

Effect of H₂S on the S-PAH formation during ethylene pyrolysis

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Abstract

The effect of the H₂S presence on the formation of six different sulphurated polycyclic hydrocarbons (S-PAH), during the pyrolysis of ethylene-H₂S mixtures, has been studied in a tubular flow reactor installation. Experiments with different inlet H₂S concentrations (0.3, 0.5 and 1%) and temperatures of reaction (between 1075 and 1475 K) have been carried out. The 16 compounds that the Environmental Protection Agency (EPA) has stated as EPA-PAH priority pollutants were also analysed. EPA-PAH compounds were the majority of quantified PAH, and also S-PAH were found and quantified. For temperatures studied, the S-PAH/EPA-PAH ratio values showed a maximum value at 1075 K and a minimum value at 1175 K. With respect to the effect of the inlet concentration of H₂S, the S-PAH/EPA-PAH ratio values increased with the increase of the H₂S concentration.

Keywords: H₂S, ethylene pyrolysis, polycyclic aromatic hydrocarbons (PAH), sulphurated polycyclic aromatic hydrocarbons (S-PAH).

1. Introduction

There is an increasing interest in the use of different non-conventional fuel mixtures due to their proved reserves [1-3], e.g. sour gas or biogas generated in anaerobic digestion,

26 in combustion processes. These gases may contain different amounts of hydrogen
27 sulphide in their composition. While expensive H₂S treatments have been traditionally
28 applied to purify the gas, nowadays, an important tendency involves not to pre-treat the
29 raw gas and devote the main efforts to the development of optimized technologies and
30 combustion processes [4], taking also the advantage of using the combustion heat of
31 H₂S, together with the downstream cleaning of the gases.

32

33 The presence of reducing zones in the combustion chamber may produce pyrolysis
34 reactions that contribute to the consumption of the fuel, and can also generate the
35 formation of appreciable amounts of unburned pollutants, such as Polycyclic Aromatic
36 Hydrocarbons (PAH) and particulate matter (soot). PAH have a fundamental role in the
37 formation of soot as they are known to participate actively in the HACA (Hydrogen
38 Abstraction Carbon Addition) route until the formation of the first soot particles [5].
39 Owing to their carcinogenic and mutagenic character [6], the Environmental Protection
40 Agency of USA (EPA) has classified 16 Polycyclic Aromatic Hydrocarbons as priority
41 pollutants, from now on called EPA-PAH. Formation of EPA-PAH may happen in
42 different processes, as in flames [e.g. 7], or during the combustion of biomass pellets in
43 domestic boilers [e.g. 8].

44

45 Moreover, sulphur compounds present in the reacting gas mixture can modify the
46 amount of soot and EPA-PAH formed during the combustion process. For example, the
47 presence of SO₂ has been demonstrated to clearly decrease both the soot and EPA-PAH
48 amounts formed in tubular reactor experiments [9-11], flames [12, 13], Claus furnaces
49 [14] and in the combustion of biomass, when sulphur compounds with different
50 functionalities were added [15]. The effect of H₂S on the pyrolysis of ethylene (known

51 as soot precursor compound) has also been studied [16], showing that the H₂S presence
52 slightly decreases the formation of soot and EPA-PAH, and in Claus furnaces [17, 18],
53 where the decrease in the EPA-PAH concentration was greater with the inlet H₂S
54 concentration increasing. Furthermore, if oxygenated compounds are present, the
55 formation of oxy-PAH can also occur.

56

57 Therefore, in the combustion of hydrocarbon fuels in the presence of sulphur species,
58 both EPA-PAH and oxy-PAH may appear, but also Sulphurated Polycyclic Aromatic
59 Hydrocarbons (S-PAH) generated from the interaction of unburnt hydrocarbons and
60 sulphur species [19, 20]. S-PAH have shown potential carcinogenic and mutagenic
61 properties [21] and highly bio-accumulative characteristics [22], with benzothiophene
62 and dibenzothiophene as the most abundant S-PAH found in the environment [19].

63

64 The joint quantification of 29 different polycyclic aromatic compounds (16 EPA-PAH,
65 7 oxy-PAH and 6 S-PAH) during pyrolysis experiments of different ethylene-SO₂
66 mixtures was carried out in a previous work of the group [11]. In that work, the
67 presence of the 7 oxy-PAH studied, from the 9-fluorenone to benzo[*cd*]pyrenone, was
68 observed, with benzanthrene and benzo[*cd*]pyrenone exhibiting the highest
69 concentrations. Likewise, five S-PAH were detected and quantified.

70

71 In this context, and considering the interest in taking advantage of different non-
72 conventional fuel sources (e.g. sour gas with high H₂S content), the objective of the
73 present work is to study the formation of EPA-PAH and S-PAH in the pyrolysis of
74 ethylene-H₂S mixtures under well controlled experimental conditions. Ethylene is well-
75 known as soot and EPA-PAH precursor in the literature, as has been chosen for

76 comparison with earlier works of our group [e.g. 9-11]. 16 EPA-PAH and 6 S-PAH
77 have been analysed. The effect of reaction temperature (1075 to 1475 K) and the inlet
78 H₂S concentration (0.3 to 1%) on their formation has been analysed. Additionally, a
79 comparison of the results obtained with those obtained in the presence of SO₂ [11] was
80 done.

81

82 **2. Experimental**

83 An experimental set-up available at the Thermochemical Processes Group (GPT) of the
84 University of Zaragoza has been used for the present experimental study. The pyrolysis
85 experiments have been carried out in a set-up that can be seen in Fig. 1 [23]. The full
86 description of the experimental set-up can be found in Sánchez et al. [23-25]. A short
87 description of the main features of the set-up is done here. The set-up used has four
88 different zones: (1) a gas feeding zone, (2) a reaction zone including a flow reactor of
89 45 mm inner diameter and 160 mm in length, (3) a soot and PAH collecting zone, and
90 (4) a gas analysis zone. Ethylene and H₂S, as reactant gases, are diluted in N₂ and fed to
91 the reaction system with a total flow rate of 1 L (STP)/min. The ethylene concentration
92 is constant in all experiments with a value of 3%.

93

94 Experiments for different reaction temperatures (1075-1475 K) were carried out.
95 Temperature is measured with a thermocouple (type S) with a ± 1.5 K of estimated
96 uncertainty. In the quasi-isothermal reaction zone, the temperature can vary ± 25 K of
97 the desired nominal temperature. Each experiment lasts a total of 3 h, which was set for
98 collecting enough S-PAH and EPA-PAH amounts for their analysis.

99

100 Table 1 shows the conditions for the experiments carried out in the present work. In
101 general, the experimental conditions are based on the conditions of the experiments of
102 pyrolysis done in a previous study [16], in which only the 16 EPA-PAH were quantified
103 using the method proposed by Sánchez et al. [24, 25]. The experiments of the present
104 work were thus planned in order to evaluate the influence of H₂S inlet concentration on
105 PAH formation for a given temperature, and to evaluate the influence of temperature on
106 PAH formation keeping a given inlet H₂S concentration. Experiments 7a and 7b of
107 Table 1 correspond to repeated experiments. Additional information about the analytical
108 method used and the compounds analysed can be found in the supplementary material
109 and in a previous work [11]. The methodology followed has been satisfactorily used in
110 other previous works of the group [23-27]. Error bars included in figures correspond to
111 the standard deviation assumed following previous works of the group [e.g. 10, 11, 16,
112 25], considering that the present work results agree fairly well the experimental results
113 of Viteri et al. [16], and since the repeated experiments of the present work (7a and 7b)
114 do also agree very well.

115

116 **3. Results and discussion**

117 Total EPA-PAH concentrations corresponding to the present study are compared with
118 the Viteri et al. results [16], under similar experimental conditions, in Fig. 2. Viteri et al.
119 did not include the determination of S-PAH and, therefore, those compounds can not be
120 compared, and thus the comparison refers to light gases and EPA-PAH. The results
121 obtained are very similar in all conditions tested and follow the same trend [16].

122

123 The total amount (in mg) of EPA-PAH and S-PAH obtained in the tests performed can
124 be seen in Fig. 3, varying the temperature of reaction (Fig. 3a) and the H₂S

125 concentration fed at 1475 K (Fig. 3b). In every test, the amount of S-PAH is lower than
126 the amount of EPA-PAH, in particular, in the tests done from 1175 to 1375 K. At 1325
127 K, the maximum formation of EPA-PAH is obtained. For S-PAH, maximum formation
128 of these compounds is found at 1375 K. Similar trends were found in the ethylene-SO₂
129 mixtures pyrolysis, but happening at lower temperatures [11].

130

131 At 1475 K, the H₂S conversion obtained by Viteri et al. [16] was 100%, and, even at
132 this temperature, the EPA-PAH amount was higher than that of S-PAH, as it can be
133 seen in Fig. 3b for different inlet H₂S concentrations. When the amount of H₂S fed to
134 the reactor increases, the S-PAH concentration slightly increases, and the EPA-PAH
135 concentration decreases. For EPA-PAH, Ibrahim et al. [17] also observed that the EPA-
136 PAH formation decreased when the concentration of H₂S was increased in the Claus
137 process.

138

139 With the amount of S-PAH and EPA-PAH formed in the ethylene-H₂S mixtures
140 pyrolysis, the mass ratio between S-PAH and EPA-PAH is calculated. Fig. 4 shows the
141 ratio values corresponding to experiments varying the temperature of reaction (Fig. 4a)
142 and the H₂S inlet concentration at 1475 K (Fig. 4b). In Fig. 4a, it can be observed that
143 this ratio presents a minimum with the temperature and it increases with H₂S
144 concentration at the reactor inlet, Fig. 4b. The main difference with the results obtained
145 in the ethylene-SO₂ mixtures pyrolysis is that the S-PAH/EPA-PAH ratio maximum
146 value is obtained at the lowest temperature studied (1075 K) in the ethylene-H₂S
147 mixtures pyrolysis, while with SO₂, it was obtained at the highest temperature
148 considered (1475 K) [11]. This maximum value in the S-PAH/EPA-PAH mass ratio is
149 obtained even with a low H₂S conversion [16]. Comparing these maximum values, the

150 S-PAH/EPA-PAH mass ratio value obtained with H₂S is a 45% higher than the
151 maximum value obtained in the ethylene-SO₂ pyrolysis experiments [11].

152

153 In Fig. 4b, it can be seen that the mass ratio of S-PAH/EPA-PAH increased with the
154 increase of H₂S inlet concentration, which is similar trend compared to that found with
155 the total S-PAH amount formed, see Fig. 3b. In the case of the experiments of ethylene-
156 SO₂ mixtures pyrolysis, the mass ratio of S-PAH/EPA-PAH increased with the increase
157 of the SO₂ fed, but S-PAH amount decreased [11].

158

159 The obtained results for the EPA-PAH and S-PAH amount formed in this work have
160 been compared with those corresponding to the study of the influence of SO₂ on the
161 formation of these products in ethylene pyrolysis [11]. The results of EPA-PAH are
162 shown in Fig. 5a as a function of temperature, and in Fig. 5b as a function of the
163 concentration of either SO₂ or H₂S. The trends are the same using H₂S or SO₂ during
164 ethylene pyrolysis. A maximum in the EPA-PAH amount is obtained with the
165 temperature, although this maximum is lower and shifted to higher temperatures when
166 H₂S is used. The total EPA-PAH amount decreases, in general, with an increase of
167 either the H₂S or SO₂ inlet concentration. This decrease is more significant with SO₂
168 than for H₂S.

169

170 Fig. 6 presents the amount of S-PAH obtained corresponding to this work compared to
171 that obtained in the presence of SO₂ [11], both as a function of the reaction temperature
172 (Fig. 6a) and the H₂S or SO₂ inlet concentration at 1475 K (Fig. 6b). In both cases, the
173 total S-PAH amount presents a maximum with the temperature, Fig. 6a. In the case of
174 H₂S, the total S-PAH amount increases until the maximum value, happening at 1375 K.

175 This fact can be attributed to the H₂S conversion increase, accompanied by the incipient
176 increase in the formation of soot [16]. At temperatures higher than 1375 K, the
177 formation of soot from S-PAH appears to be important, and this soot formation is
178 accompanied by the diminution of the amount of S-PAH.

179

180 Different trends are obtained when analysing the effect of the H₂S or SO₂ inlet
181 concentrations. The S-PAH amount increases with the H₂S concentration, but decreases
182 with the concentration of SO₂, which can be attributed to the oxidizing effect of SO₂
183 compared to H₂S. In general, the values of S-PAH are higher in the presence of H₂S
184 than in the presence of SO₂.

185

186 The yields of different elements (S, C, H) to PAH have also been determined. Figs. 7a
187 and 7b show the sulphur yield obtained in the tests done modifying the temperature and
188 the fed concentration of H₂S or SO₂, respectively. The ratio between sulphur in S-PAH
189 and sulphur in the inlet gas is defined as the sulphur yield to S-PAH (S yield). For the
190 concentration of 1% of H₂S, this yield presents a maximum at 1375 K, in the presence
191 of H₂S, Figure 7a, coinciding with the maximum of S-PAH formation, Fig. 6a. The S
192 yield values corresponding to the presence of H₂S are higher than those obtained with
193 SO₂.

194

195 Although the S-PAH amount increases with the H₂S inlet concentration (Fig. 6b), Fig.
196 7b shows that, when the H₂S inlet concentration increases from 0.3 to 1% of H₂S, the S
197 yield falls from 0.018% to 0.008%. The fact that the amount of soot decreases when the
198 fed H₂S concentration increases can explain the decrease in the S-PAH formed [14],
199 which are adsorbed on the soot. The S-PAH concentration in the soot is approximately

200 constant with the increase of the H₂S fed concentration (not shown), similarly to what
201 occurred for the ethylene-SO₂ mixtures pyrolysis [11]. Therefore, the soot formation
202 decrease is followed by an S-PAH decrease similarly to what is observed for EPA-PAH.
203 If these results are compared with those obtained with SO₂, the S yield is higher in the
204 experiments with H₂S, Fig. 7b, except for the lower concentration of sulphur compound
205 considered, for which the yield attained is higher with SO₂.

206

207 The hydrogen yield to PAH (H yield) and carbon yield to PAH (C yield), considering
208 PAH = EPA-PAH + S-PAH, can be seen in Fig. 8, for the tests done modifying the
209 temperature (Fig. 8a) and the concentration of H₂S fed (Fig. 8b). The C yield is
210 determined as the quotient of C in (EPA-PAH + S-PAH) and C fed. The H yield has
211 been determined as the quotient of H in (EPA-PAH + S-PAH) and H fed. The carbon
212 and hydrogen yields (Fig. 8a) follow the same tendency as that observed for the EPA-
213 PAH amount in Fig. 3, obtaining a maximum for both yields at 1325 K, as it happened
214 with the maximum formation of EPA-PAH. The yield values decrease at higher
215 temperatures according with the increasing transformation of EPA-PAH in soot [16].

216

217 Fig. 8b shows that both hydrogen and carbon yields suffer a slightly decrease with the
218 increase of the fed concentration of H₂S from 0.5 to 1%, similarly to the behaviour of
219 the sulphur yield to S-PAH, Fig. 7b, but much less pronounced. The C and H yields to
220 PAH decrease might be attributed to the soot formation decrease in the ethylene-H₂S
221 mixtures pyrolysis experiments with the increase of the H₂S fed concentration [16], and
222 EPA-PAH and S-PAH are found to be mostly adsorbed in soot (not shown).

223

224 The analysis of the individual total S-PAH formed has also been done in the present
225 work. The individual total S-PAH amount (in mg) and their concentration (in ppmv) can
226 be observed in Figs. 9 and 10, in the tests performed modifying the temperature and the
227 fed concentration of H₂S, respectively. As seen in Fig. 9, only 5 of the 6 S-PAH
228 analysed were detected and quantified. For all the temperatures tested, the majority
229 compound is benzothiophene (BTP), followed by dibenzothiophene (DBTP), i.e., the
230 lightest compounds, while diacenaphtho[1,2-b1',2'-d]thiophene (DACN[1,2-b,1',2']TP)
231 is not detected in any case. The main difference between the different compound results
232 in mass (Fig. 9a) or in concentration (Fig. 9b), is the numeric value, although the
233 relationship between them is not modified.

234

235 The individual total S-PAH amounts and concentrations at 1475 K and for several fed
236 concentration of H₂S can be seen in Fig. 10. An increase in the S-PAH amount occurs
237 when the inlet H₂S concentration increases, except for dibenzothiophene (DBTP),
238 which reaches a maximum for a H₂S inlet concentration of 0.5%. When the H₂S
239 concentration increases in the inlet flow, the sulphur available in the reactor increases as
240 well.

241

242 In a similar way, as for the experiments carried out varying the reactor temperature, the
243 majority S-PAH compound were the lightest compounds: benzothiophene (BTP)
244 followed by dibenzothiophene (DBP). Diacenaphtho[1,2-b1',2'-d]thiophene
245 (DACN[1,2-b,1',2']TP) was not either detected in any case. Also in this case, the main
246 difference between the different compound results in mass (Fig. 10a) or in concentration
247 (Fig. 10b), is the numeric value, although the relationship between them is not modified,
248 similarly to what happens when analysing the effect of temperature.

249

250 **Conclusions**

251 The formation, during the ethylene-H₂S mixtures pyrolysis, of EPA-PAH and S-PAH
252 has been analysed. The ethylene fed concentration was 3% and the fed concentration of
253 H₂S was modified in the range 0.3-1%. The reaction temperature studied was between
254 1075 and 1475 K.

255

256 As main results, it can be said that S-PAH were detected and quantified in all the tests
257 done. Likewise, the EPA-PAH compounds were the majority of the PAH quantified in
258 products of pyrolysis in all tests carried out. The S-PAH/EPA-PAH ratio values showed
259 a minimum at 1175 K that increased with the H₂S inlet concentration. With respect to
260 individual S-PAH, in all cases the majority compound was benzothiophene (BTP)
261 followed by dibenzothiophene (DBP), i.e., the lightest compounds, while
262 diacenaphtho[1,2-*b*1',2'-*d*]thiophene (DACN[1,2-*b*,1',2']TP) was not quantified nor
263 detected in any experiment.

264

265 The sulphur yield to S-PAH presented a maximum at 1375 K, coinciding with the
266 maximum S-PAH formation. In the other hand, when the H₂S inlet concentration
267 increased from 0.3 to 1% of H₂S, the sulphur yield to S-PAH diminished from 0.018%
268 to 0.008%. The fact that increasing the fed H₂S concentration results in a decrease of the
269 amount of soot can explain the decrease in the S-PAH formed.

270

271 The H and C yields to PAH (EPA-PAH + S-PAH) followed the same tendency as that
272 the observed for EPA-PAH, obtaining a maximum in both yields at 1325 K, equal than
273 the maximum EPA-PAH formation. The yield values decreased at higher temperatures,

274 according with the increasing EPA-PAH transformation in soot. Both yields suffered a
275 slightly decrease when the H₂S fed concentration increased, as happened to sulphur
276 yield, but much less pronounced. The C and H yields to PAH decrease might be
277 attributed to the soot formation decrease in the ethylene-H₂S mixtures pyrolysis
278 experiments.

279

280 In summary, the present results indicate the formation of S-PAH, additionally to the
281 formation of oxy-PAH and EPA-PAH, which implies that this should be beard in mind
282 when using fuels containing sulphur species in their composition.

283

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362 reaction temperature. Energy Fuels 2012;26(8):4823-9.

363

364

365

366 **Caption of Tables**

367 **Table 1.** Experimental conditions. Nitrogen is used to close the gas balance.

368

369 **Table 1.** Experimental conditions. Nitrogen is used to close the gas balance.

Set	C ₂ H ₄ (%)	H ₂ S (%)	Temperature (K)	Gas residence time (s)
1	3	0.3	1475	2.83
2	3	0.5	1475	2.83
3	3	1	1075	3.88
4	3	1	1175	3.55
5	3	1	1325	3.19
6	3	1	1375	3.05
7a	3	1	1475	2.83
7b	3	1	1475	2.83

370

371

372 **Caption of Figures**

373 **Fig. 1.** Experimental installation: (1) gas feeding system, (2) reaction system, (3) soot
374 and PAH collecting system, (4) gas analysis system [23].

375

376 **Fig. 2.** Total EPA-PAH formed in the pyrolysis of ethylene-H₂S mixtures for different
377 H₂S inlet concentrations at 1475 K.

378

379 **Fig. 3.** Total PAH (EPA-PAH and S-PAH) amounts from the pyrolysis of ethylene-H₂S
380 mixtures at: (a) 1% H₂S at different reaction temperatures; and (b) 1475 K for different
381 H₂S concentrations.

382

383 **Fig. 4.** Values of the S-PAH/EPA-PAH mass ratio in the pyrolysis of ethylene-H₂S
384 mixtures: (a) with 1% H₂S for different reaction temperatures; and (b) for 1475 K for
385 different H₂S concentrations.

386

387 **Fig. 5.** Total EPA-PAH amount formed in the pyrolysis of ethylene-H₂S or SO₂
388 mixtures: (a) Effect of the temperature, for 1% of either H₂S or SO₂; (b) Effect of the
389 H₂S or SO₂ inlet concentration at 1475 K.

390

391 **Fig. 6.** Total S-PAH amount formed in the pyrolysis of ethylene-H₂S or SO₂ mixtures:
392 (a) Effect of the temperature, for 1% of either H₂S or SO₂; (b) Effect of the H₂S or SO₂
393 inlet concentration at 1475 K.

394

395 **Fig. 7.** Sulphur yield to S-PAH formed in the pyrolysis of ethylene-H₂S: a) 1% of H₂S
396 or SO₂ at different reaction temperatures; and (b) 1475 K for different H₂S or SO₂
397 concentrations.

398

399 **Fig. 8.** Carbon and hydrogen yields to PAH formed in the pyrolysis of ethylene-H₂S
400 mixtures: a) 1% H₂S at different reaction temperatures; and (b) 1475 K for different H₂S
401 concentrations.

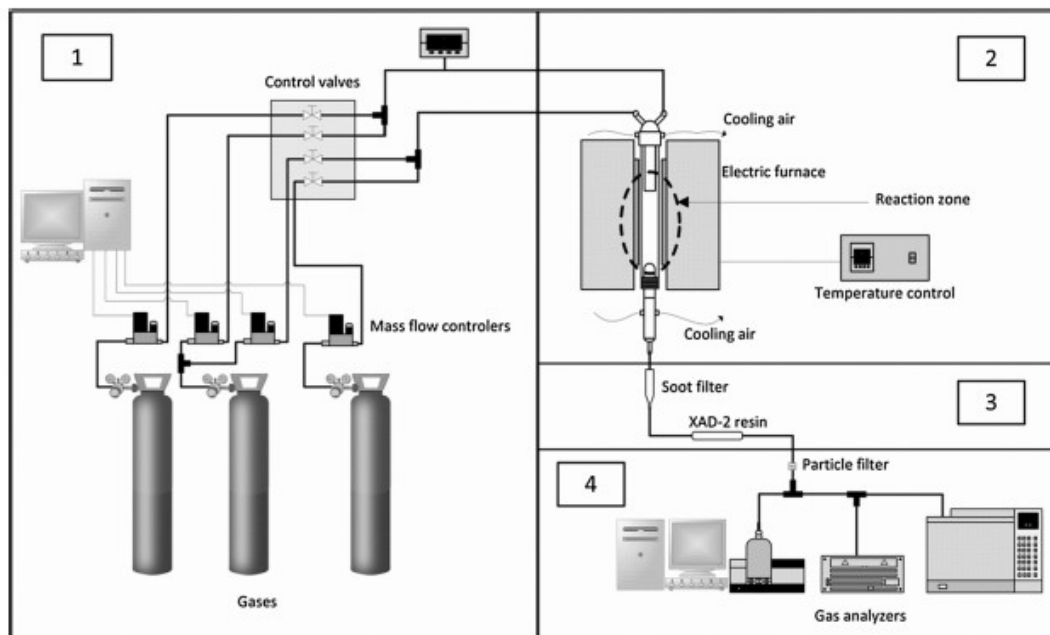
402

403 **Fig. 9.** Individual total S-PAH concentrations from the pyrolysis of ethylene-H₂S at
404 different reaction temperatures: (a) in mg and (b) in ppmv. Sets 3-7 in Table 1.

405

406 **Fig. 10.** Individual total S-PAH concentrations from the pyrolysis of ethylene-H₂S at
407 1475 K for different inlet H₂S concentrations: (a) in mg and (b) in ppmv. Sets 1, 2 and 7
408 in Table 1.

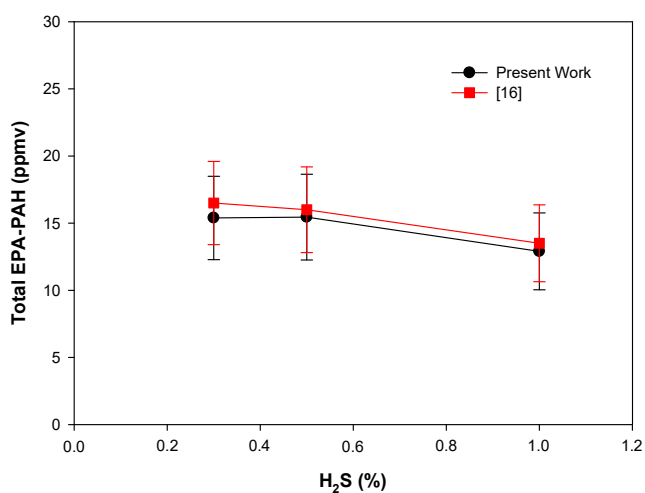
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410

411 **Fig. 1.** Experimental installation: (1) gas feeding system, (2) reaction system, (3) soot
 412 and PAH collecting system, (4) gas analysis system [23].

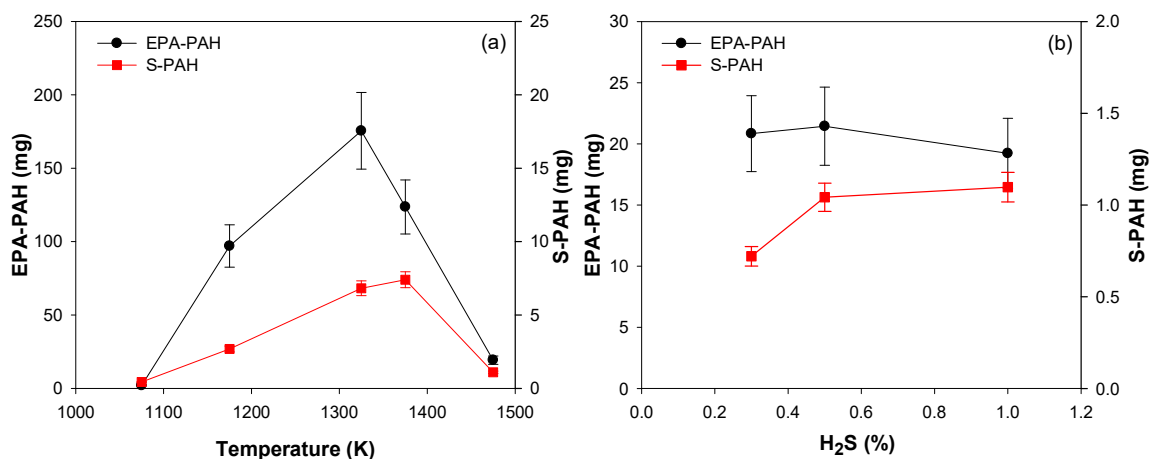
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414

415 **Fig. 2.** Total EPA-PAH formed in the pyrolysis of ethylene-H₂S mixtures for different
 416 H₂S inlet concentrations at 1475 K.

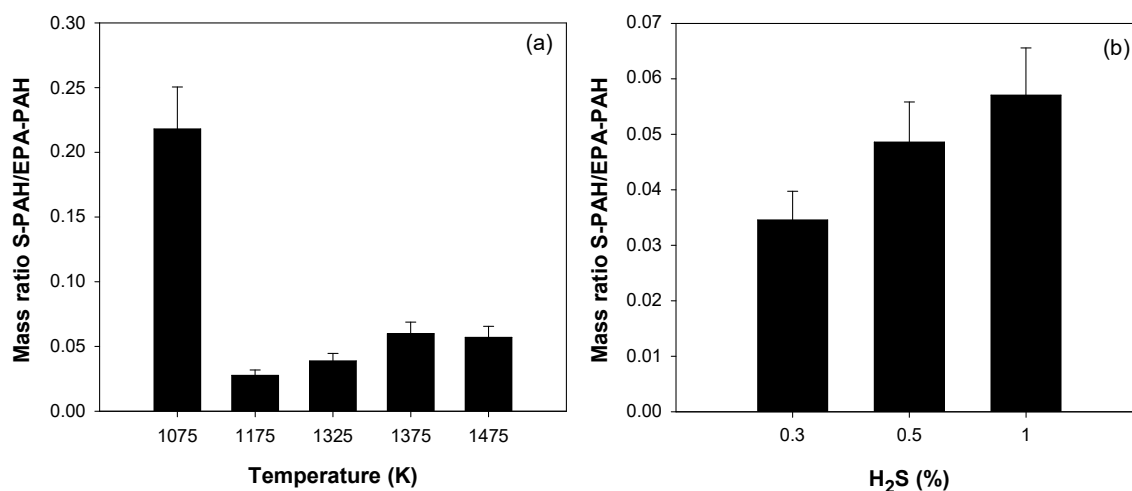
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418

419 **Fig. 3.** Total PAH (EPA-PAH and S-PAH) amounts from the pyrolysis of ethylene-H₂S
 420 mixtures at: (a) 1% H₂S at different reaction temperatures; and (b) 1475 K for different
 421 H₂S concentrations.

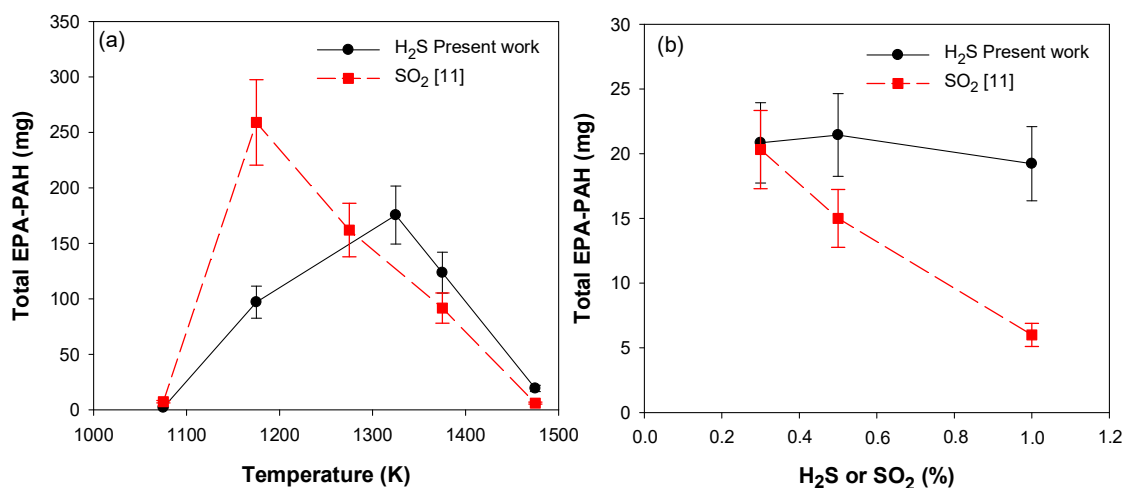
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423

424 **Fig. 4.** Values of the S-PAH/EPA-PAH mass ratio in the pyrolysis of ethylene-H₂S
 425 mixtures: (a) with 1% H₂S for different reaction temperatures; and (b) for 1475 K for
 426 different H₂S concentrations.

427



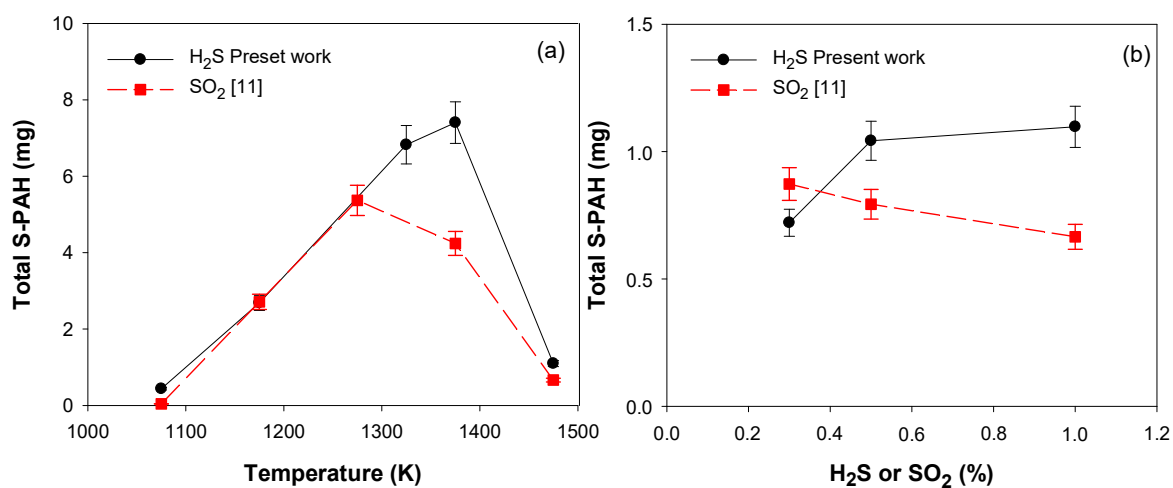
428

429 **Fig. 5.** Total EPA-PAH amount formed in the pyrolysis of ethylene-H₂S or SO₂

430 mixtures: (a) Effect of the temperature, for 1% of either H₂S or SO₂; (b) Effect of the

431 H₂S or SO₂ inlet concentration at 1475 K.

432



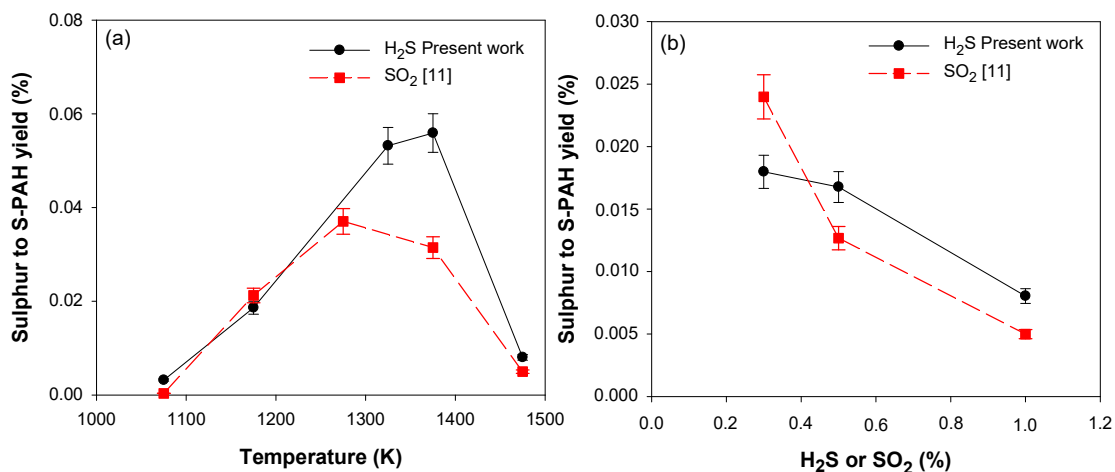
433

434 **Fig. 6.** Total S-PAH amount formed in the pyrolysis of ethylene-H₂S or SO₂ mixtures:

435 (a) Effect of the temperature, for 1% of either H₂S or SO₂; (b) Effect of the H₂S or SO₂

436 inlet concentration at 1475 K.

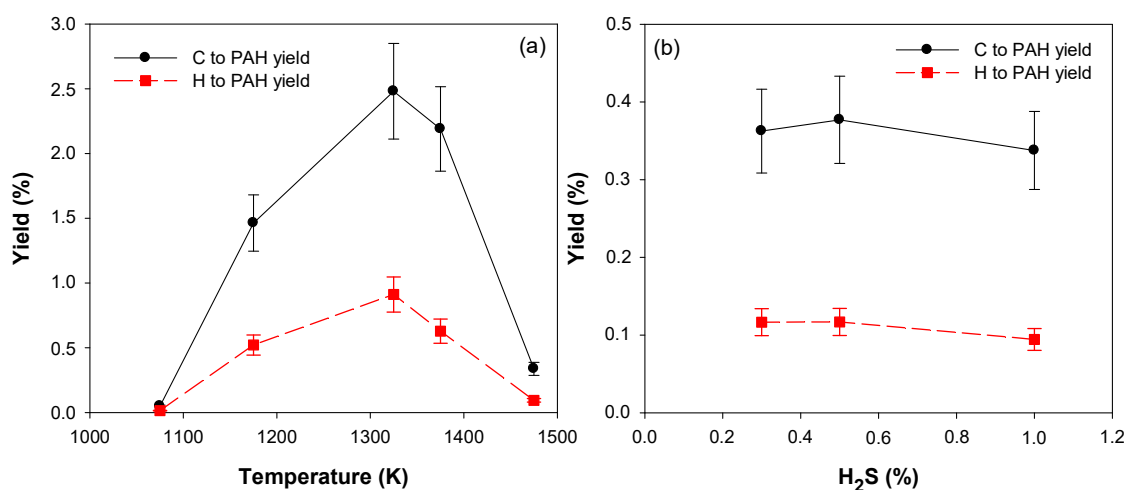
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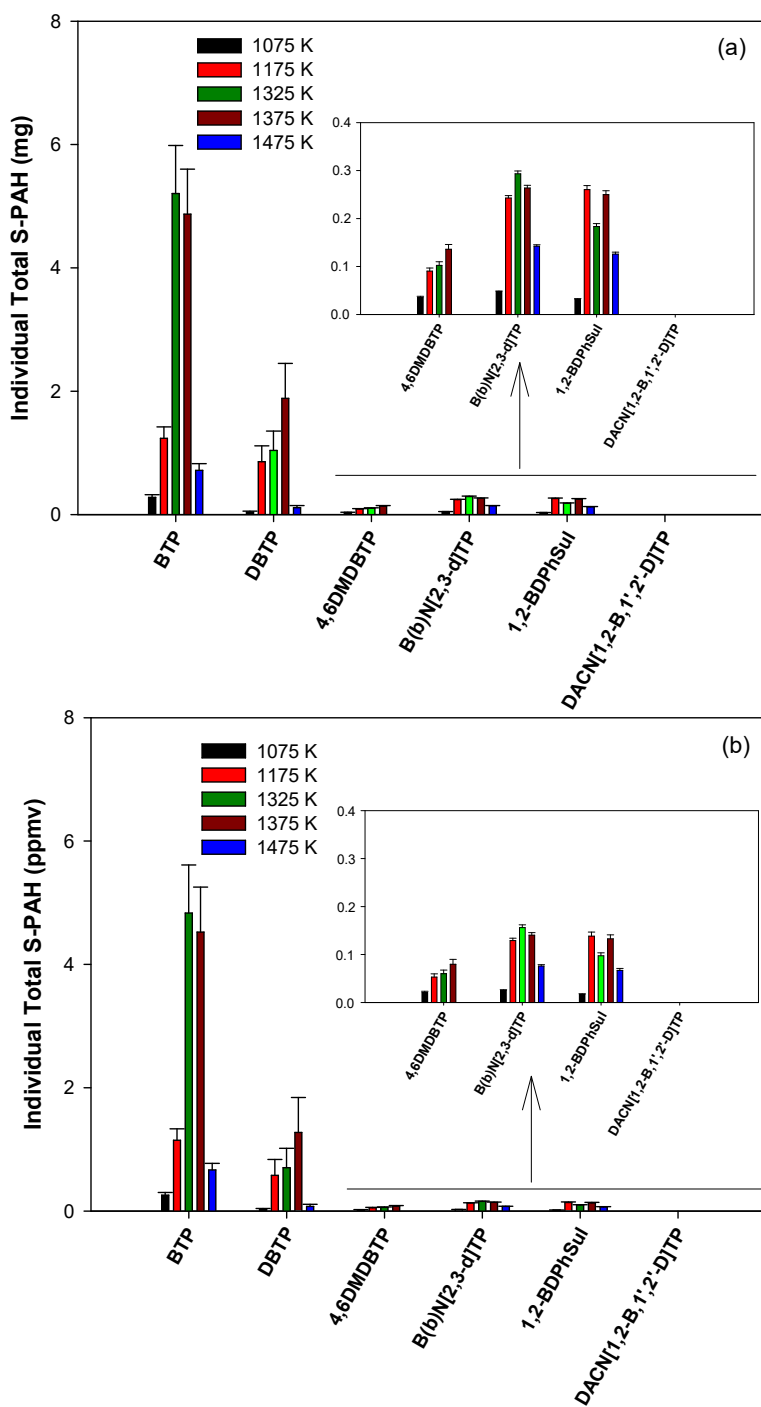
439 **Fig. 7.** Sulphur yield to S-PAH formed in the pyrolysis of ethylene-H₂S:
 440 or SO₂ at different reaction temperatures; and (b) 1475 K for different H₂S or SO₂
 441 concentrations.

442



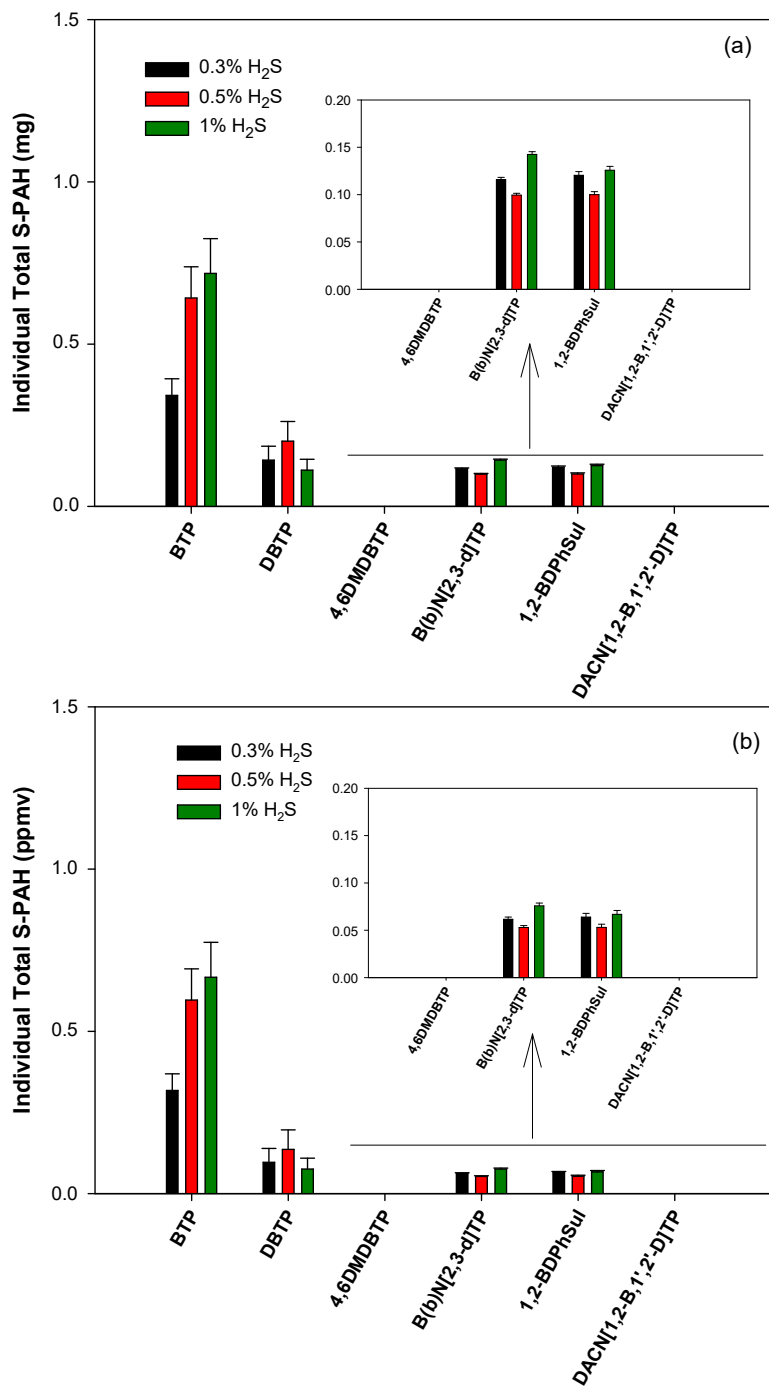
443

444 **Fig. 8.** Carbon and hydrogen yields to PAH formed in the pyrolysis of ethylene-H₂S
 445 mixtures: a) 1% H₂S at different reaction temperatures; and (b) 1475 K for different H₂S
 446 concentrations.



447

448 **Fig. 9.** Individual total S-PAH concentrations from the pyrolysis of ethylene-H₂S at
 449 different reaction temperatures: (a) in mg and (b) in ppmv. Sets 3-7 in Table 1.



450

451 **Fig. 10.** Individual total S-PAH concentrations from the pyrolysis of ethylene-H₂S at

452 1475 K for different inlet H₂S concentrations: (a) in mg and (b) in ppmv. Sets 1, 2 and 7

453 in Table 1.

454

455