the formation of styrene. A similar oxidative dehydrogenation
634 process on activated carbons has been used to synthesise styrene [23], reaffirming these
635 assumptions concerning the formation of styrene and *p*-methylstyrene. An even more extreme
636 discrepancy between the ethylbenzene and styrene yields was observed during *p*-xylene

637 pyrolysis. A portion of the large amounts of *p*-methylstyrene that formed due to *p*-ethyltoluene
638 dehydrogenation plausibly underwent demethylation, and thus increased styrene formation.

639 The analysis of secondary reaction products of *p*-xylene and toluene suggested that the main
640 side reactions accompanying compound decomposition via coking were demethylation, methyl
641 substitution (primally to the existing methyl groups rather than the aromatic ring), and
642 dehydrogenation of ethyl substituents.

643

644



645

646 Fig. 16. Demethylation and secondary reactions of methyl-substituted aromatics during
647 catalytic conversion experiments (B – benzene; T – toluene; *o*-X – *o*-xylene; *p*-X – *p*-xylene;

648 TMB – 1,2,4-trimethylbenzene; EB – ethylbenzene; ET – *p*-ethyltoluene; S – styrene; MS – *p*-
649 methylstyrene)

650

651

652 **4. Conclusions**

653 A previously-conducted toluene pyrolytic conversion experiment was re-created under a
654 reforming atmosphere in which three activated chars from different wood species were
655 examined. It was concluded that the main toluene conversion pathways, which were observed
656 under an inert atmosphere, were not influenced by the introduction of steam. The main reaction
657 led to the formation of coke on the char surface. The demethylation of toluene also occurred,
658 and the selectivity towards benzene was similar during both pyrolytic and steam reforming
659 tests. However, steam gasified the char bed and coke deposit, thus prolonging the catalytic
660 activity of char. No qualitative differences in toluene conversion over different chars were
661 observed; however, the performance of pine-derived char was worse due to its higher
662 microporosity. As one of the beneficial roles of steam, in addition to the regeneration of active
663 sites, was pore widening, the lower efficiency of pine char was less pronounced during steam
664 reforming compared with the pyrolytic tests.

665 When applied as a reforming agent, oxygen had the opposite effect to steam. The former was
666 directly consumed during ring-opening reactions with toluene, and thus, it did not cause any
667 char oxidation/activation. The different behaviours of these two oxidising agents suggest that
668 concurrent tar decomposition and catalyst regeneration can be controlled by adjusting the
669 reforming atmosphere composition.

670 The presence of a methyl group attached to an aromatic ring increased its conversion, regardless
671 of the catalyst's activity. However, a second substituent did not improve the decomposition any
672 further. Instead, two methyl groups enhanced secondary reactions, thus higher yields and wider
673 range of by-products was observed.

674

675 **Acknowledgements**

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677 number 2015/19/N/ST8/02454).

678

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