1   **Polycyclic aromatic hydrocarbons (PAHs) and soot formation in the**
2   **pyrolysis of the butanol isomers**
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10   **Abstract**

11   The formation of polycyclic aromatic hydrocarbons (PAHs) and soot from the pyrolysis

12   of the four butanol isomers: 1-butanol, 2-butanol, iso-butanol and tert-butanol, at three

13   reaction temperatures (1275, 1375 and 1475 K) has been studied. The identification and

14   quantification of the sixteen PAHs, classified by the Environmental Protection Agency

15   (EPA) as priority pollutants, were done using the gas chromatography-mass

16   spectrometry (GC-MS) technique. The soot formed was collected at the reactor outlet.

17   Light gases formed were also quantified. The harmful potential of the PAHs through the

18   benzo[*a*]pyrene equivalent, B[*a*]P-eq amount, has been evaluated. The main results

19   show that the highest formation of light gases was obtained from the pyrolysis of iso-

20   butanol at 1275 K. The formation of H_2 increases significantly as the temperature

21   increases, following the Hydrogen abstraction carbon addition (HACA) route that leads

22   to form PAHs which subsequently form soot. The tendency to soot formation, under the

23   experimental conditions of the present study, is ranked as follows: tert-butanol, 2-

24   butanol, 1-butanol and iso-butanol. The highest PAHs amount and the highest toxic

25   potential, expressed as B[*a*]P-eq amount, were found in the pyrolysis of all butanol

26   isomers at 1275 K.

27

28   ***Keywords:*** *butanol isomers pyrolysis, polycyclic aromatic hydrocarbons, PAHs, soot,*

29 *toxicity.*

30 **Highlights:**

31 • The decreasing soot formation tendency is: tert-butanol, 2-butanol, 1-butanol and

32   iso-butanol.

33 • The pyrolysis of iso-butanol produced the highest gas yield at all temperatures

34   tested.

35 • The highest PAHs amount was found in the pyrolysis of tert-butanol at 1275 K.

36 • The highest toxic potential was found at 1275 K for all butanol isomers.

37

38 **1. INTRODUCTION**

39   Nowadays, fossil fuels are the main source of energy and cover a significant amount

40 of the world primary energy consumption, although it is important to consider that they

41 are one of the main promotors of global warming and pollution in urban areas. A

42 possible scenario could indicate that fossil fuels predominance may have a peak before

43 2025 and decline thereafter [1]. In this way, different efforts have to be done in order to

44 develop alternative energies that can satisfy our demand in the near future, and can be

45 sustainable for the next generations.

46   In this context, biofuels have been chosen as an alternative way due to their

47 multiple benefits in terms of providing secure energy, economic advantages and

48 environmental protection [2]. First and second generation of biofuels can be obtained

49 from biomass feedstock, but the second generation biofuels do not pose a threat to food

50 security because these biofuels can be produced from non-edible crops or biomass

51 wastes [3].

52   1-butanol is a second generation biofuel, and could be produced through

53   fermentation [4] and nonfermentative synthesis [5], and it is very promising as

54   alternative transportation fuel or additive to conventional fuels, owing to its

55   physicochemical features such as: high energy density, low vapor pressure and low

56   hygroscopicity. Specifically, Wallner et al. [6] have analysed the properties of the

57   butanol isomers, and indicate that 1-butanol has physical properties similar to gasoline,

58   and it could be used as a substitute of gasoline. The same study points that 2-butanol is

59   not considered as a potential alternative engine fuel due to its low octane number. Tert-

60   butanol, at low volumetric fractions, can be used to improve the knock behaviour of

61   gasoline, but is not considered to be used as an alternative fuel at higher volumetric

62   concentrations, due to its high melting point. Iso-butanol can increase the octane

63   number of the gasoline in blends [7], it can also get lower brake specific fuel

64   consumption and increase the power and thermal efficiency compared to methanol and

65   ethanol blends [8].

66   Rakopoulos et al. [9] found that the use of butanol/diesel fuel blends reduced the

67   smoke, NO_x and CO, emissions, but, on the contrary, the total unburned hydrocarbons

68   were increased. Specifically 1-butanol can significantly reduce soot and CO emissions

69   in diesel engines [10].

70   Although, among the butanol isomers, the most promising candidate as biofuel is 1-

71   butanol, it is interesting to analyse the behaviour of the rest of them when butanol is

72   used as possible fuel additive, since a mixture of isomers can be obtained during butanol

73   production. In this way, different studies have been performed in order to analyse the

74   behaviour of the different butanol isomers.

Moss et al. [11] developed a detailed kinetic mechanism to describe the oxidation of the butanol isomers and ignition-delay time measurements. These authors found that the less reactive butanol isomers were tert-butanol and 2-butanol, because the formation of alkenes through dehydration reactions was preponderant. The study of the four butanol isomers combustion chemistry in flat, premixed laminar low-pressure flames presented by Yang et al. [12], indicated a significant dependence on the fuel structure regarding to formation of potential pollutants, especially oxygenated species such as acetaldehyde and formaldehyde. Besides, the tert-butanol flame produces significantly low amount of oxygenated intermediates, and high levels of hydrocarbon intermediates.

Camacho et al. [13] examined the evolution of particle size distribution function (PSDF) of nascent soot in 1-butanol, iso-butanol, n-butane and iso-butane flames to understand the impact of fuel bound oxygen and the fuel structure on the sooting behaviour of the mentioned fuels. They found that, under the same C/O ratio, butanol flames in fact nucleate soot earlier and give greater soot volume fractions than butane flames, and this faster nucleation rate also propagates into the mass growth stage of soot particles. Singh et al. [14] compared the soot formation for n-butane, iso-butane and the four butanol isomers in a counterflow non-premixed sooting flame configuration at atmospheric pressure. For the conditions studied, the sooting tendency ranking followed was: n-butane > iso-butane > tert-butanol > 1-butanol > iso-butanol > 2-butanol. The presence of the hydroxyl (-OH) group in butanol isomers affected the sooting behaviour, as the butane isomers were found to produce more soot than the butanol isomers for the conditions investigated.

Moreover, McEnally and Pfefferle [15] studied the fuel decomposition and hydrocarbon growth processes from butyl alcohols in flames. The authors explained that the decomposition of hydrocarbons in flames can take place by bimolecular H-

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100   abstraction (negligible for butanol isomers) or by unimolecular dissociation, and this

101   dissociation can occur by complex fission or by simple fission. The complex fission

102   consists of a four-center elimination that produces mainly alkenes and H_2O, while the

103   simple fission follows a scission to radicals to produce alkenes, aldehydes and ketones.

104   Each butanol isomer has different number of β H-atoms that are available to favour

105   the complex fission as it can be seen in Fig. 1.

106   tert butanol   2 butanol   1 butanol   iso butanol
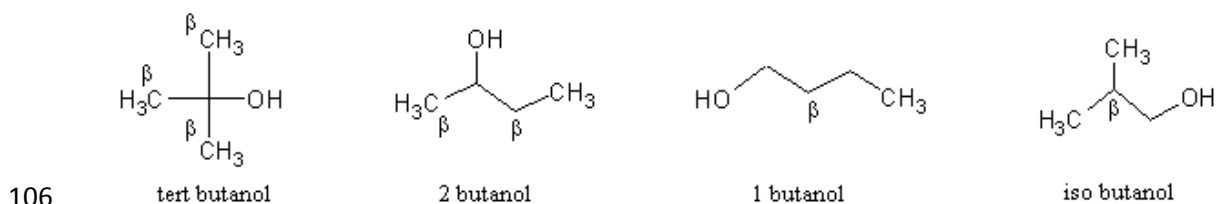
107   Fig. 1. β H-atoms of the butanol isomers.

108   In this way, the β H-atoms of each butanol isomer are: 9 H-atoms for tert-butanol, 5

109   H-atoms for 2-butanol, 2 H-atoms for 1-butanol, and 1 H-atom for iso-butanol.

110   Therefore, the complex fission for tert-butanol and soot formation are favoured.

111   The complex fission process for tert-butanol is shown in Fig. 2. The β C-atoms

112   release H-atoms to help in the water formation.

113

114   terc butanol   alqueno   agua
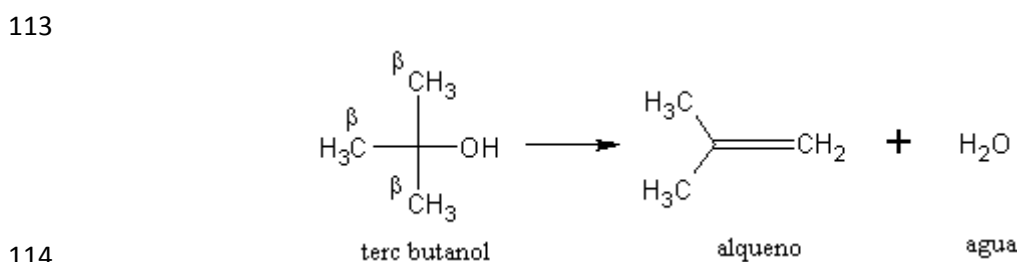
115   Fig. 2. Complex fission in tert-butanol.

116 The complex fission is dominant for tert-butanol, while simple fission is dominant

117 for the other butanol isomers. Both processes contribute to the formation of

118 intermediates, such as propargyl radicals that could form nascent soot particles [16].

119 The formation of the polycyclic aromatic hydrocarbons (PAHs), both from butane

120 isomers and butanol isomers, was analysed by Singh and Sung [17] using the planar

121 laser-induced fluorescence (PLIF) technique in a counterflow non-premixed flame

122 configuration, and a chemical kinetic model, based on the experimental data and the

123 simulated results. The authors found that, at the inception stage, the dominance of the

124 propargyl radical pathways in the PAHs formation was important.

125 In a combustion process, PAHs formation is related to the soot formation

126 mechanism through the HACA route, H-abstraction-C_2H_2 addition [18]. PAHs are of

127 important environmental concern, due to their carcinogenic and mutagenic character

128 [19]. These compounds can be found in the exhaust gases and can also be adsorbed on

129 the soot surface [20].

130 Owing to the importance of the carcinogenic potential of the PAHs, the US

131 Environmental Protection Agency (EPA) has classified sixteen PAHs as priority

132 pollutants [21], being usually considered for several studies about the toxic risk of

133 airborne that contains PAHs [22-24]. The list of these 16 priority PAHs compounds,

134 analysed in the present work, with their abbreviations, can be found as Supplementary

135 material, Table S1.

136 In this context, this work aims to study the behaviour of the four butanol isomers,

137 due to their growing importance in the combustion field, by analysing the soot, gases

138 and 16 priority PAHs formation under pyrolytic conditions. The experiments have been

139   performed in a tubular flow reactor at atmospheric pressure, using different reaction

140   temperatures.

141   **2. EXPERIMENTAL METHODOLOGY**

142   The experiments have been carried out in a tubular flow reactor, under well

143   controlled laboratory conditions, in a facility suitable for soot and PAHs collection, and

144   all the experimental details are described elsewhere [25]. The analytical methodology,

145   developed by our research group [26], has been used with success in previous works

146   addressing the quantification of PAHs [27-29], and has demonstrated recoveries higher

147   than 80 % in most cases [e.g. 30, 31]. A more detailed explanation of this methodology

148   can be found as Suplementary material.

149   The butanol isomers: 1-butanol, 2-butanol, iso-butanol and tert-butanol were fed to

150   the reaction system in a constant concentration (22500 ppmv), at three different reaction

151   temperatures (1275, 1375 and 1475 K). The feed of the butanol isomers was done

152   through an isocratic pump, with a thermally heated line with a temperature higher than

153   the boiling point of all butanol isomers. A nitrogen atmosphere was used in each

154   experiment to get a total flow rate of 1000 mL (STP)/min. Table 1 shows the

155   experimental conditions used in the present work.

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160   **Table 1:** Experimental conditions. Total flow rate is 1000 mL (STP)/min. N_2 is used to

161   balance.

Set	Butanol isomer	Reaction temperature (K)	Residence time (s)
1	1-butanol		
2	2-butanol	1275	3.27
3	Iso-butanol		
4	Tert-butanol		
5	1-butanol		
6	2-butanol	1375	3.04
7	Iso-butanol		
8	Tert-butanol		
9	1-butanol		
10	2-butanol	1475	2.83
11	Iso-butanol		
12	Tert-butanol		

162

3. RESULTS AND DISCUSSION

164   The study consists of the analysis of the formation of soot, gases and 16 priority

165   PAHs from the pyrolysis of the four butanol isomers, with a fixed concentration (22500

166   ppmv), using different reaction temperatures (1275, 1375 and 1475 K).

167   The butanol isomers present high conversion values, higher than 90 % at the

168   temperatures tested. The analysis of the yield to soot, gases, and PAHs as a function of

169   temperature is performed in order to understand the evolution of outlet products

170   obtained in the pyrolysis experiments. The values of the yields are shown in Fig. 3. The

171   yields are defined as the carbon amount in soot, gases and PAHs found in the outlet of

172   the reactor, respectively, referred to the amount of carbon fed to the reactor, in

173   percentage.

174   The yields for repeated experiments were measured. For example, for iso-butanol

175   pyrolysis at 1275 K, the yield to gases is 64.90±5.55 %, the yield to soot is 13.83±1.30

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176 %, and the yield to PAHs is 2.12±0.28 %, and for iso-butanol pyrolysis at 1375 K, the

177 yield to gases is 41.14±8.61 %, the yield to soot is 32.77±0.05 %, and the yield to PAHs

178 is 1.48±0.16 %. The values are expressed as average ± standard deviation (two

179 replicates).

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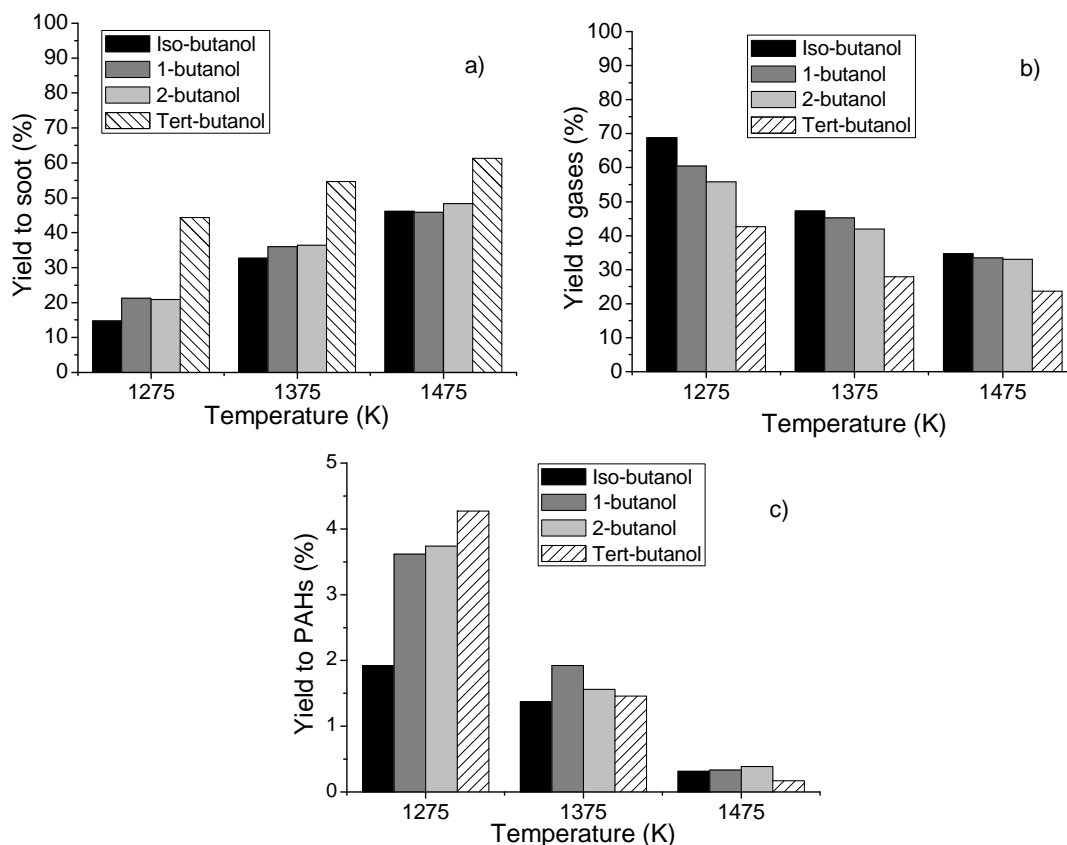
Fig. 3. a) Soot yield, b) gas yield and c) PAHs yield, obtained in the pyrolysis of the
four butanol isomers at 1275, 1375 and 1475 K.

184 In Fig. 3a, it can be seen that the soot yields increase as temperature does for any

185 alcohol isomer. The highest sooting tendency was found in the pyrolysis of tert-butanol,

186 and follows the sequence: 2-butanol, 1-butanol and iso-butanol. The highest soot

187 tendency of tert-butanol agrees with the results reported by Singh et al. [14], in a study

188   of the analysis of sooting tendency of n-butane, iso-butane and the four butanol isomers,

189   using a counterflow non-premixed flame configuration.

190   This soot formation trend could be explained by the fact that each butanol isomer

191   has different number of β H-atoms that are available for the four-center elimination

192   during the complex fission process. In this way, the soot tendency ranking agrees with

193   the highest number of β H-atoms available to the complex fission process of each

194   isomer as it was pointed previously [15]. Thus, tert-butanol could form more alkenes

195   necessary for the HACA route through complex fission process, producing subsequently

196   more soot formation.

197   On the other hand, the gas yield decreases as temperature increases for a given

198   isomer, Fig. 3b, since as the soot formation processes are enhanced, the availability of

199   carbon to take part in the formation of gas products decreases. Thus, the gas yield

200   decreases as the soot yield increases. Moreover, the evolution of the gas yield for each

201   butanol isomer agrees with the evolution of the corresponding soot yield.

202   As it can observed in Fig. 3c, the PAHs yield decreases as the temperature

203   increases. At the lowest temperature tested, 1275 K, the highest soot and PAHs

204   formation is found in the pyrolysis of tert-butanol. At 1375 and 1475 K, differences

205   among the yields to PAHs of the different isomers tested are smaller, in particular at

206   1475 K.

207   The formation of gases is an important issue in the pyrolysis of butanol isomers. In

208   most of the cases, the gas yield is higher than 30 %. For this reason, it is interesting the

209   identification and quantification of the gases formed during the process. Fig. 4 shows

210   the concentration of the major gases from the pyrolysis of the four butanol isomers at

211   1275, 1375 and 1475 K.

212   The formation of CO and CO_2 in the butanol isomers pyrolysis is due to the

213   presence of oxygen in the alcohol molecules. The formation of CO, Fig. 4a, from the

214   pyrolysis of tert-butanol is lower than from the rest of butanol isomers. In general, CO

215   shows a slight increase as the temperature increases. On the other hand, the formation of

216   CO_2 is very similar for the four isomers, Fig. 4b, showing also a significant increase of

217   CO_2 concentration as the temperature increases. The formation of CO and CO_2 is

218   important because, for the formation of these compounds, the carbon is removed from

219   the reaction pathways that would lead to the soot formation, especially in the pyrolysis

220   of alcohols [32, 33].

221   The formation of C_2H_4 is observed in Fig. 4c, where the pyrolysis of tert-butanol

222   shows the lowest formation of ethylene at all temperatures tested. The same behaviour

223   is observed in the formation of C_2H_2, Fig. 4d, and in the formation of CH_4, Fig. 4e. In

224   general, the concentration of C_2H_4 and CH_4 decreases as the temperature increases.

225   On the other hand, the trend of C_2H_2 is different in the pyrolysis of each butanol

226   isomer. C_2H_2 is one of the most important soot precursors, and could be very reactive to

227   form other soot intermediates such as propargyl radicals, or other cyclic compounds

228   [34]. It is important to point that C_2H_2 is an intermediate compound in the pyrolysis of

229   organic compounds, and it could follow different reaction pathways according to the

230   experimental conditions employed.

231   The formation of H_2, Fig. 4f, increases as the temperature increases, being similar in

232   the pyrolysis of all butanol isomers. Richter and Howard [35] explained that H_2 is

233   released during the formation of soot intermediates such as cyclohexadiene and

234   benzene, in the well-known HACA mechanism, and therefore the increased amount of

235   H_2 and soot are related as the temperature increases.

236   The concentration of benzene decreases as the temperature increases, Fig. 4g.

237   Moreover, it is appreciable that pyrolysis of tert-butanol forms lower concentration of

238   benzene than the rest of the isomers. This could be attributed to the fact that most of the

239   tert-butanol carbon continues its reaction pathways, through different intermediates, up

240   to the formation of soot [35], more quickly than the rest of the butanol isomers.

241   Fig. 5 shows the formation of minor gases in the pyrolysis of the butanol isomers at

242   1275, 1375 and 1475 K. It can be seen that the concentration of most of the minor gases

243   decreases as the temperature increases. On the other hand, C_4H_6 (1,3-butadiene) slightly

244   increases as the temperature increases (Fig. 5d). This behaviour was also observed in

245   flames where a further dehydrogenation of the linear butenes can lead to 1,3-butadiene
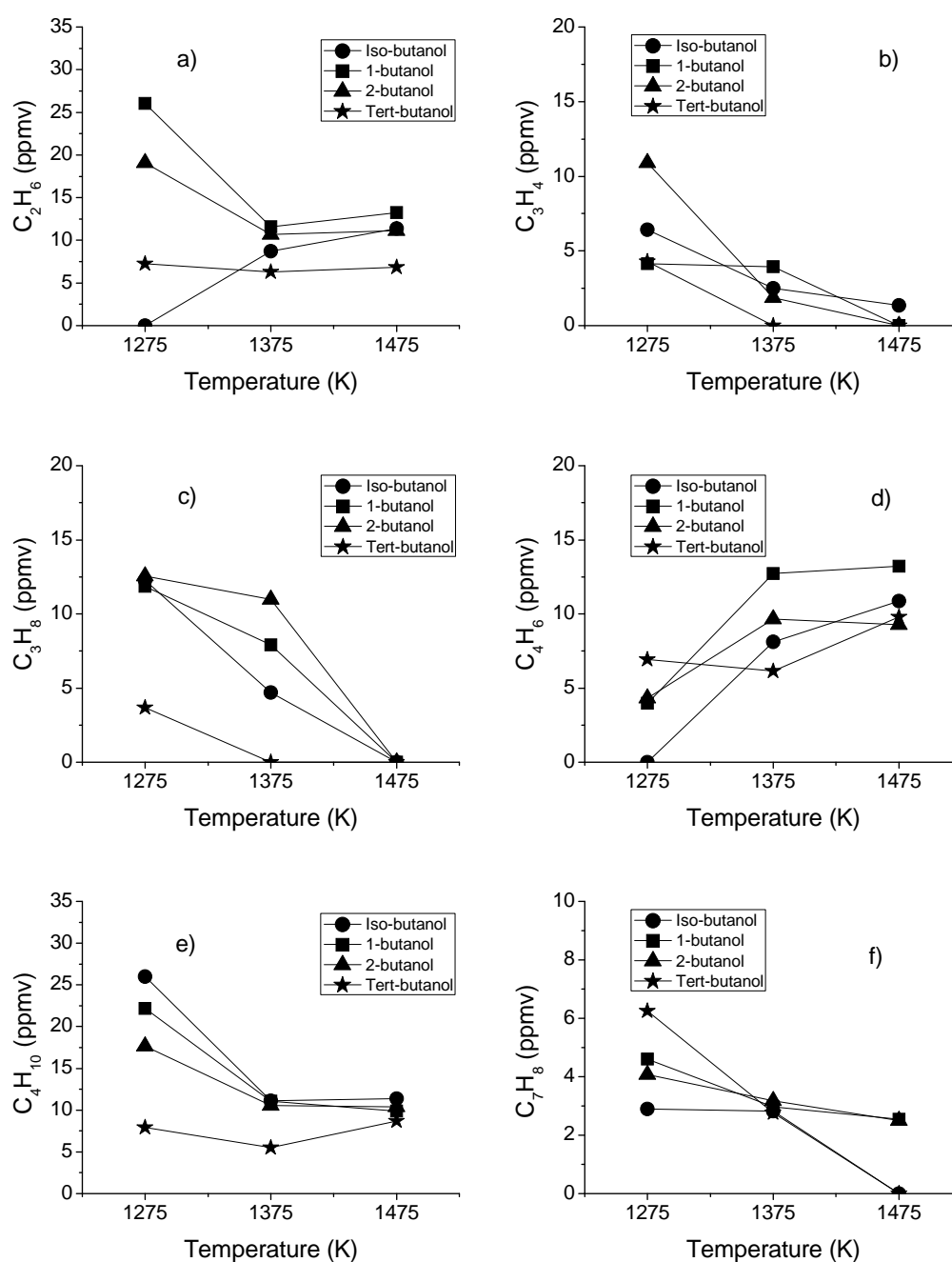
246   [36].

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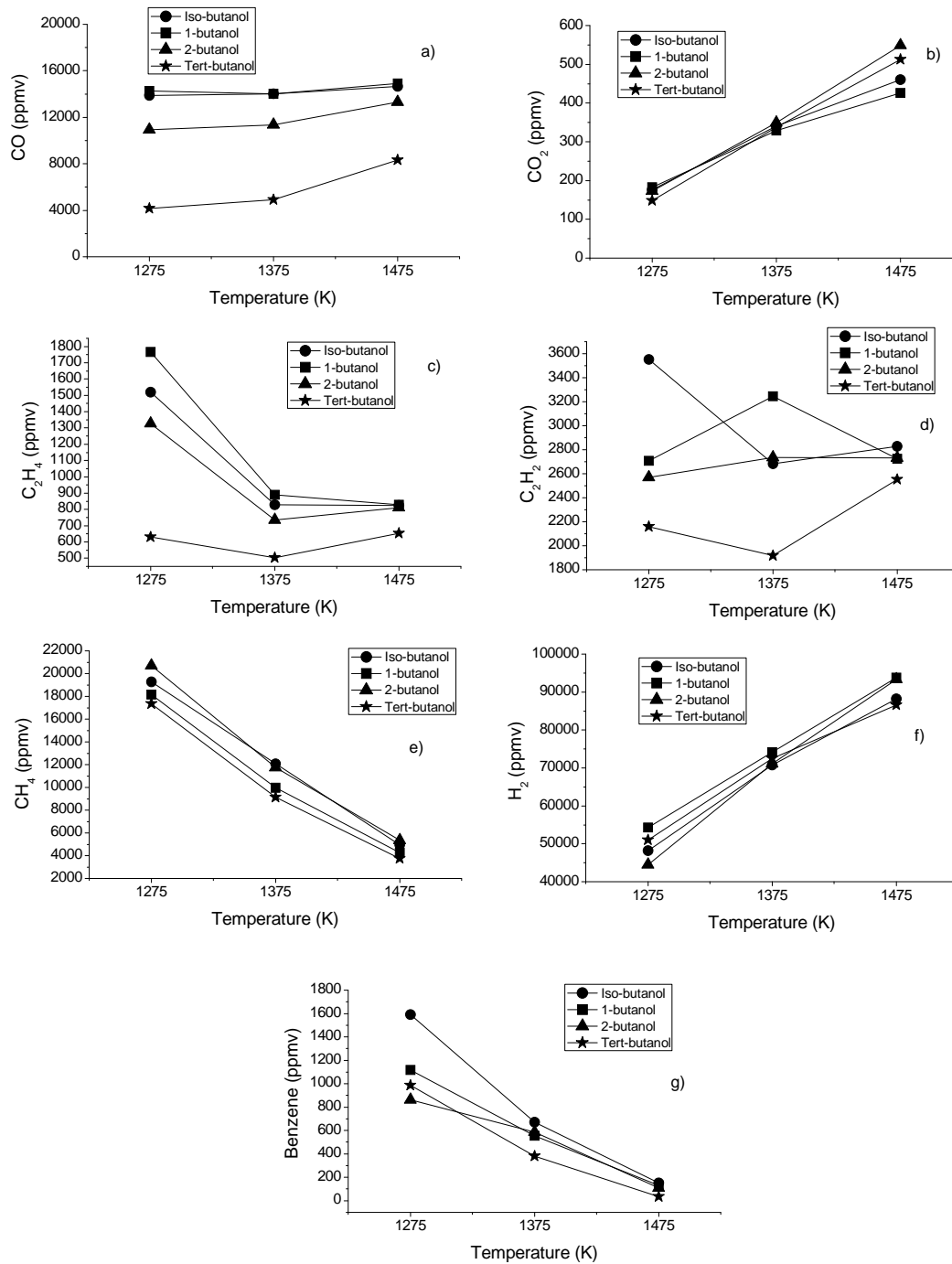
Fig. 4. Major gases formed as a function of the temperature: a) CO, b) CO_2, c) C_2H_4, d)

C_2H_2, e) CH_4, f) H_2 and g) benzene, from the pyrolysis of the four butanol isomers at

1275, 1375 and 1475 K.

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Fig. 5. Minor gases formed as a function of the temperature: a) C_2H_6, b) C_3H_4 (propadiene), c) C_3H_8, d) C_4H_6, e) C_4H_{10}, and f) C_7H_8, from the pyrolysis of the four butanol isomers at 1275, 1375 and 1475 K.

Because the PAHs species present different toxicity and since the PAHs are important soot precursors, and thus can be involved in the complex mechanism to form

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259   soot particles, it is important to show the PAHs speciation obtained, in the different

260   pyrolysis experiments. Fig. 6 shows the individual total PAHs concentration at the

261   different temperatures studied, that refers to the concentration of each individual PAH,

262   determined as the sum of each individual compound found either in the XAD-2 resin,

263   adsorbed on soot and stuck on the reactor walls in each experiment.

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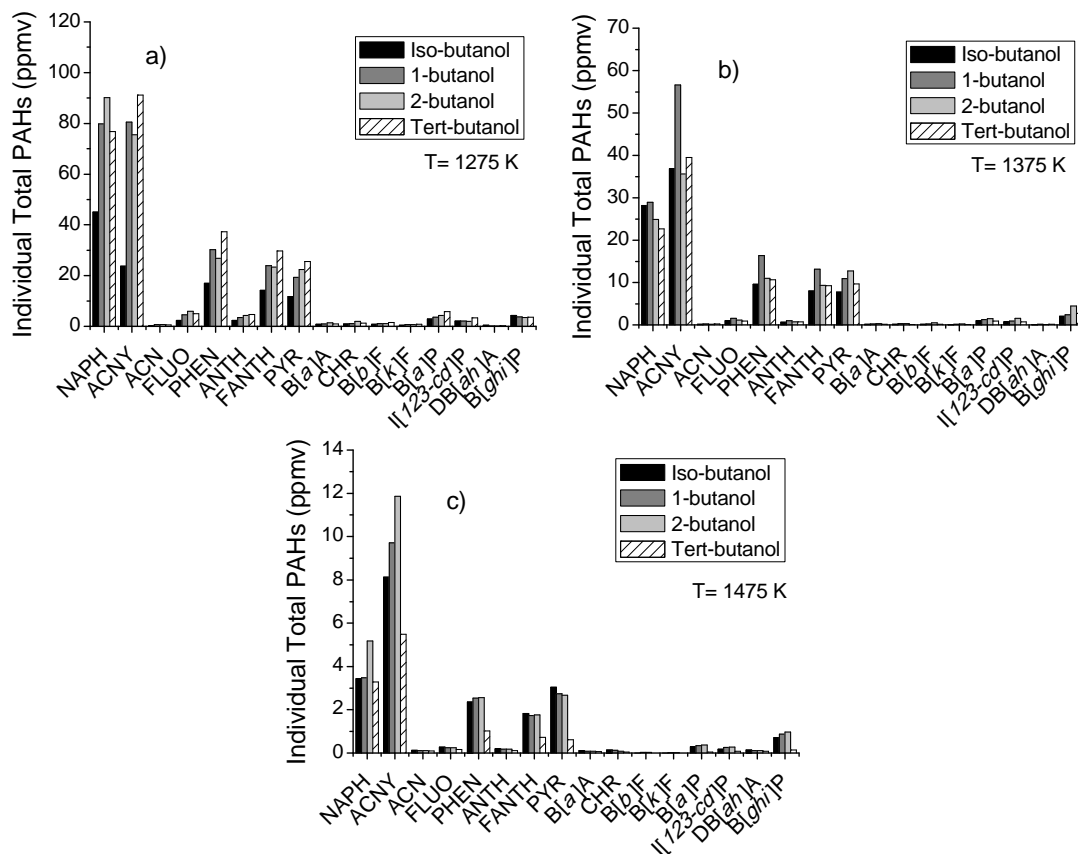
Fig. 6. Concentration of individual total PAHs as a function of reaction temperature in

the pyrolysis of the butanol isomers: a) 1275 K, b) 1375 K and c) 1475 K.

267   The highest formation of the different PAHs was found at 1275 K. At this

268   temperature, Fig. 6a, NAPH and ACNY were found in higher concentrations. Other

269   PAHs, such as PHEN, FANH and PYR were also obtained in significant concentrations.

270   High molecular weight PAHs were found in very low concentrations, except B[*a*]P,

271   I[*123-cd*]P and B[*ghi*]P which were found in higher concentrations. The same PAHs

272   trend is shown. At higher temperatures, Figs. 6b and 6c, but in lower concentrations.

273   The influence of each butanol isomer on PAHs speciation is analysed at 1275 K in

274   Fig. 6a, temperature at which the high PAHs concentration is obtained. The formation

275   of the different PAHs from tert-butanol is higher in most of the cases. The highest

276   formation of PAHs from the pyrolysis of tert-butanol at 1275 K could be related with

277   their highest formation of soot, Fig. 3a, and it could be due to a greater trend to form

278   alkenes and aromatics, through the complex fission, of these butanol isomers [15].

279   In order to determine the PAHs speciation in each phase (resin, soot or reactor

280   walls), Figs. 7, 8, 9 and 10 show the individual PAHs distribution found in each phase

281   analysed, at different reaction temperatures, from the pyrolysis of iso-butanol, 1-

282   butanol, 2-butanol and tert-butanol, respectively.

283   The PAHs formed from the pyrolysis of iso-butanol are shown in Fig. 7. It can be

284   seen that NAPH has the highest concentration at 1275 K in the resin, but it decreases as

285   the temperature increases, Figs. 7b and 7c, being ACNY the compound with the highest

286   concentration on soot at 1375 and 1475 K. Low molecular weight PAHs, such as

287   PHEN, FANTH and PYR, were found in greater concentration than high molecular

288   weight PAHs at all temperatures tested. High molecular weight PAHs were found in

289   significant concentrations in soot and reactor walls phases at 1275 K, Fig. 7a. Above

290   this temperature, these high molecular weight PAHs decrease their concentration as the
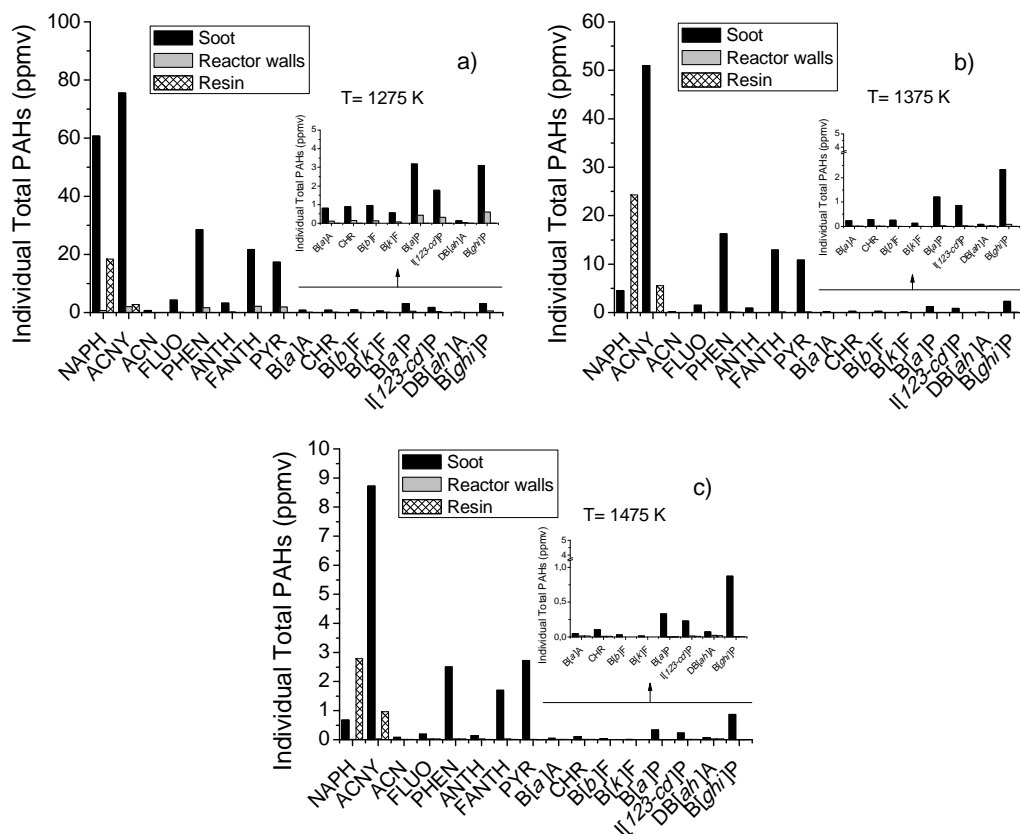
291   temperature increases.
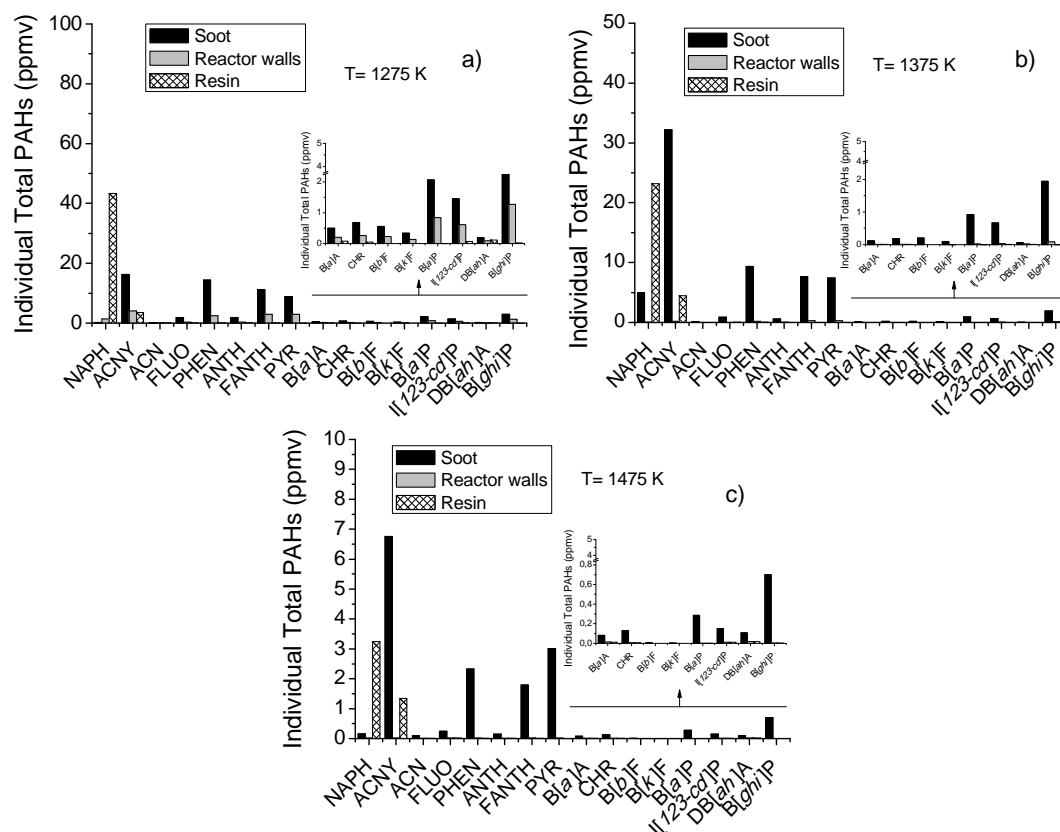
Fig. 7. Individual PAHs distribution on the soot, reactor walls, and resin in the pyrolysis of iso-butanol: (a) 1275 K, (b) 1375 K and (c) 1475 K.

Fig. 8 shows the PAHs formed from the pyrolysis of 1-butanol. As it can be observed, PAHs concentration decreases as temperature increases. ACNY is the compound found adsorbed on the soot in the highest concentration at all temperatures tested. The reactor walls phase shows the lowest amount of PAHs. The resin phase shows significant concentrations of NAPH and ACNY. In addition, the formation of PAHs with higher molecular weight were principally found at 1275 K, Fig. 8a, and it coincides with the lowest amount of soot obtained at this temperature, Fig. 3a.
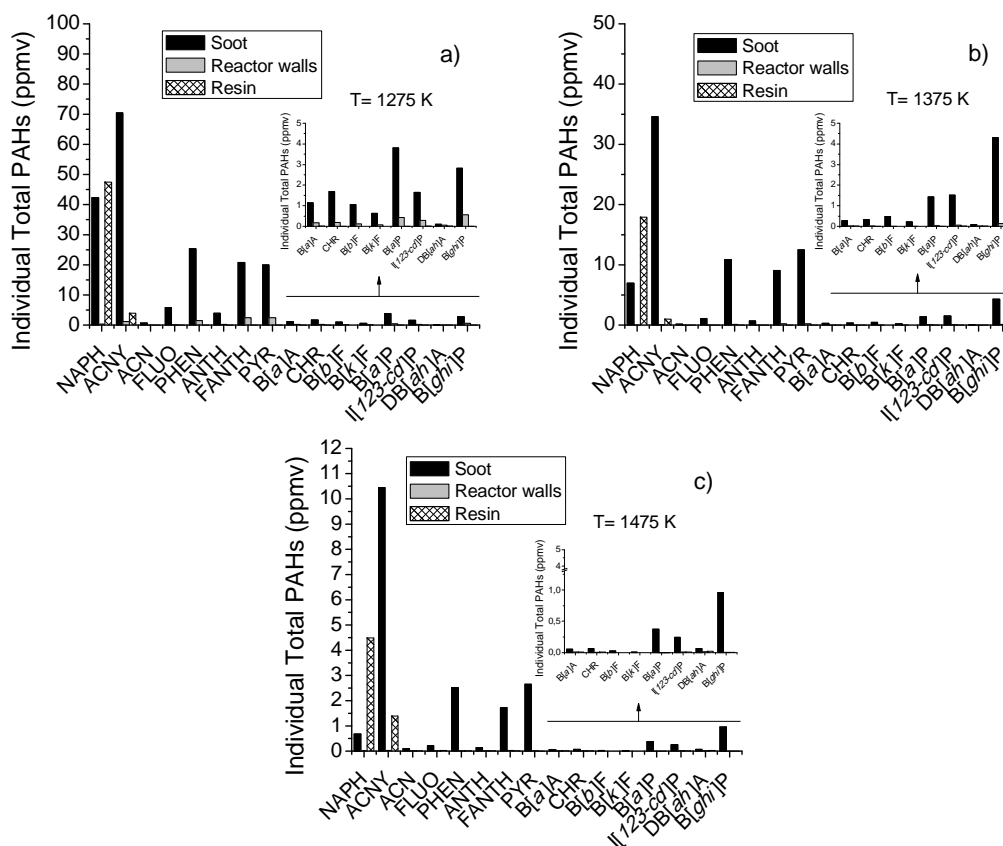
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Fig. 8. Individual PAHs distribution on the soot, reactor walls, and resin in the pyrolysis
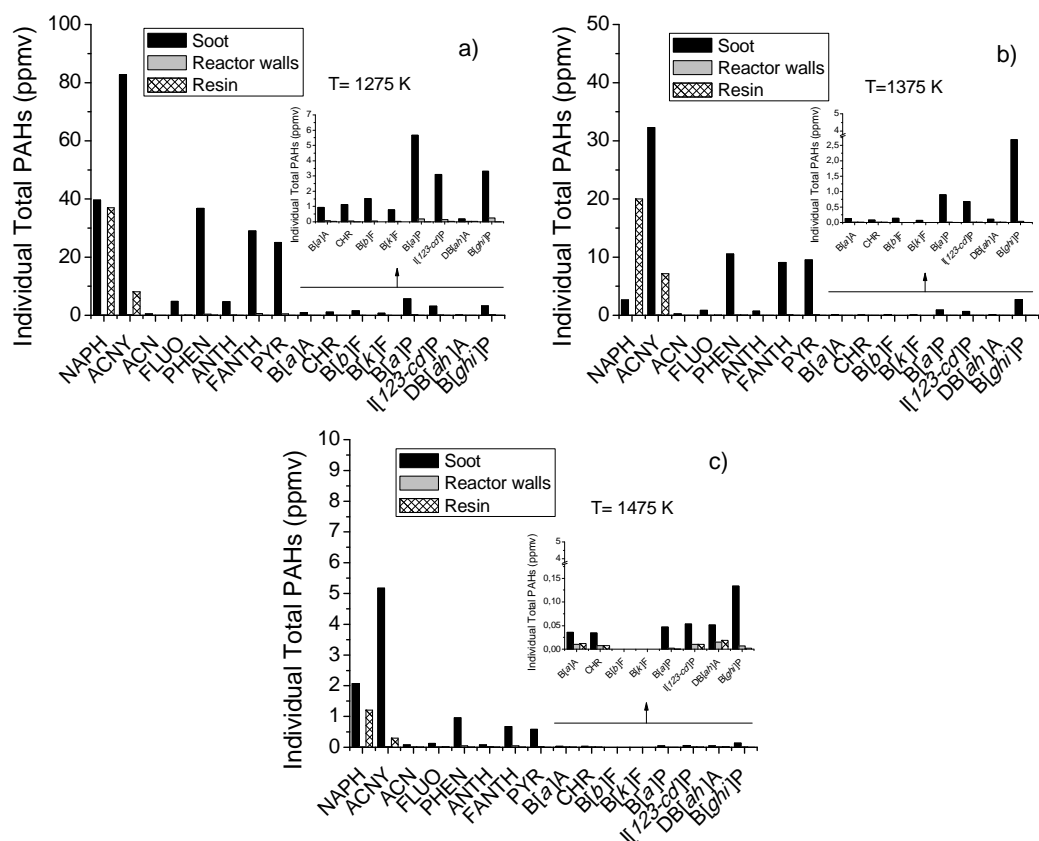
of 1-butanol: (a) 1275 K, (b) 1375 K and (c) 1475 K.

Fig. 9 shows the PAHs found in the pyrolysis of 2-butanol, where PAHs found on

soot were the highest at all temperatures. ACNY is the PAH that shows the highest

concentration found on soot, as in 1-butanol pyrolysis, at all temperatures tested.

Furthermore, NAPH, PHEN, ANTH and PYR (low molecular weight PAHs) were

obtained in significant concentrations. On the other hand, PAHs with high molecular

weight were found in low concentrations at all temperature tested.

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Fig. 9. Individual PAHs distribution on the soot, reactor walls, and resin in the pyrolysis

of 2-butanol: (a) 1275 K, (b) 1375 K and (c) 1475 K.

In the pyrolysis of tert-butanol, Fig. 10, most of the PAHs were found on soot, and

ACNY was found in the highest concentration in this phase. The same trend was

observed previously in 1-butanol pyrolysis, Fig. 8, and in 2-butanol pyrolysis, Fig. 9.

The same low molecular weight PAHs: NAPH, PHEN, ANTH, and PYR were found in

significant concentrations. On the other hand, it is notable that B[*a*]P, a high molecular

weight PAH, was found in a comparatively high concentration at 1275 K, Fig. 10a.

Fig. 10. Individual PAHs distribution on the soot, reactor walls, and resin in the pyrolysis of tert-butanol: (a) 1275 K, (b) 1375 K and (c) 1475 K.

As it can be noticed in the above analysis, the same PAHs evolution was found from the pyrolysis of all butanol isomers, except for slight differences. In summary, 1-butanol, 2-butanol and tert-butanol showed higher concentrations of ACNY than NAPH, which could be explained by the reaction of 1-naphthylacetylene up to the formation of ACNY at high temperatures [37], and could also be attributed to the structural configuration of these isomers that allows them to release more β H-atoms than iso-butanol [15], facilitating the occurrence of the HACA route.

In the pyrolysis of all butanol isomers, the same low molecular weight PAHs: NAPH, ACNY, PHEN, ANTH, and PYR, were found in significant concentrations at all temperatures analysed.

334   The concentrations of PAHs found on reactor walls were low. The same behaviour

335   was found on resin, except for high amounts of NAPH and ACNY.

336   PAHs are well-known for their mutagenic and carcinogenic properties, especially

337   B[a]P. In this way, the benzo[a]pyrene equivalent amount (B[a]P-eq) was taken as a

338   reference [38-40], for comparing the cancer risk attributed to the inhalation of PAHs

339   airborne. The toxicity equivalent factor (TEF) is used to express the toxicity of each

340   PAH in terms of B[a]P, the reference compound. In this work, the TEF values proposed

341   by Nisbet and Lagoy [40] were taken, Table S1.

342   The value of B[a]P-eq, in mg, is calculated from the Eq. (1), where i corresponds to

343   each PAH amount, in mg, and its corresponding TEF value.

$$344 \qquad\qquad\qquad \text{B}[a]\text{P-eq} = \sum_{i=1}^{n}(TEF_i) \times (\text{PAH}_i) \qquad\qquad (1)$$

345   The comparison between B[a]P-eq amount values obtained in the pyrolysis of the

346   four butanol isomers as a function of the temperature is shown in Fig. 11.

347   It is observed that B[a]P-eq amounts decrease as the temperature increases. The

348   highest values of B[a]P-eq amount at 1275 K was found in the pyrolysis of tert-butanol.

349   On the other hand, at 1375 and 1475 K there was no significant differences, for B[a]P-

350   eq amounts, among the pyrolysis of the different isomers tested.

351
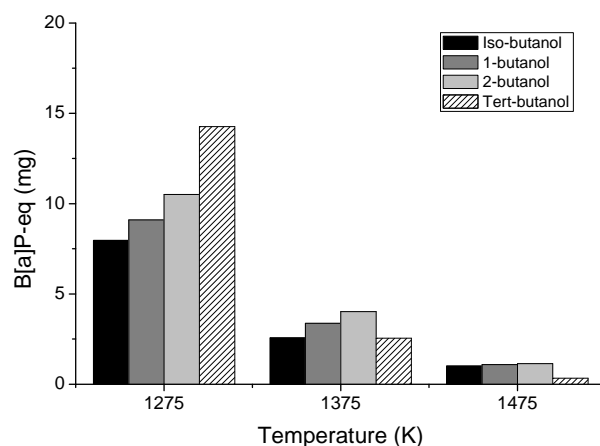
Fig. 11. B[*a*]P-eq amounts from the pyrolysis of the four butanol isomers as a function

of the temperature.

The comparison of the PAHs and B[*a*]P-eq amounts in each phase analysed:

adsorbed on soot, stuck on reactor walls and adsorbed on resin, is shown in Fig. 12.

In Fig. 12a, the iso-butanol pyrolysis shows that the PAHs amounts found on soot

are higher than the ones found on the resin and reactor walls at all temperatures tested,

and this trend decreases as the temperature increases. Although the amount of PAHs

found on the resin was high at 1275 and 1375 K, the B[*a*]P-eq amounts found in the

resin were low. The highest B[*a*]P-eq amount was found on soot at 1275 K.

In Fig. 12b, the 1-butanol pyrolysis shows that the highest PAHs and B[*a*]P-eq

amounts were obtained adsorbed on soot, being at 1275 K the highest ones.

In Figs. 12b, 12c and 12d, PAHs and B[*a*]P-eq amount values from the pyrolysis of

1-butanol, 2-butanol and tert-butanol, present similar trends. The highest values for both

parameters analysed were found from the pyrolysis of tert-butanol at 1275 K on soot.

22

366
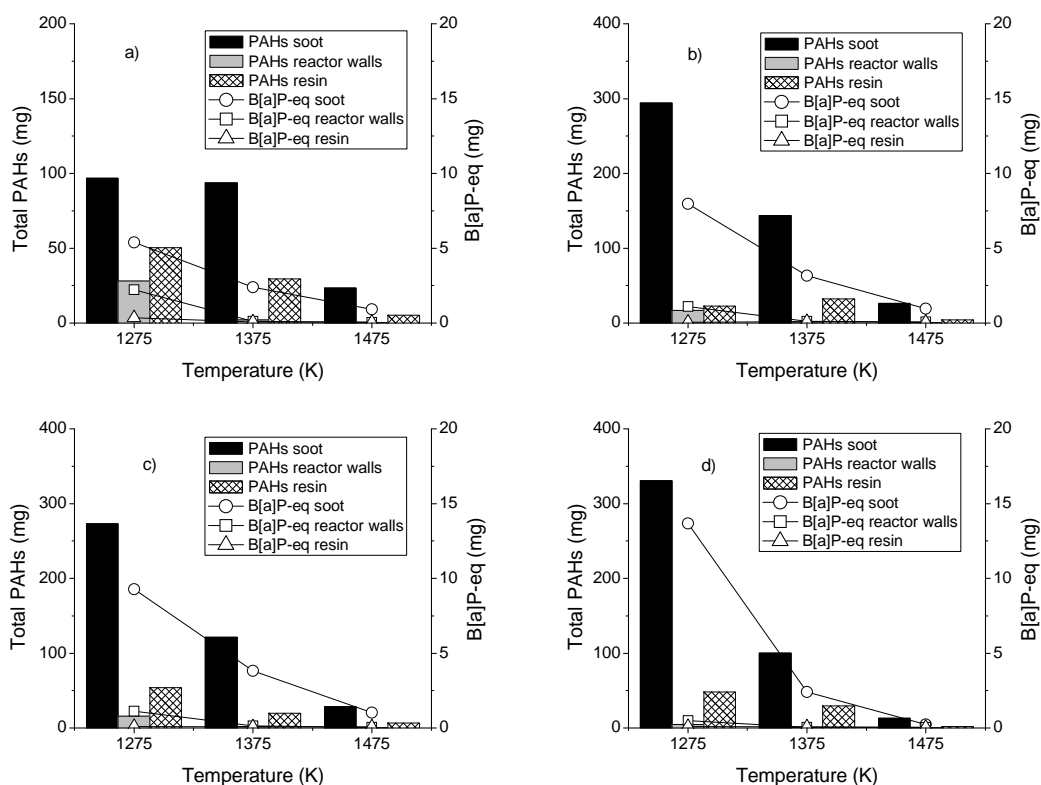
Fig. 12. Total PAHs and B[*a*]P-eq amount distribution in the different phases analysed, from the butanol isomers pyrolysis at different reaction temperatures: a) Iso-butanol, b) 1-butanol, c) 2-butanol and d) Tert-butanol.

In general, PAHs were found predominantly on soot, especially at 1275 K. The highest PAHs amount was found on soot from the pyrolysis of tert-butanol at 1275 K, Fig. 12d. The highest toxic potential, evaluated through the B[*a*]P-eq amount, was also found on soot at 1275 K in the pyrolysis of tert-butanol, shown in Fig. 12d. Although the B[*a*]P-eq amounts on the reactor walls were low in the pyrolysis of 1-butanol, 2-butanol and tert-butanol for all temperatures tested, only in the case of the pyrolysis of iso-butanol at 1275 K a significant B[*a*]P-eq amount is found on the reactor walls.

378   The toxic potential, analysed in the present study, shows that the soot formed from

379   the pyrolysis of butanol isomers, at low temperatures, increases the toxicity risk of the

380   effluent.

381

382   4. CONCLUSIONS

383   The present work analyses the formation of soot, gases and PAHs from the

384   pyrolysis of the four butanol isomers: iso-butanol, 1-butanol, 2-butanol and tert-butanol.

385   The experiments were performed with a given inlet concentration of butanol isomer,

386   22500 ppmv, and a temperature range from 1275 to 1475 K.

387   In this temperature range and for all the butanol isomers, an increase of the

388   pyrolysis temperature produces an increase of soot formation, while the gas and PAHs

389   yields decrease.

390   The soot formation tendency increases according to the importance of the complex

391   fission process, in the decomposition of butanol isomers, which depends on the number

392   of β H-atoms that are available to the four-center elimination. In this way, the tendency

393   to soot formation was ranked, under the experimental conditions of the present study, as

394   follows: tert-butanol, 2-butanol, 1-butanol and iso-butanol. This same trend was found

395   in the formation of PAHs at 1275 K, where the tert-butanol was the isomer with the

396   highest formation of PAHs.

397   The formation of high amounts of CO and CH_4 is important due to their role to

398   remove carbon from the typical pathways leading to PAHs and soot formation. The

399   formation of H_2 increases significantly as the temperature increases, according to the

400   HACA route that leads to form PAHs which subsequently form soot.

401   The PAHs analysis in each phase showed that most of the PAHs were found on the

402   soot phase, at all the temperatures tested. In this phase, the PAHs with the highest

403   concentrations are: NAPH, ACNY, PHEN, FANTH and PYR, while the PAHs with

404   higher molecular weight were found in low concentrations. There is a relationship

405   between the amount of PAHs and B[a]P-eq. The higher is the formation of PAHs, the

406   higher are the values of B[a]P-eq found at 1275 K in the pyrolysis of all butanol

407   isomers.

408

5. ACKNOWLEDGEMENTS

6. REFERENCES

418

419   [1]   Mohr SH, Wang J, Ellem G, Ward J, Giurco D. Projection of world fossil fuels

420   by country. Fuel 2015;141:120-35.

421   [2]   Jess A. What might be the energy demand and energy mix to reconcile the

422   world's pursuit of welfare and happiness with the necessity to preserve the

423   integrity of the biosphere?. Energy Policy 2010;38:4663-78.

424   [3]   Naik SN, Goud VV., Rout PK, Dalai AK. Production of first and second

425   generation biofuels: A comprehensive review. Renew. Sust. Energ. Rev.

426   2010;14:578-97.

427   [4]   Lee SY, Park JH, Jang SH, Nielsen LK, Kim J, Jung KS. Fermentative butanol

428   production by *Clostridia*. Biotechnol. Bioeng. 2008;101:209-28.

429   [5]   Atsumi S, Hanai T, Liao JC. Non-fermentative pathways for synthesis of

430   branched-chain higher alcohols as biofuels. Nature 2008;451:86-9.

431   [6]   Wallner T, Miers SA, McConnell S. A comparison of ethanol and butanol as

432   oxygenates using a direct-injection, spark-ignition engine. J. Eng. Gas. Turbines

433   Power-Trans. ASME 2009;131:32802-1-32802-9.

434   [7]   Li Y, Yu Y, Wang Z, Wang J. Physical and chemical properties of isobutanol-

435   gasoline blends. Environ. Prog. Sustain. Energy 2014;34: 908-14.

436   [8]   Popuri S, Bata R. A Performance Study of Iso-Butanol-, Methanol-, and Ethanol-

437   Gasoline Blends Using a Single Cylinder Engine. SAE Tech. Pap. 1993;932953.

438   [9]   Rakopoulos DC, Rakopoulos CD, Hountalas DT, Kakaras EC, Giakoumis EG,

439   Papagiannakis RG. Investigation of the performance and emissions of bus engine

440   operating on butanol/diesel fuel blends. Fuel 2010;89:2781-90.

441 [10] Yao M, Wang H, Zheng Z, Yue Y. Experimental study of n-butanol additive and

442   multi-injection on HD diesel engine performance and emissions. Fuel

443   2010;89:2191-201.

444 [11] Moss JT, Berkowitz AM, Oehlschlaeger MA, Biet J, Warth V, Glaude PA, et al.

445   An experimental and kinetic modeling study of the oxidation of the four isomers

446   of butanol. J. Phys. Chem. A 2008;112:10843-55.

447 [12] Yang B, Oßwald P, Li Y, Wang J, Wei L, Tian Z, et al. Identification of

448   combustion intermediates in isomeric fuel-rich premixed butanol–oxygen flames

449   at low pressure. Combust. Flame 2007;148:198-209.

450 [13] Camacho J, Lieb S, Wang H. Evolution of size distribution of nascent soot in n-

451   and i-butanol flames. Proc. Combust. Inst. 2013;34:1853-60.

452 [14] Singh P, Hui X, Sung CJ. Soot formation in non-premixed counterflow flames of

453   butane and butanol isomers. Combust. Flame 2016;164:167-82.

454 [15] McEnally CS, Pfefferle LD. Fuel decomposition and hydrocarbon growth

455   processes for oxygenated hydrocarbons: butyl alcohols. Proc. Combust. Inst.

456   2005;30:1363-70.

457 [16] Wang H, Frenklach M. A detailed kinetic modeling study of aromatics formation

458   in laminar premixed acetylene and ethylene flames. Combust. Flame

459   1997;110:173-221.

460 [17] Singh P, Sung CJ. PAH formation in counterflow non-premixed flames of butane

461   and butanol isomers. Combust. Flame 2016;170:91-110.

462 [18] Frenklach M. Reaction mechanism of soot formation in flames. Phys. Chem.

463   Chem. Phys. 2002;4:2028-37.

464   [17]   Agency for Toxic Substances and Disease Registry ATSDR. Toxicological

465   profile for polycyclic aromatic hydrocarbons, Atlanta, GA; 1995. Available on

466   line: <http://www.atsdr.cdc.gov/toxprofiles/tp69.pdf > [accessed: 05.10.16].

467   [20]   Ochsenkühn-Petropoulou M, Staikos K, Matuschek G, Kettrup A. On-line

468   determination of polycyclic aromatic hydrocarbons in airborne particulate matter

469   by using pyrolysis/GC-MS. J. Anal. Appl. Pyrolysis 2003;70:73-85.

470   [21]   US Environmental Protection Agency EPA. Health assessment document for

471   diesel engine exhaust; 2002. Available on line: <http://hero.epa.gov/index.cfm

472   /reference/download/reference_id/42866> [accessed: 05.10.16].

473   [22]   Walgraeve C, Chantara S, Sopajaree K, De Wispelaere P, Demeestere K, Van

474   Langenhove H. Quantification of PAHs and oxy-PAHs on airborne particulate

475   matter in Chiang Mai, Thailand, using gas chromatography high resolution mass

476   spectrometry. Atmos. Environ. 2015;107:262-72.

477   [23]   Ballesteros R, Hernández JJ, Lyons LL. An experimental study of the influence

478   of biofuel origin on particle-associated PAH emissions. Atmos. Environ.

479   2010;44:930-8.

480   [24]   Wang W, Jariyasopit N, Schrlau J, Jia Y, Tao S, Yu T, et al. Concentration and

481   photochemistry of PAHs, NPAHs, and OPAHs and toxicity of PM 2.5 during the

482   Beijing Olympic Games. Environ. Sci. Technol. 2011;45:6887-95.

483   [25]   Sánchez NE, Millera Á, Bilbao R, Alzueta MU. Polycyclic aromatic

484   hydrocarbons (PAH), soot and light gases formed in the pyrolysis of acetylene at

485   different temperatures: Effect of fuel concentration. J. Anal. Appl. Pyrolysis

486   2013;103:126-33.

487   [26]   Sánchez NE, Salafranca J, Callejas A, Millera Á, Bilbao R, Alzueta MU.

488   Quantification of polycyclic aromatic hydrocarbons (PAHs) found in gas and

489   particle phases from pyrolytic processes using gas chromatography-mass

490   spectrometry (GC-MS). Fuel 2013;107:246-53.

491 [27] Viteri F, Abián M, Millera Á, Bilbao R, Alzueta MU. Ethylene-SO$_2$ interaction

492   under sooting conditions: PAH formation. Fuel 2016;184:966-72.

493 [28] Viteri F, Baena C, Millera Á, Bilbao R, Alzueta MU. Formation of polycyclic

494   aromatic hydrocarbons in the pyrolysis of 2-methylfuran at different reaction

495   temperatures. Combust. Sci. Technol. 2016;188:611-22.

496 [29] Viteri F, Salinas J, Millera Á, Bilbao R, Alzueta MU. Pyrolysis of dimethyl

497   carbonate: PAH formation. J. Anal. Appl. Pyrolysis 2016;122:524-530.

498 [30] Sánchez NE, Callejas A, Millera Á, Bilbao R, Alzueta MU. Polycyclic aromatic

499   hydrocarbon (PAH) and soot formation in the pyrolysis of acetylene and

500   ethylene: Effect of the Reaction Temperature. Energy Fuels 2012;26:4823-9.

501 [31] Sánchez NE, Callejas A, Millera Á, Bilbao R, Alzueta MU. Formation of PAH

502   and soot during acetylene pyrolysis at different gas residence times and reaction

503   temperatures. Energy 2012;43:30-6.

504 [32] Pepiot-Desjardins P, Pitsch H, Malhotra R, Kirby SR, Boehman AL. Structural

505   group analysis for soot reduction tendency of oxygenated fuels. Combust. Flame

506   2008;154:191-205.

507 [33] Esarte C, Abián M, Millera Á, Bilbao R, Alzueta MU. Gas and soot products

508   formed in the pyrolysis of acetylene mixed with methanol, ethanol, isopropanol

509   or n-butanol. Energy 2012;43:37-46.

510 [34] Kennedy IM. Models of soot formation and oxidation. Prog. Energy Combust.

511   Sci. 1997;23:95-132.

512   [35]   Richter H, Howard J. Formation of polycyclic aromatic hydrocarbons and their

513   growth to soot-a review of chemical reaction pathways. Prog. Energy Combust.

514   Sci. 2000;26:565-608.

515   [36]   Oßwald P, Güldenberg H, Kohse-Höinghaus K, Yang B, Yuan T, Qi F.

516   Combustion of butanol isomers - A detailed molecular beam mass spectrometry

517   investigation of their flame chemistry. Combust. Flame 2011;158:2-15.

518   [37]   Richter H, Mazyar OA, Sumathi R, Green WH, Howard JB, Bozzelli JW.

519   Detailed kinetic study of the growth of small polycyclic aromatic hydrocarbons.

520   1. 1-Naphthyl + Ethyne. J. Phys. Chem. A 2001;105:1561-73.

521   [38]   World Health Organization WHO. Air quality guidelines for Europe,

522   Copenhagen, 2000. Available on line:

523   <http://www.euro.who.int/__data/assets/pdf_file/0005/ 74732/E71922.pdf>

524   [accessed: 05.10.16].

525   [39]   Jia Y, Stone D, Wang W, Schrlau J, Tao S, Simonich SLM. Estimated reduction

526   in cancer risk due to PAH exposures if source control measures during the 2008

527   Beijing olympics were sustained. Environ. Health Perspect. 2011;119:815-20.

528   [40]   Nisbet ICT, LaGoy PK. Toxic equivalency factors (TEFs) for polycyclic

529   aromatic hydrocarbons (PAHs). Regul. Toxicol. Pharmacol. 1992;16:290-300.

530