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1 **Steam reforming of different biomass tar model compounds**
2 **over Ni/Al₂O₃ catalysts**

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13 **Abstract**

14 This work focuses on the removal of the tar derived from biomass gasification by
15 catalytic steam reforming on Ni/Al₂O₃ catalysts. Different tar model compounds
16 (phenol, toluene, methyl naphthalene, indene, anisole and furfural) were individually
17 steam reformed (after dissolving each one in methanol), as well as a mixture of all of
18 them, at 700 °C under a steam/carbon (S/C) ratio of 3 and 60 min on stream. The
19 highest conversions and H₂ potential were attained for anisole and furfural, while
20 methyl naphthalene presented the lowest reactivity. Nevertheless, the higher reactivity
21 of oxygenates compared to aromatic hydrocarbons promoted carbon deposition on the
22 catalyst (in the 1.5-2.8 wt. % range). When the concentration of methanol is decreased
23 in the feedstock and that of toluene or anisole is increased, the selectivity to CO is
24 favoured in the gaseous products, thus increasing coke deposition on the catalyst and
25 decreasing catalyst activity for the steam reforming reaction. Moreover, an increase in
26 Ni loading in the catalyst from 5 to 20 % enhances carbon conversion and H₂ formation
27 in the steam reforming of a mixture of all the model compounds studied, but these
28 values decrease for a Ni content of 40 %. Coke formation also increased by increasing
29 Ni loading, attaining its maximum value for 40 % Ni (6.5 wt. %).

30 **Keywords:** Ni/Al₂O₃ catalyst, biomass gasification, tar model compound, steam
31 reforming

32

33

34 **1. Introduction**

35 Biomass gasification is regarded as a promising technology in the development of a
36 worldwide sustainable energy system. The major product in this thermochemical
37 process is a combustible gas (also called syngas) that may be used for power generation
38 (gas turbines, fuel cells or engines) or as feedstock for the synthesis of liquid fuels via
39 Fischer-Tropsch and various chemical products [1]. However, this syngas also contains
40 some impurities, such as fine particles, organic tars, NO_x and SO₂, which need to be
41 removed before its application [2].

42 In particular, tars are the main contaminants in the gas produced and their content
43 ranges from 5 to 100 g/Nm³, depending on the type of gasifier. However, their
44 maximum allowable content is 5 mg/Nm³ in gas turbines and 100 mg/Nm³ in internal
45 combustion engines [3, 4]. Tars are a complex mixture of aromatic and oxygenated
46 hydrocarbons that may cause several operational problems, such as condensation and
47 subsequent plugging of downstream equipment, clogging filters, metal corrosion,
48 polymerization into more complex structures and coke deposition on the catalyst [5, 6].
49 Hence, tar elimination is essential in order to implement any technology for syngas
50 exploitation.

51 Amongst the different strategies to remove tars from the gas [4], catalytic steam
52 reforming seems to be a promising alternative from an economic and technical point of
53 view, given that a high degree of gas purity can be attained and, at the same time, the
54 product gas heating value is increased [6, 7]. This process involves the oxidation of the
55 tar components using steam to produce a useful gas (mainly H₂ and CO) and the
56 presence of a catalyst allows a more effective tar removal at lower temperatures than
57 non-catalytic tar conversion. Ni-based catalysts have been widely applied in the steam
58 reforming of biomass tars due to their low cost, high activity for C-C and O-H bond

59 rupture and better performance in terms of H₂ production [8-13]. The high activity of
60 Ni/Al₂O₃ catalysts is attributed to the high metal surface area and high thermal stability
61 [14]. However, these types of catalysts are usually deactivated by coke deposition on
62 the active sites and sintering on the catalyst surface [15]. Several strategies have been
63 proposed in order to minimize catalyst deactivation, such as process configuration (one
64 or two stages) [16], optimization of operating conditions (temperature, S/C ratio and
65 space time) [17, 18] and catalyst improvement (with different Ni loadings, additives or
66 supports) [19].

67 Although there are papers in the literature dealing with the steam reforming of real
68 biomass tars [19-22], the complexity of tar composition makes it difficult to ascertain
69 both the reaction mechanism and the main species responsible for catalyst deactivation
70 by coke deposition. Therefore, most of the literature focuses on the conversion of
71 individual model molecules, usually toluene, benzene, phenol or naphthalene on
72 supported metal catalysts [5, 7, 9, 23, 24], but only few papers compare their reactivities
73 and trends towards coke formation [3, 25-27]. Furthermore, since tar is a mixture of
74 organic compounds with different structure and molecular weight affecting product
75 distribution and coke nature, a deeper understanding on the behaviour of tar main
76 components and their mixture is required in the steam reforming process.

77 Based on this background, this paper focuses on a systematic and detailed comparison
78 of a series of model compounds and their mixture in the catalytic steam reforming
79 process in terms of hydrogen production and catalyst deactivation. The components
80 selected are representative of the major chemical families contained in the tar derived
81 from biomass gasification, i.e., phenol, toluene, methyl naphthalene, indene, anisole and
82 furfural. In addition, as the steam reforming reactions were carried out over a typical
83 reforming catalyst (Ni/Al₂O₃), the influence of Ni loading was also investigated by

84 feeding a mixture of all the model compounds studied. The operating conditions were
85 based on the results of a previous work about phenol steam reforming, in which
86 temperature, space time and reaction time were optimized in order to maximize
87 conversion and minimize coke deposition [18]. The study is conducted not only with the
88 aim of eliminating biomass gasification tars and converting them into higher value
89 added products, such as hydrogen, but also with the aim of contributing to a better
90 understanding of the steam reforming behavior of the most representative tar
91 compounds on a low-cost and high activity catalyst like Ni/Al₂O₃, by considering the
92 influence each compound has on the catalyst deactivation by coke deposition. This issue
93 is essential in order to find the species responsible for the different reactivity and coke
94 formation, with the latter hindering the good performance of the catalysts in the tar
95 reforming process

96 **2. Experimental**

97 2.1. Model compounds

98 Six compounds were selected: phenol, toluene, methyl naphthalene, indene, anisole and
99 furfural. These compounds cover a wide range of one- and two-ring aromatic
100 hydrocarbons and oxygen containing compounds present in the tars derived from
101 biomass gasification. In addition, given that some model compounds were solid at room
102 temperature, methanol was used as solvent in all the experiments and, in order to assess
103 its contribution to the final product stream, it was previously steam reformed alone.

104 2.2. Catalyst preparation

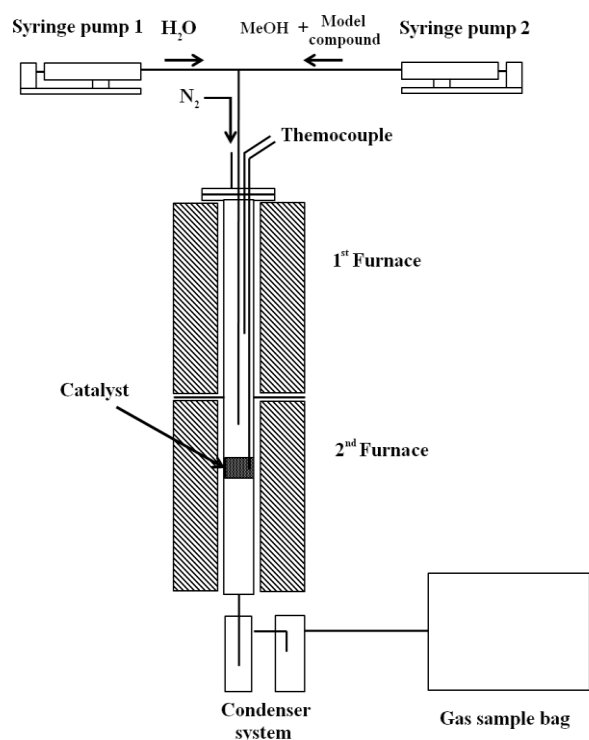
105 The Ni/Al₂O₃ catalysts were prepared by the impregnation method, in which the γ -
106 Al₂O₃ (96% Alfa Aesar) support was impregnated with an aqueous solution of
107 Ni(NO₃)₂·6H₂O (Sigma-Aldrich). The resulting solution was continuously stirred for 30

108 min at 100 °C followed by drying at 105 °C overnight, and it was then calcined
109 following a heating rate of 20 °C min⁻¹ in an air atmosphere at 750 °C for 3 h. Finally,
110 the catalysts prepared were ground and sieved to a size between 0.18 and 0.24 mm and
111 reduced in-situ by the process gases (H₂ and CO) generated during the reaction, as was
112 reported in previous papers, [15, 18]. The catalysts were formulated with Ni loadings of
113 5, 10, 20 and 40 wt. %, respectively.

114 2.3. Experimental equipment and procedure

115 The steam reforming experiments of the model compounds and their mixture on
116 Ni/Al₂O₃ catalysts were performed in a two-stage stainless steel tube reactor (both 16
117 cm in length and 2.2 cm in internal diameter), placed within two independently heated
118 electric furnaces, as shown in Figure 1. The water and the blend of the model
119 compound with methanol were fed into the first reactor by means of syringes 1 and 2,
120 respectively. This reactor was maintained at 250 °C in order to ensure a complete
121 vaporization of the feedstock before entering the next reactor containing the catalyst. In
122 addition, a nitrogen flow rate of 80 ml min⁻¹ was introduced to sweep the volatiles
123 formed in the reactor. The model compounds and their mixture were steam reformed at
124 750 °C for 60 min in the second reactor, in which 1.5 g of Ni/Al₂O₃ catalyst were
125 previously placed. The products generated in the steam reforming process were cooled
126 by passing through two condensers filled with dry ice, which gathered the liquid water
127 and the unconverted model compounds. All the non-condensable gases were collected
128 using a 10 L TeldarTM gas sample bag. After finishing each experiment, the gases were
129 collected for another 20 min to ensure the reaction was complete. The amount of
130 unconverted reactant was calculated by weighing both syringes and the condensers
131 before and after the experiments. The gases collected in the gas sample bag were
132 analysed off-line by gas chromatography following the same methodology reported in

133 previous papers [15, 18]. All the experiments were repeated at least twice to ensure
134 reproducibility of the results.



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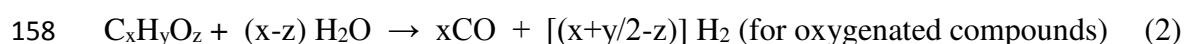
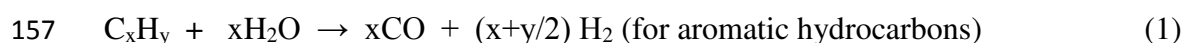
136

Figure 1

137 The catalyst loaded with 10 wt% Ni was used to investigate the reactivity of the
138 different tar compounds in the steam reforming process and their influence on the
139 product distribution and catalyst deactivation. In these experiments, the atomic ratio for
140 model compound carbon atoms / solvent carbon atoms (C_{cc}/C_s) was kept always at 1. In
141 addition, in order to investigate the effect of C_{cc}/C_s ratio in the steam reforming
142 reaction, experiments were performed by feeding toluene and anisole with a C_{cc}/C_s
143 ratio of 2. Moreover, the influence of Ni loading (5, 10, 20 and 40 wt%) on the
144 conversion of a mixture of all the tar model compounds was also analyzed, by keeping
145 in this case the C_s/C_{cc} ratio at 1. All the experiments were carried out at a S/C ratio of 3,
146 which meant that water flow rate was always 6.64 ml h^{-1} . However, the flow rate for

147 each model compound was different: 4.97 ml min⁻¹ for methanol, 3.41 ml min⁻¹ for
148 toluene, 2.48 ml min⁻¹ for phenol, 3.28 ml min⁻¹ for indene, 3.44 ml min⁻¹ for anisole,
149 3.26 ml min⁻¹ for methylnaphthalene, 3.5 ml min⁻¹ for furfural and 3.1 ml min⁻¹ for the
150 mixture of all the model compounds used in the experiments involving different Ni
151 loadings. It should be noted that these flow rates are based on the mixture of methanol
152 and the model compound(s).

153 Many parallel reactions may occur during the catalytic steam reforming process and
154 product distribution is the result of their competition [28], with the most important
155 being those of steam reforming (Eq. 1 and 2) and water gas shift (WGS) (Eq. 3), as
156 shown below [27]:



160 In order to quantify the products of the reforming process, conversion and product
161 yields have been taken as reaction indices. The carbon conversion of the model
162 compounds was defined as the moles of carbon in the gaseous product stream divided
163 by the moles of carbon in the feed. Furthermore, the moles of CO, CO₂ and C₁- C₄
164 hydrocarbons formed during the reaction have been determined from GC analyses,
165 which allowed calculating the total amount of carbon moles in the gas. The moles of
166 carbon in the feed were calculated based on the total amount of model compound or
167 mixture introduced into the reactor, i.e, weighing the syringe before and after the
168 experiment. The product yields were calculated as the ratio between the grams of each
169 product (H₂, CO, CO₂ and CH₄) in the gaseous stream and the grams of the model
170 compound in the feed.

171 C conversion (%) = $\frac{\text{moles of carbon in the product gas}}{\text{moles of carbon in the feed}} \times 100$ (4)

172 Yield (%) = $\frac{\text{g of the compound in the product gas}}{\text{g of the model compound in the feed}} \times 100$ (5)

173 Moreover, H₂ potential was also determined as the ratio between the concentration of H₂
174 in the effluent gas and the maximum allowed by stoichiometry:

175 $H_2 \text{ potential} = \frac{\text{moles of } H_2 \text{ in the product gas}}{\text{maximum moles of } H_2 \text{ allowed by stoichiometry}} \times 100$ (6)

176 The maximum number of H₂ moles allowed by stoichiometry was calculated by
177 considering reforming and WGS reactions i.e. reactions 1 and 3 for aromatic
178 hydrocarbons and reactions 2 and 3 for oxygenated compounds. Thus, H₂ potential is
179 defined based on the maximum number of H₂ moles obtained when model compounds
180 are fully reformed to CO₂ and H₂.

181 2.4. Characterization of the used catalyst

182 The amount and nature of the coke deposited on the catalyst were determined by
183 temperature-programmed oxidation (TPO) using a thermogravimetric analyzer
184 (Shimadzu TGA-50). The catalyst was fully recovered after the reaction and around 20
185 mg were used for determining the coke content by TPO. The sample was heated in an
186 atmosphere of air at 15 °C min⁻¹ to a final temperature of 800 °C and maintained at this
187 temperature for 10 min. In addition, a Hitachi SU8230 high-resolution scanning electron
188 microscope (SEM) was used to analyze the surface morphology of the used catalyst and
189 the nature of the coke deposited on it.

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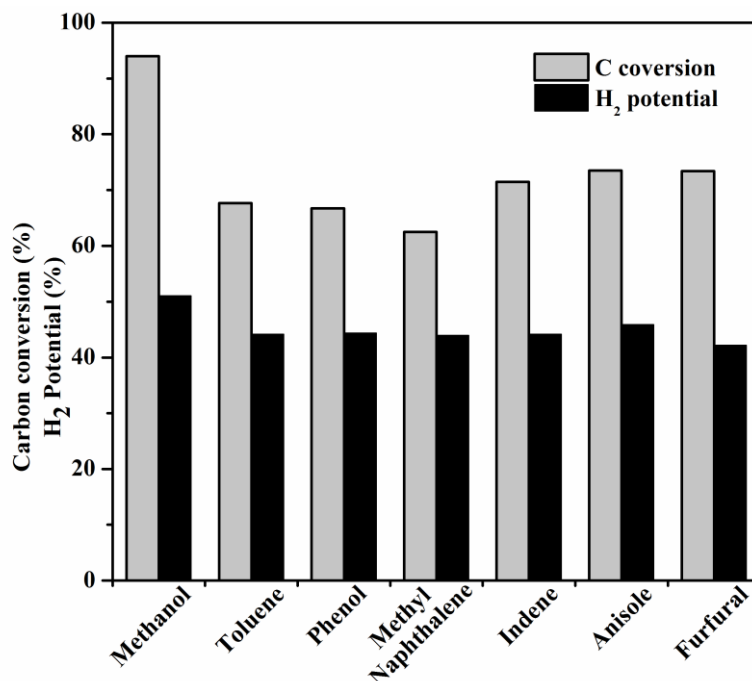
191 3. Results and discussion

192 3.1. Steam reforming of model compounds

193 The catalytic steam reforming of different tar model compounds was carried out on a
194 Ni/Al₂O₃ catalyst and Figure 2 shows a comparison of their conversions and H₂
195 potential at 750 °C catalyst temperature and after 60 min on stream. The mechanism of
196 catalytic steam reforming involves the absorption of model molecules and water vapour
197 on the catalyst surface, where they react with CO, CO₂ and H₂, as observed in reactions
198 (1-3). S/C ratio of 3 is an adequate value for tar conversion and product gas
199 composition, given that although a high water concentration will promote the WGS
200 reaction, most active sites on the catalyst surface would be occupied by H₂O molecules
201 at very high S/C ratios, thereby resulting in a lower adsorption capacity and lower tar
202 conversion. Given that all the compounds were dissolved in methanol, Figure 2 also
203 provides information on the conversion and H₂ potential for this solvent in the steam
204 reforming process. As observed, the conversion of all the model compounds was in the
205 63-75 % range, which is lower than that of methanol (94 %). The most reactive
206 compounds were furfural and anisole, followed by indene and toluene, with the most
207 refractory one being methyl naphthalene. Also, the H₂ potential for all the model
208 compounds studied was very similar, with values between 42 and 45 %.

209 These results obtained in this work suggest that there are significant differences in the
210 steam reforming mechanism of hydrocarbons and oxygenates. Thus, larger cyclic
211 hydrocarbons with higher molecular weight are less reactive, whereas those containing
212 oxygen-carbon bonds are more easily reformed [29]. In addition, these oxygenates are
213 more thermally unstable, thereby undergoing homogeneous (gas-phase) thermal
214 decomposition, as well as cracking reactions on the acid sites on the catalyst support,
215 competing with the steam reforming to H₂ [30]. It is noteworthy that phenol underwent
216 the lowest conversion among the oxygenated compounds. According to Wang et al.

217 [17], the formation of more stable intermediates during the reforming of phenol
218 increases the difficulty in decomposing this compound on the Ni surface compared to
219 the other oxygenates, such as furfural or hydroxyacetone.



220

221

Figure 2

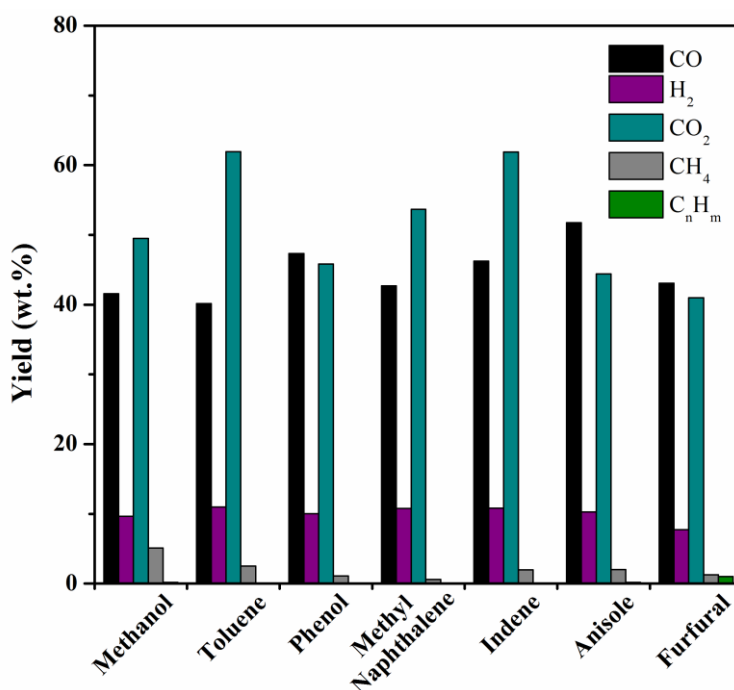
222 Similar results have been reported in the literature for the steam reforming of model
223 compounds, i.e., naphthalene is reported to be less reactive than other tar compound
224 models, such as toluene, benzene, pyrene or anthracene [3, 19, 26, 28]. In addition, Hu
225 and Lu [31] and Davda et al [32] concluded that oxygen containing hydrocarbons, such
226 as glucose (with a C/O ratio of 1), may be completely and faster converted than
227 hydrocarbons with a similar number of carbon atoms, given that the steam reforming of
228 these compounds to CO and H₂ is thermodynamically favoured at low temperatures.

229 The yields of the gaseous compounds obtained in the steam reforming of the model
230 compounds are displayed in Figure 3. As observed, the major products are CO and CO₂
231 followed by H₂, which makes clear that the main reaction taking place on the Ni/Al₂O₃
232 catalyst is that of steam reforming (Eq. 1 and 2) followed by WGS (Eq. 3). The

233 common reaction scheme proposed in the literature [19] for the steam reforming process
234 consists of C-H or C-C bond cleavage onto the metal surface to form carbon (C*) and
235 H₂. Then, the C* species react with the hydroxyl groups derived from the dissociation
236 of H₂O (OH*) on the support to form CO, which will further react with the remaining
237 H₂O to give more H₂ and CO₂ [9]. The highest yields of CO₂ are obtained from
238 aromatic hydrocarbons, i.e., toluene (62 wt. %), indene (61 wt. %) and
239 methylnaphthalene (53 wt. %), whereas CO formation is more favoured for oxygenated
240 hydrocarbons like anisole (52 wt. %) and phenol (47 wt. %). The parallel formation of
241 CO intermediate from the direct decomposition of each compound due to presence of
242 oxygen atoms in the molecule would promote the production of CO in the gaseous
243 stream [12]. Furthermore, the CO/CO₂ ratio depends on the WGS equilibrium reaction
244 and, as observed, the higher amount of CO in the gaseous stream derived from phenol,
245 anisole and furfural and the lower content of CO₂ and H₂ are evidences that these
246 oxygenated compounds enhance the reverse WGS reaction by displacing the
247 thermodynamic equilibrium to the endothermic route [6, 33]. In this context, two
248 possible mechanisms for phenol decomposition on nickel surface were explained in a
249 previous paper [18], in which it was concluded that both mechanisms lead mainly to the
250 formation of CO and H₂. Other authors have also highlighted that the carbon deposited
251 on the catalyst may further react with steam to generate additional CO and so contribute
252 to keeping catalyst activity [5].

253 In addition, the content of CH₄ was very low and that of C₂-C₄ hydrocarbons almost
254 negligible in all the experiments. These results confirm that these model compounds,
255 especially those with aromatic rings, are quite refractory to cracking reactions (more
256 refractory as the number of rings is increased). In fact, methyl naphthalene with 2
257 aromatic rings (more than any other model compound studied) leads to the lowest CH₄

258 yield (0.6 wt. %). It should be noted that the reforming of toluene and anisole leads to a
259 slightly higher concentrations of CH₄ than the other model compounds due to the
260 dealkylation of the methyl group in its structure [28]. The CH₄ formed may also be
261 derived from the decomposition of the model compound itself or from CO through the
262 methanation reaction [3, 12, 23]. However, these reactions are almost irrelevant because
263 the CH₄ content in the product gases was less than 4 %.



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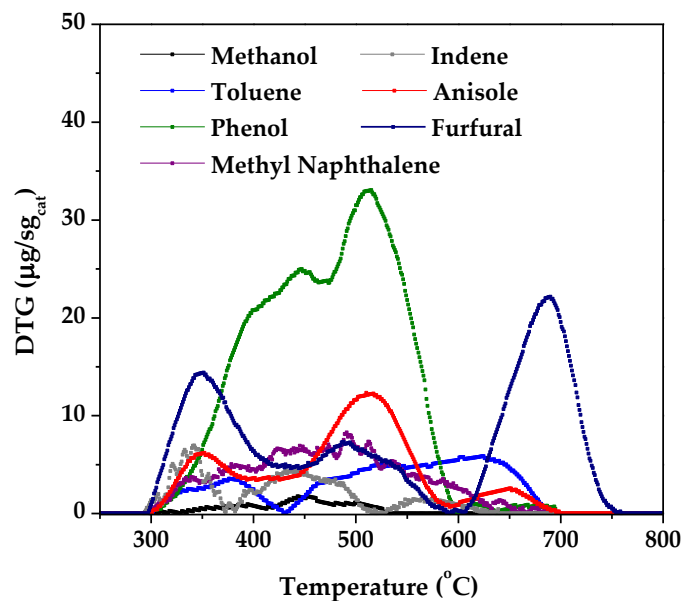
Figure 3

266 The nature and amount of the coke deposited on the catalyst in the steam reforming of
267 different model compounds were determined by temperature programmed oxidation
268 (DTG-TPO) curves (Figure 4). This coke blocks the pores and poisons the active sites,
269 which leads to a loss of activity in the catalyst, and consequently hydrogen production is
270 reduced. However, the addition of steam reduces coke deposition on the catalyst, given
271 that the carbon generated may further react with the water in the medium. Thus, the low
272 amount of coke formed on the used catalysts is noteworthy (lower than 2.8 wt. % in all
273 cases), which is evidence that the operating conditions selected (1.5 g of catalyst, 750

274 °C and S/C=3) limit coke development. The content of coke deposited was higher in
275 those experiments performed with oxygenated compounds, being 2.8, 2.7 and 1.5 wt. %
276 for phenol, furfural and anisole, respectively. On the contrary, the steam reforming of
277 aromatic hydrocarbons resulted in lower coke deposition (in the 0.5-0.8 wt. % range).
278 The tar compounds studied tend to undergo thermal decomposition and/or cracking
279 reactions together with the Boudouard reaction ($2\text{CO} \leftrightarrow \text{CO}_2 + \text{C}_{\text{solid}}$), which compete
280 with the steam reforming reaction. Therefore, the higher reactivity of oxygenated
281 compounds compared to hydrocarbons would enhance these unwanted reactions, thus
282 favouring coke formation [29]. The carbon formed via decomposition usually tends to
283 accumulate at the initial section of the catalytic bed due to the high partial pressure of
284 the reactants, whereas that produced via CO disproportionation would be accumulated at
285 the final section due to the high CO partial pressure at this position in the catalytic bed.
286 Other papers have also reported the higher coke deposition from oxygen containing
287 model compounds. For example, Koike et al. [9] determined that the carbon deposition
288 originated from the steam reforming of phenol was higher than that from toluene and
289 benzene. Remón et al. [34] concluded that furfural had the highest influence in terms of
290 carbon deposition on the catalyst in the reforming of the aqueous fraction of bio-oil on a
291 Ni-Co/Al-Mg catalyst. Trane-Restrup and Jensen [27] also found a higher coke
292 deposition rate on Ni/CeO₂-K/MgAl₂O₄ catalyst for furfural and guaiacol than for 2-
293 methylfuran and ethanol, which is explained by their lower molecular weight.

294 As observed in Figure 4, the number of peaks observed in the TPO profiles and the
295 temperatures corresponding to these peaks (between 250 and 700 °C) provide
296 information about the heterogeneity of the coke (more heterogeneous coke as the
297 number of peaks is higher). The results in the literature about coke deposition on
298 Ni/Al₂O₃ reforming catalyst [16, 18, 35] allow establishing the hypothesis that coke is

299 heterogeneous, with mainly three preferential oxidation peaks: i) around 350-400 °C
300 oxidation temperature, which can be attributed to the amorphous external coke (also
301 known as encapsulating coke) deposited over Ni particles, which is easily accessible for
302 gasification during the steam reforming and to oxygen during its combustion activated
303 by these Ni particles; ii) the shoulder around 500 °C oxidation temperature may be
304 related to a polymerized coke (graphitic and aromatic) with a more condensate structure
305 due to self condensation reactions of each compound. This coke is generally less
306 reactive and progressively separates from Ni sites, thus requiring higher temperatures
307 for its combustion (above 450 °C), and; iii) between 500 and 700 °C oxidation
308 temperature, associated with the filamentous coke, which is not adsorbed on Ni sites
309 and is combusted above 500 °C. This coke grows towards the outside of the catalyst
310 particles without significantly contributing to catalyst deactivation. From Figure 4 it can
311 be concluded that the type of model compound significantly affects the nature of the
312 coke deposited on the catalyst. Thus, the coke derived from oxygenated steam
313 reforming presented the most heterogeneous structure, with the coke from furfural being
314 the most filamentous and that derived from phenol and anisole more polymerized. On
315 the contrary, the coke derived from aromatic hydrocarbons was less developed with a
316 lower number of shoulders detected in the TPO analysis.

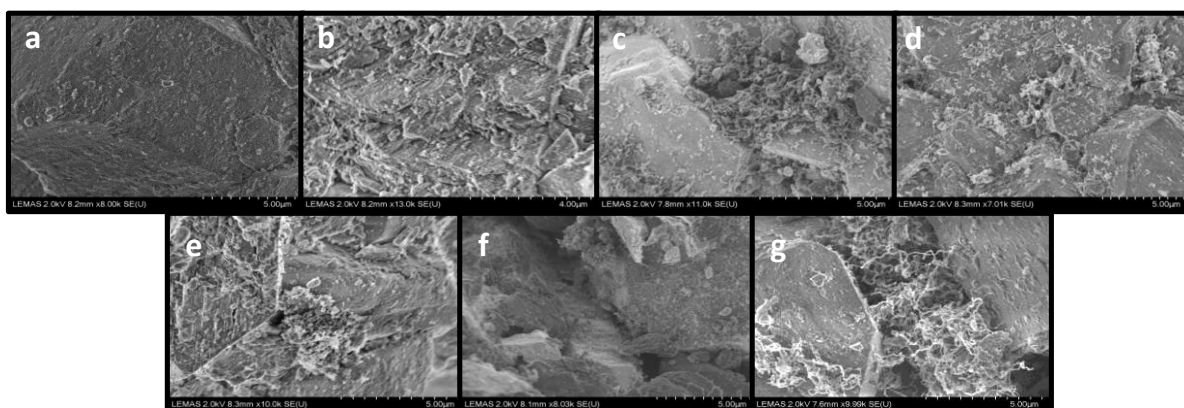


317

318

Figure 4

319 Figure 5 shows SEM images of the fresh (a) and the used catalyst in the steam
 320 reforming of toluene (b), phenol (c), methyl naphthalene (d), indene (e), anisole (f) and
 321 furfural (g) after reaction. As observed, the SEM analysis confirmed that furfural leads
 322 to highly developed filamentous type carbon deposits on the catalyst surface. Besides,
 323 some filamentous coke is observed on the catalyst used in phenol steam reforming, but
 324 this coke seems to be less structured than that derived from furfural. The steam
 325 reforming of aromatic hydrocarbons led to mainly non-structured carbon deposits,
 326 similar to those reported by Josuinkas et al. [28] for toluene/naphthalene steam
 327 reforming on Ni catalysts prepared from hydrotalcite-like precursors.



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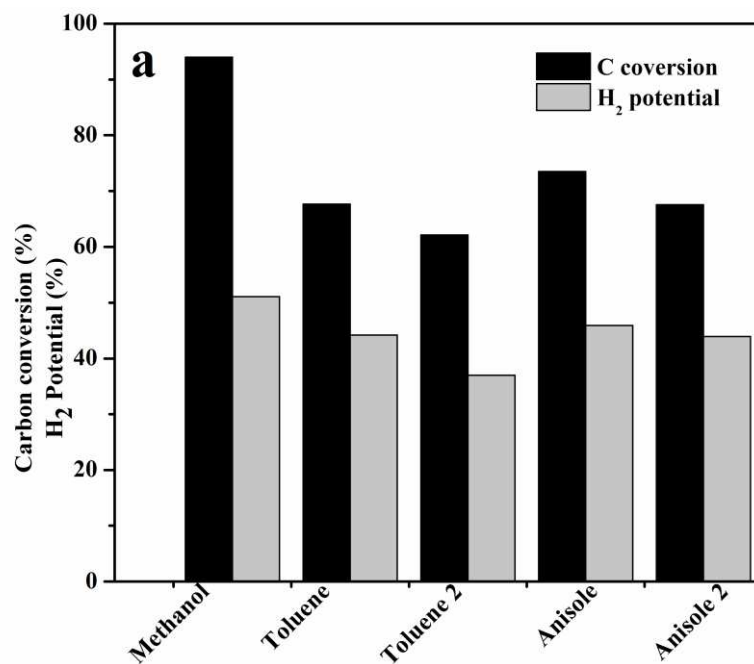
Figure 5

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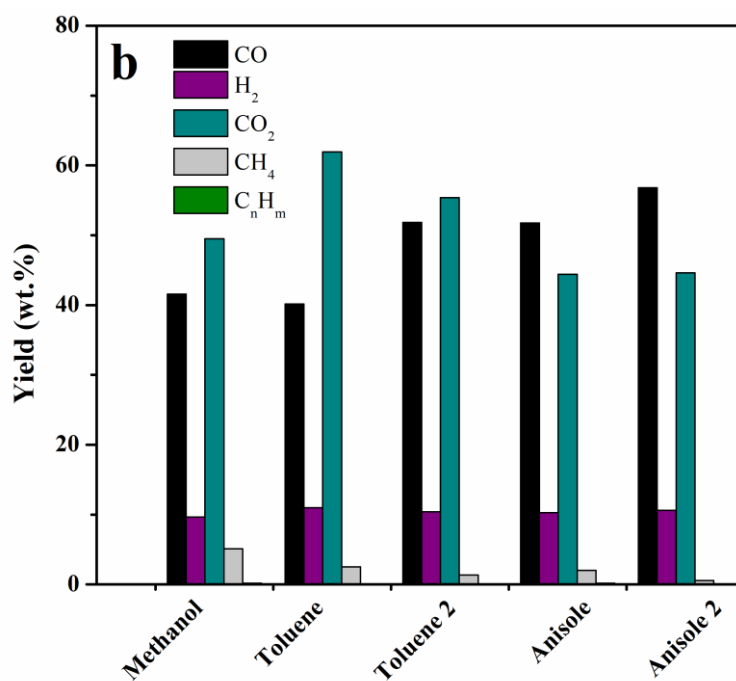
330 3.2. Effect of C_{cc}/C_s ratio on the feedstock

331 Figure 6(a) shows the conversion and H_2 potential and (b) shows the gaseous compound
332 yields in the steam reforming experiments performed with toluene/methanol and
333 anisole/methanol mixtures with a C_{cc}/C_s ratio of 2. Furthermore, Figure 6 also
334 compares these results with those obtained with a C_{cc}/C_s ratio of 1. In this figure, the
335 terms anisole1 and toluene 1 correspond to $C_{cc}/C_s=1$, whereas anisole 2 and toluene2
336 correspond to $C_{cc}/C_s=2$. As observed in Figure 6(a), when the content of toluene or
337 anisole increases in the reaction medium, carbon conversion decreases from 67 to 62 wt.
338 % and from 73 to 67 wt. %, respectively. Likewise, H_2 potential also decreases by
339 increasing the C_{cc}/C_s ratio, with this trend being more pronounced in the steam
340 reforming of toluene (from 44 to 37 %). Therefore, by increasing the concentration of
341 tar-like compounds in the feedstock and decreasing that of methanol (which is more
342 reactive and more easily reformed), the steam reforming activity of the mixtures to CO,
343 CO_2 and H_2 is moderately reduced.

344 A low content of methanol also changes the composition of the gas, as observed in
345 Figure 6(b). When the content of toluene is increased in the feedstock, formation of CO
346 is favoured (from 40 to 51 %) and that of CO_2 is reduced (from 62 to 55 %). When
347 anisole content is increased, a similar increasing trend is observed for CO yield (from
348 52 % to 57 %). However, the yield of CO_2 remained almost constant in the gaseous
349 stream (around 44 %). It is noteworthy that, in both cases, the yields of H_2 remained
350 almost constant and those of CH_4 were moderately reduced. These results suggest that
351 an increase in C_{cc}/C_s ratio in the feedstock leads to a reduction in the catalyst activity,
352 especially for WGS reaction, given that higher coke depositions reduce catalyst activity
353 for this reaction.



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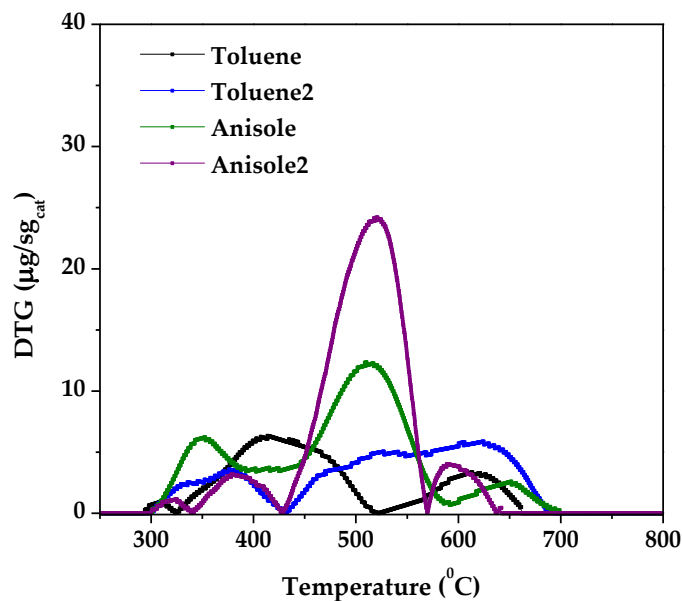
356

Figure 6

357 The steam reforming literature contains mainly global data for different catalysts on the
 358 conversion of tar model compounds, but very few reports deal with the influence of
 359 their concentration in the feedstock. Thus, only Ma et al. [36] established that higher

360 loadings of benzene or naphthalene in the biomass gasification derived tar resulted in a
361 reduction of their conversion in a catalytic tar removal system.

362 DTG-TPO results for the Ni/Al₂O₃ catalyst used in the catalytic reforming of toluene
363 and anisole with a C_{cc}/ C_s ratio of 2 (Figure 7) showed an increase in the coke amount
364 formed compared to the results obtained with a C_{cc}/ C_s ratio of 1, i.e., from 0.81 % to
365 1.4% in the reforming of toluene and from 1.49 % to 2.75 % in the reforming of
366 anisole. Although the deactivation of the catalyst is not significant, a higher
367 concentration of the model compound in the feedstock implies a lower conversion along
368 with an increase in CO selectivity, thus promoting carbon deposition by CO
369 disproportionation [31]. Moreover, the nature of the coke deposited on the catalyst
370 changes depending on the reactant loading. The catalyst used for toluene with a C_{cc}/ C_s
371 ratio of 2 presents a higher shoulder at low temperatures (400 °C) and a lower peak at
372 higher temperatures (500-600 °C), whereas this peak is considerably higher when the
373 C_{cc}/ C_s ratio of anisole increases from 1 to 2 in the feedstock. Thus, Figure 7 suggests
374 that an increase in the content of toluene results in an increase in the amorphous coke
375 (which can be more easily removed), whereas a higher amount of anisole leads to the
376 formation of a more condensed and structured coke (with higher degree of
377 graphitization).



378

379

Figure 7

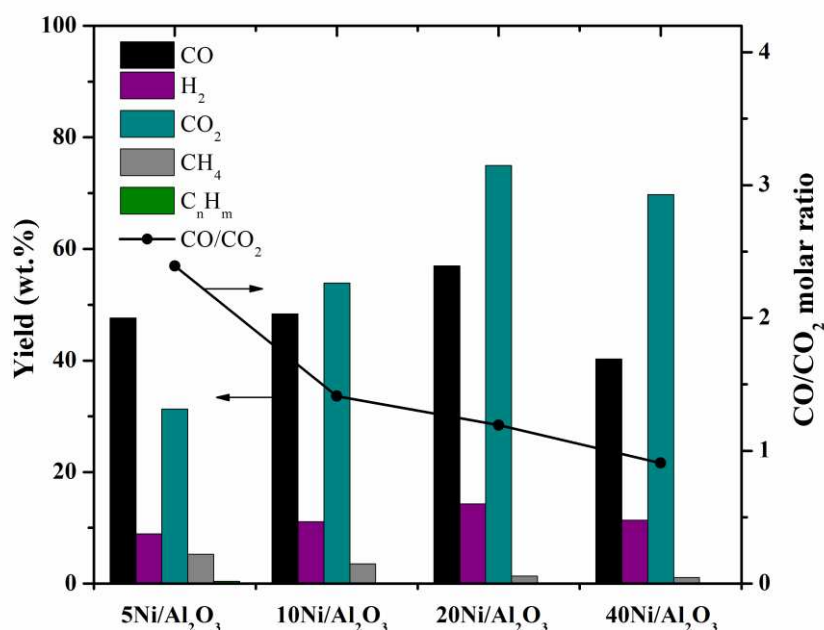
380 3.3. Effect of Ni loading on the catalyst

381 The influence of Ni content on the reforming performance of a mixture of all the model
 382 compounds previously studied separately (maintaining a C_s/C_{cc} ratio of 1) is discussed
 383 in this section. The sample notation indicates the amount of Ni deposited on the support,
 384 for example, 5Ni/Al₂O₃ means that the catalyst contains 5 wt.% Ni. Figure 8 shows the
 385 carbon conversion and H₂ potential obtained at 750 °C and for a reaction time of 60 min
 386 using the Ni/Al₂O₃ catalyst with different Ni loadings. As observed, the conversion of
 387 the mixture increases from 65 to 90 % when Ni loading is increased from 5 to 20 wt.%.
 388 As Ni content is further increased to 40 wt.%, the conversion of the mixture decreases
 389 to 73 %. The same trend was observed for the H₂ potential, attaining its maximum value
 390 (63 %) with 20Ni/Al₂O₃ catalyst. Thus, by increasing Ni content to 20 wt.%, more
 391 active sites will be available for the reforming and WGS reactions, which would result
 392 in higher carbon conversions and H₂ yields [37]. However, higher Ni contents in the
 393 catalyst may contribute to higher coke formation, thereby deactivating faster
 394 40Ni/Al₂O₃ catalyst, and consequently lowering tar conversion for 60 min reaction.

395 According to Li et al. [39], an increase in Ni loading promotes the activity of the
396 catalyst, but cannot prevent the deactivation in the acetic acid steam reforming. These
397 authors observed that nickel species probably aggregate in the catalyst preparation
398 process when Ni loadings are higher than 20 %, thus forming large size particles (with a
399 significant presence of crystallites), and therefore leading to faster metal sintering and
400 coke deposition on the catalyst. Similarly, Yue et al. [39] and Josuinkas et al. [28]
401 suggested that a decrease in tar conversion for high Ni contents is associated with an
402 increase in Ni particle size and the consequent decrease in the catalyst surface area and
403 activity.

404 **Figure 8**

405 Figure 9 shows the gaseous product yields and CO/CO₂ molar ratios obtained in the
406 steam reforming of the mixture with different Ni loadings. The CO, CO₂ and H₂ yields
407 by mass unit in the feed increase as Ni content is increased to 20 wt.% due to the
408 enhancement of steam reforming and WGS reactions as well as decomposition reactions
409 [39]. However, a further increase in Ni content above 20 wt.% leads to a decrease of
410 their yields, given that the total conversion of the feed is reduced, as was previously
411 reported (Figure 8). In addition, Figure 9 shows that CO/CO₂ molar ratio decreases by
412 increasing Ni content, even for 40Ni/Al₂O₃ catalyst, indicating that the WGS reaction is
413 more favoured [40]. It should be noted that the drop of CO/CO₂ ratio, especially when
414 Ni content increases from 20 to 40 %, may also be attributed to the Boudouard reaction
415 occurring when the catalyst undergoes a severe coke deposition. Furthermore, when Ni
416 content in the catalyst was 20 wt.% and 40 wt.%, the yields of CH₄ were almost
417 negligible (1.3 and 1.0 wt. %, respectively). These results suggest that 20Ni/Al₂O₃
418 catalyst is the most suitable for reforming the tars derived from biomass gasification.



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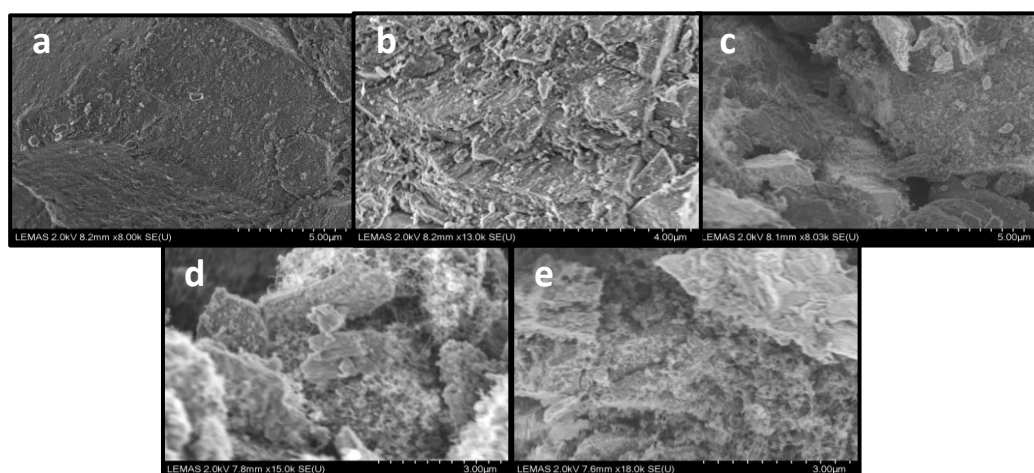
420

Figure 9

421 Other papers in the literature also report an optimum Ni content in the catalyst for tar
 422 conversion to H₂ and CO. Seyedeyn-Azad et al. [40] found that the highest catalytic
 423 activity for the steam reforming of biomass derived bio-oil, both in terms of hydrogen
 424 production and selectivity, was for a Ni/Al₂O₃ catalyst with a Ni content of 14.1 %. For
 425 higher Ni loadings (18 %), the results did not change significantly. Yue et al. [39]
 426 performed the steam reforming of toluene on NiO/MgO-γAl₂O₃ and observed 100%
 427 conversion when Ni content was 10 %, but an increase to 15 % led to conversion
 428 decrease to 86 %. Similarly, Wang et al. [37] obtained the highest conversion and H₂
 429 yield in the steam reforming of acetic acid and hydroxyacetone with a Ni/nano- Al₂O₃
 430 catalyst loaded with 10 % Ni. Nevertheless, other works concluded that the catalytic
 431 activity in the reforming reactions increased with higher Ni contents. For example,
 432 Garbarino et al. [33] determined that the conversion of a phenol-ethanol mixture on Ni
 433 supported catalysts was as follows: Ni₃₉>Ni₁₆>Ni₅.

434 The amounts of coke deposited on 5, 10, 20 and 40 Ni/Al₂O₃ catalysts, considering that
435 total weight loss during TPO analysis corresponds to carbon oxidation, are 0.6, 0.85, 2.2
436 and 6.5 wt. %, respectively. Carbon deposition increases by increasing Ni content and,
437 although the 40Ni/Al₂O₃ catalyst still promotes the steam reforming activity, it cannot
438 prevent the higher coke formation rates. As shown in Figure 9, Ni loading significantly
439 affects the distribution of reforming products, which will further affect coke formation,
440 since some compounds, such as CO, will be potential coke precursors. Furthermore, it
441 seems that a bigger Ni particle size in 40Ni/Al₂O₃ catalyst would favour CO
442 disproportionation, thus leading to a higher catalyst deactivation [38].

443 Figure 10 shows in detail the morphology of the carbon species in the fresh (a) and used
444 catalysts containing 5 (b), 10 (c), 20 (d) and 40 (e) wt.% Ni. As observed, the SEM
445 analysis confirmed the presence of filamentous type carbon deposits on the catalysts
446 surface, with the amount of deposited coke being higher as Ni loading is increased.
447 These results are consistent with those obtained in the TPO, in which the highest coke
448 yields have been obtained with 40Ni/Al₂O₃ catalyst.



449

450

Figure 10

451 **4. Conclusions**

452 Steam reforming of different aromatic and oxygenated tar model compounds and their
453 mixture has been studied on Ni/Al₂O₃ catalysts. The highest conversions and H₂
454 potentials were obtained for oxygenated compounds, and specifically for anisole,
455 whereas methylnaphthalene presented the lowest reactivity. Although carbon deposition
456 on the catalyst was low in all the experiments, the amount of coke was higher with
457 oxygenate reactants due to their higher reactivity favouring unwanted reactions that
458 promoted its formation. Increasing the C_{cc}/ C_s ratio to 2, the steam reforming activity to
459 CO, CO₂ and H₂ was slightly lower for toluene than anisole and the coke deposited on
460 the catalyst increased due the higher CO selectivity. Besides, the nature of the coke was
461 disparate using toluene and anisole, increasing the amorphous coke with the former and
462 the graphitization degree with the latter. Moreover, Ni loading increase enhances
463 reforming and WGS reactions, thereby increasing carbon conversion and H₂ potential.
464 However, for a Ni loading of 40 %, conversion decreases due the reduction in the
465 catalyst specific surface area, which can be associated with an increase in Ni particle
466 size. Besides, higher Ni loading lead to higher amount of coke with a more developed
467 filamentous structure.

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588

589

590 **Figure captions**

591 Figure 1. Schematic diagram of the experimental system.

592 Figure 2. Carbon conversion and H₂ potential in the steam reforming of different tar
593 model compounds.

594 Figure 3. Gaseous compound yields in the steam reforming of different tar model
595 compounds.

596 Figure 4. DTG-TPO curves of the coke deposited on the catalyst used with each tar
597 model compounds.

598 Figure 5. SEM imagines of the fresh (a) and the used catalyst used with toluene (b),
599 phenol (c), methyl naphthalene (d), indene (e), anisole (f) and furfural (g).

600 Figure 6. Effect of C_{cc}/ C_s ratio on carbon conversion and H₂ potential (a) and on gas
601 compounds yields (b) in the steam reforming of toluene and anisole.

602 Figure 7. DTG-TPO curves of the coke deposited on the catalyst used with different
603 C_{cc}/ C_s ratios in the feedstock of toluene and anisole.

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