

1 **Pollutant emissions during the pyrolysis and combustion of starch/poly(vinyl**
2 **alcohol) biodegradable films**

3 *J. Moltó, B. López-Sánchez, D. Domene-López, A. I. Moreno, R. Font, M. G.*

4 *Montalbán**

5 Chemical Engineering Department, University of Alicante, P.O. Box 99, 03080

6 Alicante, Spain. *Corresponding author: mercedes.garciam@ua.es

7 **Abstract**

8 The massive use of petroleum-based polymers and their improper waste treatment has
9 brought on significant global environmental problems due to their non-biodegradable
10 nature. Starch/poly(vinyl alcohol) (PVA) bioplastics are suitable substitutes for
11 conventional polymers, such as polyethylene, due to their full biodegradability and
12 excellent mechanical properties. Knowledge of the pollutant emissions during pyrolysis
13 and combustion of starch/PVA films is important because they can arrive at landfills
14 mixed with conventional polymers and be thermally degraded in uncontrolled fires. On
15 the other hand, controlled thermal treatments could result in thermal valorization of the
16 waste. Pyrolysis and combustion experiments were carried out at 650, 750, 850 and 950°C
17 in a laboratory furnace. The analysis of carbon oxides, light hydrocarbons, and
18 semivolatile compounds, including polycyclic aromatic hydrocarbons (PAHs), is shown.
19 Experiments showed lower pollutant emissions than those found with conventional
20 polymers, such as polyethylene and polyester, in the same equipment. Nevertheless, the
21 pyrolysis run at 950°C showed the highest light hydrocarbon yield (123013 mg kg⁻¹), but
22 this is considerably lower than the values found for polyethylene. The main semivolatile
23 compounds (not PAHs) emitted, with maximum yields ranging from 1351 to 4694 mg kg⁻¹,
24 were benzaldehyde, phenol, indene, and acetophenone. Specifically, the total

25 semivolatile compounds emitted after pyrolysis and combustion of starch/PVA samples
26 represent only 38 and 50%, respectively, of those emitted with polyethylene. Further, the
27 main PAHs were naphthalene, acenaphthylene, and phenanthrene with maximum values
28 of 4694, 2704 and 1496 mg kg⁻¹, respectively. The PAH yield was considerably higher in
29 experiments with low oxygen content.

30 **Keywords:** starch/PVA films; pyrolysis; combustion; emission; PAHs.

31 **1. Introduction**

32 In the past few years, there has been increasing interest in the removal or minimization
33 of environmental problems caused by non-degradable petroleum-based polymers, such as
34 polyethylene (PE) and polypropylene (PP). They have seriously contributed to pollution
35 and global warming, due to the increased waste disposal and landfilling. Moreover,
36 harmful pollutant emissions, such as polycyclic aromatic hydrocarbons (PAHs), are
37 generated when their residues are burned and incinerated without control (Tak et al.,
38 2019). Recently, in order to reduce the massive consumption of one-use conventional
39 plastics and their impact on the environment, the European Commission has approved
40 Directive 2019/904/EU, which will ban the commercialization of several common single-
41 use plastic products by 2021. During the last few years, great efforts have been
42 concentrated on the replacement of conventional polymers with polymers that are
43 biodegradable and more environmentally friendly, such as starch and its derivatives
44 (polylactic acid, etc.), cellulose, chitosan, alginate, collagen, or lignin (Domene-López et
45 al., 2020). Among the natural biopolymers mentioned, starch is a promising candidate as
46 it is highly available, is inexpensive, has good biocompatibility, and can be readily
47 transformed into thermoplastic starch (TPS) (Domene-López et al., 2019a; Domene-
48 López et al., 2019b). One of the main drawbacks of TPS is its lack of mechanical
49 resistance. For this reason, blending it with other biodegradable compounds, such as

50 poly(vinyl alcohol) (PVA), is a good alternative because of its relatively low cost,
51 suitability for food and medical applications, excellent chemical resistance, and physical
52 and optical properties (Domene-López et al., 2018; Shi et al., 2008; Tak et al., 2019).

53 Currently, disposal of starch/PVA films have received far less attention than their
54 preparation, characterization, or application. It seems clear that, based on its
55 biodegradability, the waste from starch/PVA films is environmentally-friendly, as it can
56 be easily degraded by microorganisms if it is accumulated or composted in landfills
57 (Ishigaki et al., 1999; Tang and Alavi, 2011; Cano et al., 2016). Alternatively, the waste
58 can be dissolved in aqueous medium if released into freshwater streams or oceans
59 (Domene-López et al., 2018). Ideally, waste starch/PVA films are more suitable for
60 composting, landfilling, or recycling than for thermal treatments, pyrolysis and
61 combustion, which could lead to air pollution. However, thermal treatments can be used
62 to produce energy and, hopefully, to obtain thermal valorization of the waste. In order to
63 achieve effective and safe waste-burning, minimizing the emission of harmful pollutants
64 from incomplete combustions is required. In addition, uncontrolled fires in landfills are
65 quite usual and can create a serious hazard for human health and for the environment due
66 to the emission of PAHs (Conesa et al., 2009). Therefore, the evaluation of the possible
67 pollutant emissions associated with thermal treatments of any waste must be determined.
68 PAHs are formed in any thermal process of an organic compound (Font et al., 2003), and
69 they are of special interest due to their carcinogenic nature and toxicity. Studies on the
70 thermal degradation of biopolymers and the formation of air pollutants after their
71 combustion are scarce in the literature. Chien et al. (2010) studied the combustion kinetics
72 and emission factors of the 16 priority PAHs in polylactic acid combustion. To the best
73 of our knowledge, no studies regarding the pollutant emissions produced when
74 starch/PVA films are burnt or incinerated at the end of their life cycle can be found in the

75 literature. However, a high number of papers concerning the analysis of pollutant
76 emissions in the combustion and pyrolysis of conventional plastics, such as PE (Mastral
77 et al., 2002; Wang et al., 2003; Font et al., 2003, 2004), PP (Rotival et al., 1994), or
78 polyvinyl chloride (Wang et al., 2003; Aracil et al., 2005) have been reported.

79 The aim of this work is to study the emission of pollutants from the thermal degradation
80 of starch/PVA biodegradable films under different temperature and atmosphere
81 conditions in a laboratory scale reactor. The analysis, identification, and quantification of
82 gases, volatile compounds, and semivolatile compounds (PAHs and others) have been
83 carried out. Due to the potential for starch/PVA films to replace some conventional
84 plastics, especially PE, the results of the emissions have been compared with those
85 obtained with non-biodegradable materials. Comparison with other wastes of similar
86 oxygen content, such as polyesters, have been also carried out. In order to make an
87 accurate comparison between the emissions originated by the thermal treatments of two
88 different wastes, similar experimental equipment is usually necessary (Moltó et al., 2005).

89 **2. Experimental**

90 *2.1. Materials*

91 Potato starch was provided by Across Organics (Geel, Belgium). PVA (M_w : 125000) was
92 purchased from Sigma-Aldrich (Madrid, Spain), and the plasticizer, glycerol, was
93 supplied by Fisher Chemical (Geel, Belgium). Zinc stearate, which was used as a
94 lubricant, was provided by Sigma-Aldrich (Madrid, Spain). All chemicals were used
95 without further purification.

96 *2.2. Preparation and characterization of the starch/PVA film*

97 The preparation and composition of the starch/PVA film was described in a previous work
98 (Domene-López et al., 2018). Briefly, starch, PVA, water, and glycerol were weighed and

99 manually pre-mixed at room temperature for 3 min. The content of glycerol and water in
100 the sample was fixed at 30 and 20 wt.%, respectively, and the solid materials, starch and
101 PVA, each represented 25 wt.%. A small amount (0.5 wt.% with respect to the above
102 formulation) of zinc stearate was also added to the formulation. Next, the mixture was
103 processed by melt-compounding at 110 °C in a HAAKE™ PolyLab™ QC Modular
104 Torque Rheometer (ThermoFisher Scientific, Waltham, MA, USA) for 25 min at 100
105 rpm. The film was hot pressed into 1 mm thick plates at 160 °C and under a pressure of 6
106 ton for 10 min. Then, the starch/PVA film was cooled under pressure.

107 The water content of the film sample was determined as described by Domene-López et
108 al. (2018) and was found to be 18.03%. The rest of the experiments were carried out with
109 the dried sample, i.e., after drying in an oven for 5 h at 110 °C. Elemental analysis of the
110 starch/PVA film was completed in a FlashEA 1112 Series elemental microanalyzer
111 (Thermo Fisher Scientific, Waltham, MA, USA). Nitrogen and sulfur were not detected,
112 and the oxygen plus ash content was determined from the difference. The amount of ash
113 was also determined by mass loss at 850 °C, following the norm UNE-EN ISO 3451-
114 1:2008 for plastics. A semi-quantitative analysis of other elements was carried out with a
115 PW2400 automatic sequential X-ray fluorescence spectrometer (Philips Co.,
116 Westborough, MA, USA). Table 1 shows the results of these analyses. The net calorific
117 value of the starch/PVA film was determined to be 17177 kJ kg⁻¹ (dry basis) using an AC-
118 350 calorific bomb (Leco Corporation, St. Joseph, MI, USA).

119 **Table 1.** Characterization of the starch/PVA film used (on a dry basis).

wt.%	Starch/PVA film
Elemental analysis ^a	
C	46.9
H	8.4
N	nd

S	nd
O and ash (by difference) ^a	44.7
Ash ^b	0.83
X-ray fluorescence analysis	
Ca	0.035
Si	0.017
Al	0.009
P	0.032
Mg	0.011
Na	0.035
S	0.006
Cl	0.023

nd: not detected

^aObtained by combustion in pure oxygen at 1000 °C.

^bDetermined by norm UNE-EN ISO 3451-1:2008 at 850 °C.

120
121
122
123

2.3. Experimental setup for the pyrolysis and combustion experiments

124
125
126
127
128
129
130
131
132
133
134
135
136
137
138

Pyrolysis and combustion experiments were performed in a horizontal tubular reactor, which has previously been described in detail (Font et al., 2003; Aracil et al., 2005; Moltó et al., 2006; Conesa et al., 2013). Briefly, these experiments used a moving quartz-type reactor (25 mm internal diameter), which is located inside a laboratory furnace with temperature control. A horizontal actuator was employed to introduce the sample, previously placed in a holder, into the system at a constant speed. Four different temperatures (650, 750, 850 and 950 °C) were chosen to conduct these pyrolysis and combustion experiments. During each experiment, once the nominal temperature inside the furnace was reached, 50–200 mg of sample were introduced into the reactor at a speed of 1 mm s⁻¹. Nitrogen (pyrolysis experiments) or synthetic air (combustion experiments) was introduced in parallel with the sample movement at a constant flow of 300 mL min⁻¹ (1 atm, 20 °C). From the gas flow rate, gas residence times were calculated at each temperature: 4.9 s at 650 °C, 4.3 s at 750 °C, 3.8 s at 850 °C and 3.4 s at 950 °C. For each set of experimental conditions, a control run, without a sample (blank), was carried out.

139 In this work, the influence of the presence of oxygen in pollutant emissions was studied
 140 by examining the variation of the oxygen ratio (λ), which is defined as the ratio between
 141 the actual air flow and the stoichiometric air flow necessary to obtain complete
 142 combustion (Soler et al., 2018). λ was calculated using equation (1):

$$143 \quad \lambda = \frac{(m_{air})_{used} \times 23}{(m_{sample}) \times \left(\frac{\%C}{12} + \left(\%H - \frac{\%Cl}{35.5} \right) \times \frac{1}{4} + \frac{\%S}{32} - \frac{\%O}{32} \right) \times 32} \quad (1)$$

144 where m_{air} and m_{sample} are the inlet mass flow of the air and sample, respectively, and
 145 $\%C$, $\%H$, $\%Cl$, $\%S$ and $\%O$ are the mass percentages of carbon, hydrogen, chlorine,
 146 sulfur, and oxygen, respectively, in the sample. In this equation, all the parameters are
 147 known, except m_{sample} . In order to obtain the value of this parameter, we assume that
 148 the mass of the sample, M_{sample} , is introduced in the furnace at a speed, v , of 1 mm s⁻¹
 149 and is uniformly distributed in the sample holder, which has a length, l , of 41 mm. We
 150 also assume the sample is burnt following a fully-defined front and that the reaction is
 151 very fast. With this, m_{sample} can be calculated with equation (2):

$$152 \quad m_{sample} = M_{sample} \times \frac{v}{l} \quad (2)$$

153 Therefore, $\lambda=0$ for pyrolytic processes; $\lambda=1$ for complete combustion processes, i.e.,
 154 when the amount of oxygen present is stoichiometric; and $\lambda>1$ for processes with excess
 155 oxygen. Specifically, in this study, the experiments were carried out at $\lambda=0$ (pyrolysis),
 156 $\lambda=0.2$, and $\lambda=0.6$. λ was varied by changing the feed mass of the film sample and was
 157 calculated with equation (1), in order to study the evolution of volatiles under
 158 substoichiometric oxygen conditions, which can occur in uncontrolled processes.

159 In order to evaluate the reproducibility of the results, some of the pyrolysis and
 160 combustion experiments (with two oxygen ratios: $\lambda=0.2$ and $\lambda=0.6$) at 650, 850 and 950
 161 °C were carried out in duplicate (9 runs were duplicated in total). A standard deviation of

162 15% (or below) with respect to the mean concentration values was obtained for the
163 different compounds analyzed.

164 *2.4. Analytical procedure*

165 The compounds leaving the reactor were sampled to analyze the gases, volatile
166 compounds, and semivolatile compounds emitted, focusing especially on the formation
167 of the 16 U.S. Environmental Protection Agency (EPA) priority PAHs (US EPA, 1998)
168 during the starch/PVA film pyrolysis or combustion.

169 *2.4.1. Gases and volatile compounds*

170 After collecting the exit gas for 3 min using Tedlar® bags (Restek, Bellefonte, USA), the
171 gases and volatile compounds were analyzed. Concentrations of CO₂ and CO were
172 determined by gas chromatography with a thermal conductivity detector (GC-TCD,
173 Agilent 7820A GC) and two packed columns from Teknocroma (Barcelona, Spain), Haye
174 Sep Q80/100 and Molecular Sieve 5A 80/100, which were both coupled with a pneumatic
175 valve. The rest of volatile compounds, mainly light hydrocarbons, were analyzed by gas
176 chromatography with a flame ionization detector (GC-FID, Shimadzu GC-17A) using an
177 Alumina KCl Plot capillary column (Sigma Aldrich, Missouri, USA). The identification
178 and quantification of gases and volatile compounds was performed by external standard
179 calibration. Different gas standards containing known amounts of aliphatic hydrocarbons
180 C₁-C₇ and benzene, toluene and xylenes together with CO₂ and CO, were used to calibrate
181 the gas chromatographs. With the calibration, the retention time and the response factor
182 of each compound are determined. After the experiments, the identification of a
183 compound in the sample was carried out by comparison with its retention time in the
184 calibration curve and its quantification is obtained from its peak area in the chromatogram
185 and response factor.

186

2.4.2. Semivolatile compounds

187 In each experiment, for the analysis of semivolatile compounds, including PAHs, the
188 outlet gas stream was collected in a polyaromatic Amberlite® XAD-2 resin (Supelco,
189 Bellefonte, USA), located at the exit of the furnace, for 10 min. The Tedlar® bag, for the
190 collection of gases and volatile compounds, was placed after this resin. A solution of
191 deuterated internal standards (Standard Mix 26) in dichloromethane was provided by Dr.
192 Ehrenstorfer-Schäfers (Augsburg, Germany) and used to calculate the concentration of
193 PAHs in the samples. The standards were added to the resin before the solid-liquid
194 extraction. The extraction of the resin was performed using an Accelerated Solvent
195 Extraction (ASE-100 Dionex-Thermo Fisher Scientific, California, USA), following the
196 U.S. EPA 3545A method (EPA, 2007a). The resin was extracted with a mixture of
197 dichloromethane/acetone (1:1 v/v). After the extraction, the sample was concentrated to
198 approximately 1.5 mL, and a recovery standard (anthracene-d₁₀ from AccuStandard Inc.,
199 USA) was added. The sample was analyzed by gas chromatography (model 6890N,
200 Agilent, California, USA) coupled with a mass spectrometer (model 5976N, Agilent,
201 California, USA) with an Agilent HP5-MS (30 m x 0.25 mm i.d. x 0.25 µm) in the SCAN
202 mode (35-550 uma). The injection volume was 1 µL with a split of 1:25, and the He flow
203 was 1 mL min⁻¹. The oven temperature program consisted of an isothermal step at 40 °C
204 (5 min hold), a heating step up to 290 °C at 12 °C/min (6 min hold), and, then, a heating
205 step up to 320 °C at 20 °C min⁻¹ (10 min hold). The identification and quantification of
206 the PAHs was performed with a standard of each compound and using the peak area of
207 the corresponding primary ion, following the U.S. EPA 8270D method (EPA, 2007b).
208 Other semivolatile compounds were identified by comparing results with the NIST mass
209 spectral database and interpolating between the calculated response factors (mass/area
210 ratio) from the two nearest deuterated standards for semi-quantification.

211 During all the experimental processes, i.e., sampling, extraction, concentration and
212 analysis, the samples were protected from light with aluminum foil to avoid degradation
213 of the studied compounds.

214 *2.5. Statistical analysis*

215 As stated before, data of some analysis were presented as mean \pm standard deviation,
216 calculated from two independent experiments by using GraphPad Prism 8.0.1 software
217 (GraphPad Software, San Diego, CA, USA). In these cases, and, as normality
218 (Kolmogorov-Smirnov, $p > 0.05$) and homoscedasticity (Levene, $p > 0.05$) were met, the
219 statistical significance was determined using analysis of variance (one-way ANOVA) and
220 the parametric test of Tukey ($p < 0.05$).

221 **3. Results and discussion**

222 *3.1. Gases and volatile compounds*

223 Table 2 shows the analysis of the gases and volatile compounds emitted during pyrolysis
224 and combustion of the starch/PVA films at the four temperatures (650, 750, 850 and 950
225 °C). For the duplicate pyrolysis and combustion runs, the standard deviations can be also
226 observed. CO and CO₂ were the most abundant gaseous compounds in all the
227 experiments, with the CO₂ yields being higher than the CO yields in the combustion
228 experiments. This is due to an increased oxygen content in the atmosphere, i.e., an
229 increase of λ , which intensifies the film combustion. However, under inert atmosphere,
230 the CO yields were the highest. CO and CO₂ emissions detected in the pyrolysis
231 experiments were due to the oxygen content of the polymeric film. Similar results have
232 been found, using the same equipment, for other residues containing biomass (Soler et
233 al., 2018).

234 Aliphatic (C₁ to C₇ chains) and aromatic (benzene, toluene, and xylenes) hydrocarbons
235 were identified in the emissions. In general terms, the most abundant light hydrocarbons
236 (see Table 2) were methane, ethane, 2-butyne, benzene, and toluene, though methane was
237 the primary hydrocarbon in all runs. We found that the proportion of light hydrocarbons
238 in the emissions was considerably higher in the pyrolysis experiments than in the
239 combustion experiments. This is due to the presence of oxygen in the atmosphere in the
240 combustion runs, contributing to the oxidation of the light hydrocarbons and giving
241 higher CO₂ yields. Similar results have been found in previous works with other materials
242 (Ortuño et al., 2014a, 2014b; Soler et al., 2018). Combustion runs with $\lambda=0.6$ showed the
243 lowest values of light hydrocarbons.

244 The presence of oxygen during the experiments had two opposite effects. On the one
245 hand, oxygen favors the formation of free radicals, which leads to higher reaction rates
246 and, therefore, an increase in the light hydrocarbon yield. On the other hand, oxygen also
247 has an effect on oxidative destruction of the hydrocarbons, leading to a decrease in their
248 yields. At low temperatures, the first effect prevails, while, at high temperatures, the
249 second effect is more important (Font et al., 2003; Aracil et al., 2005). Consistent with
250 this, we observed the expected behavior. In general terms, as seen in Table 2, a higher
251 content of light hydrocarbons was found at lower temperatures, being even negligible in
252 some cases from 850–950 °C. The highest light hydrocarbon yield, 123013 mg kg⁻¹, was
253 found for the pyrolysis run performed at 950 °C.

254 **Table 2.** Yields of gases and volatile compounds during thermal decomposition of starch/PVA films (mg kg sample⁻¹). Mean values ± standard
 255 deviation of the measurements of the duplicated experiments are shown.

Experiment	Pyrolysis ($\lambda=0$)				$\lambda=0.2$				$\lambda=0.6$			
	650 °C	750 °C	850 °C	950 °C	650 °C	750 °C	850 °C	950 °C	650 °C	750 °C	850 °C	950 °C
<i>Carbon oxides</i>												
CO ₂	59946		77886		636393		734565	699361	1381207		1831959	
	± 1128 ^a	74635	± 1346 ^a	75595 ± 1277 ^a	± 10589 ^b	691034	± 10685 ^c	± 6726 ^c	± 14126 ^d	1678933	± 23869 ^e	1654474 ± 19651 ^f
CO	100179		302657		172947		218987	234129				
	± 2045 ^a	251711	± 7175 ^b	284401 ± 5574 ^b	± 3412 ^c	209870	± 5975 ^d	± 6961 ^d	89258 ± 2352 ^a	72427	63800 ± 1659 ^e	49020 ± 1396 ^e
CO/(CO+CO ₂)	0.626	0.771	0.795	0.790	0.214	0.233	0.230	0.251	0.061	0.041	0.034	0.029
<i>Light hydrocarbons</i>												
Methane	16089		79576		82294 ± 18164		43233	43738				
	± 3464 ^a	63221	± 1654 ^b	82294 ± 975 ^b	± 401 ^a	34651	± 1671 ^c	± 1864 ^c	5591 ± 269 ^d	17367	5472 ± 198 ^d	32668 ± 1524 ^e
Ethane	3517 ± 244 ^a	8157	nd	nd	3535 ± 136 ^a	4243	2419 ± 189 ^b	nd	1183 ± 89 ^c	nd	nd	nd
Ethylene	166 ± 12 ^a	578	652 ± 45 ^b	538 ± 31 ^c	207 ± 18 ^{ad}	357	405 ± 21 ^e	291 ± 16 ^d	81 ± 9 ^{af}	177	43 ± 5 ^f	214 ± 17 ^{ad}
Propane	743 ± 67 ^a	999	245 ± 15 ^b	14 ± 2 ^c	655 ± 41 ^a	557	111 ± 9 ^c	nd	275 ± 17 ^b	97	nd	nd
Propylene	158 ± 17 ^a	192	59 ± 6 ^b	8 ± 1 ^c	100 ± 12 ^d	98	32 ± 4 ^{bc}	4	23 ± 2 ^c	13	1	2
Acetylene	34 ± 4 ^a	5971	9968 ± 695 ^b	14666 ± 1521 ^c	5528 ± 391 ^d	6731	9054 ± 599 ^b	15119 ± 988 ^c	nd	nd	nd	nd
<i>trans</i> -2-Butene	7009 ± 467 ^a	5674	nd	20 ± 2 ^b	4947 ± 277 ^c	nd	nd	nd	nd	nd	nd	nd
Isobutene	505 ± 31 ^a	nd	181 ± 19 ^b	nd	356 ± 21 ^c	1319	nd	12 ± 1 ^d	464 ± 25 ^a	118	nd	nd
<i>cis</i> -2-Butene	555 ± 54 ^a	744	144 ± 9 ^b	6 ± 0.8 ^c	358 ± 19 ^d	385	nd	nd	76 ± 6 ^{bc}	35	nd	nd
Isopentane	nd	16	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd

<i>n</i> -Pentane	28 ± 4	nd	nd	nd	21 ± 3	9	nd	nd	nd	nd	nd	nd
Propyne	243 ± 16 ^a	179	43 ± 5 ^b	16 ± 2 ^b	177 ± 15 ^c	114	nd	nd	102 ± 7 ^d	nd	nd	nd
1-Pentene	9 ± 1	1	nd	nd	5	1	nd	nd	1	nd	nd	nd
2-Butyne	1372 ± 125 ^a	573	781 ± 53 ^b	1047 ± 61 ^c	666 ± 31 ^b	579	649 ± 77 ^b	677 ± 36 ^b	153 ± 14 ^d	236	127 ± 15 ^d	833 ± 61 ^{bc}
1-Butyne	162 ± 11 ^a	118	16 ± 1 ^b	nd	116 ± 15 ^c	63	nd	nd	nd	nd	nd	nd
<i>n</i> -Hexane	2798 ± 213 ^a	5140	2886 ± 115 ^a	481 ± 30 ^b	2143 ± 172 ^c	nd	1449 ± 118 ^d	339 ± 27 ^{be}	25 ± 2 ^e	128	nd	212 ± 14 ^{be}
1-Hexene	2	nd	nd	nd	2	nd	nd	nd	nd	nd	nd	nd
cis-2-Hexene	143 ± 12 ^a	26	nd	nd	85 ± 10 ^b	nd	nd	nd	27 ± 1 ^c	nd	nd	nd
<i>n</i> -Heptane	501 ± 35 ^a	621	60 ± 4 ^b	nd	471 ± 33 ^a	392	nd	nd	nd	nd	nd	nd
Benzene	3195 ± 248 ^a	11044	17246 ± 426 ^b	20718 ± 1125 ^c	4695 ± 320 ^a	9312	12606 ± 641 ^d	14724 ± 1158 ^{bd}	2150 ± 207 ^a	7073	2163 ± 188 ^a	13007 ± 680 ^d
1-Heptene	2	nd	nd	nd	1	nd	nd	nd	nd	nd	nd	nd
Isooctane	115 ± 10 ^a	100	31 ± 2 ^b	nd	97 ± 11 ^a	nd	nd	nd	nd	nd	nd	nd
Toluene	3854 ± 198 ^{ac}	10233	9760 ± 713 ^b	3176 ± 121 ^{ac}	4332 ± 148 ^c	7316	7498 ± 653 ^d	2707 ± 98 ^{ae}	1387 ± 75 ^{ef}	2257	354 ± 20 ^f	1390 ± 105 ^{ef}
Xylene (<i>p</i> -, <i>m</i> -, <i>o</i> -)	636 ± 61 ^a	2208	1158 ± 81 ^b	29 ± 4 ^c	742 ± 61 ^a	925	423 ± 31 ^d	34 ± 4 ^c	320 ± 28 ^d	13740	nd	nd
Total light hydrocarbons	41836	115795	122806	123013	47403	67052	77879	77645	11858	41241	8160	48326

256 nd: not detected or lower than detection limit (<1 mg kg sample⁻¹). ^{a,b,c,d,e,f} Means within each row with different letters are significantly different
257 (*p*<0.05), Tukey's test.

258

259 *3.2. Semivolatile compounds and PAHs*

260 The yields of the semivolatile compounds, including the 16 PAHs emitted during the
261 pyrolysis and combustion experiments, are reported in Table 3. For the duplicate
262 pyrolysis and combustion runs, the standard deviations have been also reported. The
263 semivolatile compounds identified can be classified in four groups:

264 i) Linear aliphatic hydrocarbons, such as undecane, dodecane, and tetradecane and its
265 derivatives.

266 ii) Substituted monoaromatic compounds, such as 1-ethenyl-3-methylbenzene and 1-
267 ethenyl-4-methylbenzene.

268 iii) Partially oxygenated compounds, such as benzaldehyde and acetophenone, and
269 aromatic alcohols, such as phenol and 2-methylphenol.

270 iv) PAHs with two to six aromatic rings, which are naphthalene, acenaphthylene,
271 acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene,
272 benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene,
273 benzo(a)pyrene, indeno(1,2,3-cd)pyrene, dibenz(a,h)anthracene, and
274 benzo(g,h,i)perylene.

275 As can be seen in Table 3, the main semivolatile compounds (not PAHs) emitted, with
276 maximum yields ranging from 1351 to 4694 mg kg⁻¹, are benzaldehyde, phenol, indene,
277 and acetophenone. The most abundant PAHs in all runs include naphthalene,
278 acenaphthylene, and phenanthrene. The yield of PAHs can also be observed in Figure 1.
279 As seen in previous studies, naphthalene is the most abundant PAH formed in the thermal
280 degradation of different materials (Ortuño et al., 2014a, 2014b; Soler et al., 2018). This

281 is because naphthalene is the PAH with the lowest boiling point and highest stability
282 (Chien et al., 2010). The formation of PAHs is considerably higher in runs with low
283 oxygen content (pyrolysis and combustion at $\lambda=0.2$) than in the combustion runs with
284 higher oxygen content ($\lambda=0.6$), as expected. Afterall, it is widely known that pyrolytic
285 processes are the primary sources of PAH emissions (Thomas et al., 2007). As seen in
286 Table 3, the maximum formation of the 16 PAHs occurs in the pyrolysis run at the highest
287 temperature (950 °C), with a value of 13560 mg kg⁻¹. This trend was previously identified
288 for other samples analyzed with the same equipment (Ortuño et al., 2014a, 2014b). No
289 data were found in the literature regarding yields obtained for PAHs in the thermal
290 decomposition of starch or starch/PVA films.

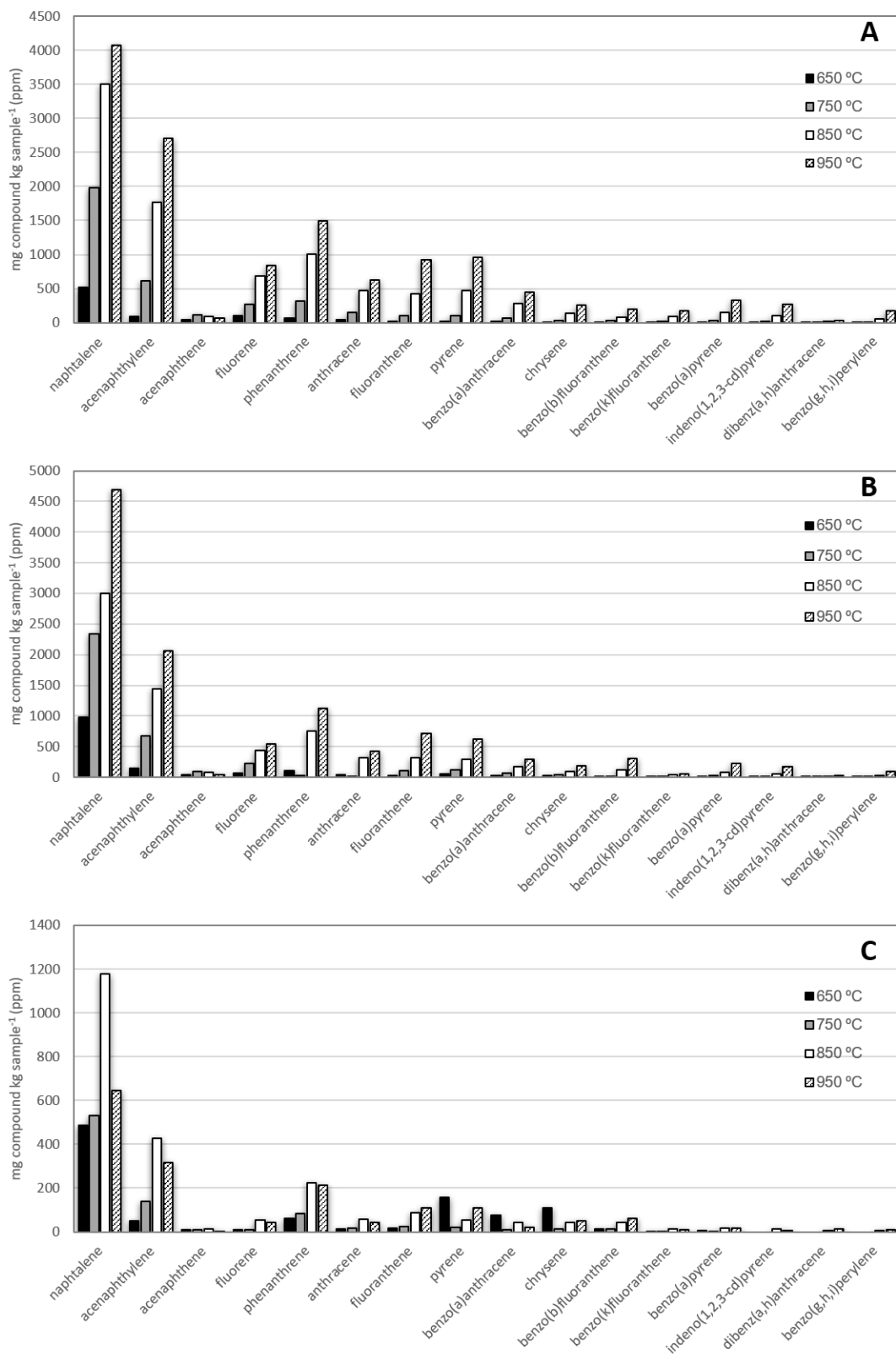
291 **Table 3.** Yields of semivolatile and PAH (italicized) compounds during thermal decomposition of starch/PVA films (mg kg sample⁻¹). Mean values
 292 ± standard deviations of the measurements of the duplicated experiments are shown.

Experiment	Pyrolysis ($\lambda=0$)			$\lambda=0.2$				$\lambda=0.6$				
	650 °C	750 °C	850 °C	950 °C	650 °C	750 °C	850 °C	950 °C	650 °C	750 °C	850 °C	950 °C
Benzaldehyde ^b	1090 ± 35 ^a	459	78 ± 5 ^{bc}	47 ± 4 ^c	1088 ± 37 ^a	2299	157 ± 12 ^b	80 ± 7 ^{bc}	1429 ± 39 ^d	621	801 ± 32 ^e	381 ± 17 ^f
Phenol ^b	375 ± 17 ^a	38	550 ± 20 ^b	24 ± 2 ^c	742 ± 21 ^d	3829	40 ± 3 ^c	nd	615 ± 19 ^e	199	341 ± 17 ^a	nd
1-Ethenyl-3-Methylbenzene ^d	nd	736	nd	nd	523 ± 25	3381	nd	nd	62 ± 5	nd	nd	nd
Benzofuran ^d	nd	nd	482 ± 21 ^a	86 ± 5 ^b	nd	nd	514 ± 22 ^a	112 ± 9 ^b	360 ± 13 ^c	153	112 ± 13 ^b	nd
Indene ^b	608 ± 23 ^a	1352	117 ± 9 ^b	1428 ± 32 ^c	607 ± 19 ^a	1775	1680 ± 37 ^d	997 ± 25 ^e	78 ± 6 ^b	nd	nd	nd
1-Ethenyl-4-Methylbenzene ^d	nd	nd	nd	nd	nd	nd	nd	nd	nd	40	91 ± 9	69 ± 8
2-Methylphenol ^c	232 ± 13 ^a	346	47 ± 5 ^b	nd	304 ± 17 ^c	539	52 ± 4 ^b	nd	nd	nd	nd	nd
Undecane ^d	nd	nd	nd	nd	nd	nd	nd	nd	73 ± 5	26	nd	49 ± 5
Acetophenone ^b	1075 ± 41 ^a	819	74 ± 7 ^b	nd	1144 ± 39 ^a	1351	121 ± 12 ^b	nd	325 ± 12 ^c	56	nd	nd
1-Methyl-1H-indene ^d	522 ± 25	nd	nd	nd	nd	893	nd	nd	nd	nd	nd	nd
2-Methylindene ^b	401 ± 19 ^a	592	116 ± 9 ^b	2	466 ± 17 ^c	nd	123 ± 10 ^b	nd	nd	nd	nd	nd
<i>Naphtalene</i> ^a	520 ± 27 ^a	1976	3506 ± 102 ^b	4072 ± 113 ^c	978 ± 31 ^d	2336	3005 ± 97 ^e	4694 ± 125 ^f	485 ± 20 ^a	532	1178 ± 29 ^d	646 ± 31 ^a
4-Methyl-3-Heptanol ^d	nd	nd	nd	nd	nd	nd	nd	nd	83 ± 7	45	nd	50 ± 5
Dodecane ^d	nd	nd	nd	4	nd	nd	nd	nd	18 ± 2	9	nd	23 ± 3
Ethylamine Morpholine ^d	nd	nd	nd	nd	nd	nd	nd	nd	nd	90	184 ± 15	nd
1-Methylnaphtalene ^b	229 ± 11 ^a	701	850 ± 31 ^b	338 ± 15 ^c	302 ± 16 ^{cd}	644	636 ± 27 ^e	231 ± 12 ^{ad}	67 ± 4 ^f	46	122 ± 14 ^f	nd

2-Methylnaphtalene ^b	218 ± 10 ^{ac}	576	590 ± 21 ^b	222 ± 17 ^{ac}	278 ± 19 ^c	545	486 ± 22 ^d	160 ± 15 ^a	61 ± 5 ^e	38	87 ± 9 ^e	nd
2,6,11-Trimethyldodecane ^d	nd	nd	nd	nd	nd	nd	nd	nd	49 ± 3	nd	nd	51 ± 4
Tetradecane ^c	nd	nd	nd	8 ± 1 ^a	nd	nd	nd	10 ± 1 ^a	46 ± 3 ^b	2	nd	44 ± 3 ^b
Biphenyl ^b	101 ± 9 ^{ac}	226	448 ± 19 ^b	455 ± 19 ^b	131 ± 14 ^c	282	27 ± 2 ^d	437 ± 18 ^b	61 ± 4 ^{ad}	55	183 ± 15 ^c	49 ± 5 ^{ad}
2-Vinylnaphtalene ^b	79 ± 7 ^a	320	82 ± 7 ^a	385 ± 23 ^b	nd	339	365 ± 17 ^b	280 ± 16 ^c	nd	nd	nd	nd
Acenaphthylene ^a	95 ± 8 ^{af}	616	1765 ± 99 ^b	2704 ± 112 ^c	141 ± 15 ^a	676	1436 ± 75 ^d	2066 ± 102 ^e	50 ± 3 ^f	138	428 ± 20 ^g	315 ± 19 ^{ag}
Acenaphthene ^a	46 ± 5 ^a	113	92 ± 5 ^b	67 ± 4 ^c	41 ± 4 ^a	95	79 ± 5 ^{bc}	44 ± 5 ^a	11 ± 1 ^d	9	13 ± 1 ^d	3
Dibenzofuran ^b	44 ± 4 ^{ae}	nd	44 ± 3 ^{ae}	49 ± 2 ^{ace}	86 ± 7 ^b	31	61 ± 4 ^{cde}	45 ± 3 ^{ae}	64 ± 3 ^{de}	43	57 ± 2 ^e	44 ± 3 ^{ae}
Fluorene ^a	98 ± 8 ^a	275	681 ± 27 ^b	834 ± 31 ^c	73 ± 5 ^a	230	440 ± 13 ^d	537 ± 22 ^e	9 ± 1 ^f	8	54 ± 2 ^{af}	42 ± 4 ^{af}
Diethyl phthalate ^d	nd	nd	nd	nd	nd	nd	nd	nd	34 ± 2	16	25 ± 1	nd
Benzophenone ^d	140 ± 11 ^a	130	nd	nd	126 ± 11 ^a	103	nd	nd	21 ± 2 ^b	6	nd	nd
1-Chlorotetradecane ^d	nd	nd	nd	nd	nd	nd	nd	nd	34 ± 3	16	25 ± 2	nd
Phenanthrene ^a	65 ± 6 ^a	316	1001 ± 31 ^b	1496 ± 45 ^c	102 ± 10 ^a	24	755 ± 28 ^d	1128 ± 35 ^e	62 ± 5 ^a	85	223 ± 16 ^f	214 ± 11 ^f
Anthracene ^a	42 ± 5 ^a	151	475 ± 23 ^b	625 ± 24 ^c	45 ± 3 ^a	9	324 ± 11 ^d	428 ± 16 ^b	15 ± 2 ^a	18	57 ± 4 ^a	43 ± 5 ^a
6H-Cyclobuta(jk)phenanthrene ^d	nd	nd	nd	nd	nd	nd	nd	168 ± 11	nd	nd	nd	13 ± 1
4H-Cyclopenta(def)phenanthrene ^c	nd	nd	281 ± 13 ^a	271 ± 11 ^a	nd	54	171 ± 9 ^b	nd	nd	nd	nd	nd
2-Phenylnaphtalene ^b	nd	75	187 ± 11 ^a	182 ± 9 ^a	40 ± 2 ^b	79	141 ± 8 ^c	131 ± 12 ^c	nd	10	24 ± 3 ^b	5
Fluoranthene ^a	18 ± 2 ^a	103	428 ± 22 ^b	926 ± 31 ^c	31 ± 2 ^{af}	111	316 ± 10 ^d	712 ± 23 ^e	17 ± 2 ^a	26	87 ± 8 ^{fg}	108 ± 9 ^g
Pyrene ^a	19 ± 2 ^a	106	476 ± 20 ^b	960 ± 35 ^c	53 ± 5 ^{ag}	116	296 ± 9 ^d	622 ± 19 ^e	158 ± 14 ^{fg}	22	55 ± 6 ^{ag}	108 ± 7 ^g
Benzo(a)anthracene ^a	16 ± 1 ^a	66	277 ± 14 ^b	445 ± 23 ^c	33 ± 2 ^{ae}	73	168 ± 11 ^d	293 ± 15 ^b	75 ± 6 ^c	10	42 ± 5 ^{ae}	21 ± 2 ^a
Triethylene glycol monododecyl ether ^d	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	467 ± 23	nd

<i>Chrysene</i> ^a	8 ± 1 ^a	32	140 ± 10 ^b	257 ± 17 ^c	22 ± 1 ^{ag}	39	92 ± 7 ^d	181 ± 11 ^e	108 ± 10 ^{bd}	15	44 ± 4 ^g	49 ± 4 ^g
<i>Benzo(b)fluoranthene</i> ^a	9 ± 1 ^a	35	77 ± 8 ^b	198 ± 13 ^c	4	20	122 ± 8 ^d	302 ± 16 ^e	12 ± 1 ^a	13	41 ± 3 ^{af}	62 ± 5 ^{bf}
<i>Benzo(k)fluoranthene</i> ^a	6	16	93 ± 5 ^a	179 ± 15 ^b	5	21	40 ± 5 ^{cd}	60 ± 5 ^c	4	3	12 ± 1 ^{de}	9 ± 1 ^e
<i>Benzo(a)pyrene</i> ^a	7 ± 1 ^a	27	151 ± 11 ^b	329 ± 16 ^c	7 ± 1 ^a	31	85 ± 7 ^d	223 ± 13 ^e	6	4	16 ± 2 ^a	16 ± 2 ^a
<i>Indeno(1,2,3-cd)pyrene</i> ^a	3	20	99 ± 7 ^a	267 ± 21 ^b	11 ± 1 ^c	21	57 ± 6 ^d	174 ± 11 ^e	nd	nd	15 ± 1 ^c	5
<i>Dibenz(a,h)anthracene</i> ^a	2	5	17 ± 2 ^a	27 ± 2 ^b	1	5	9 ± 1 ^c	23 ± 2 ^{ab}	nd	nd	5	13 ± 1 ^{ac}
<i>Benzo(g,h,i)perylene</i> ^a	2	11 ± 1 ^a	58 ± 5 ^b	174 ± 15 ^c	3	11	28 ± 3 ^{ab}	100 ± 9 ^d	nd	nd	6	10 ± 1 ^a
Total PAHs	956	3868	9336	13560	1550	3818	7252	11587	1012	883	2276	1664
Total semivolatile compounds	6070	10238	13282	17061	7387	19962	11826	14238	4492	2354	4795	2442

293 nd: not detected or lower than detection limit (<1 mg kg sample⁻¹). ^aAuthentic quantitative standard. ^bForward values (forward value = 100 × [$\sum(I_{LIB}$
294 × $I_{UKN})^{1/2}$]²/ $\sum I_{LIB}$ × $\sum I_{UKN}$; I_{LIB} is the intensity of the spectrum of the proposed compound at a given mass; I_{UKN} is the intensity of the unknown
295 spectrum at a given mass) larger than 90 and quantifications using an internal standard. ^cForward values (see definition in footnote b) between 80
296 and 90 and quantifications using an internal standard. ^dForward values (see definition in footnote b) between 70 and 80 and quantifications using
297 an internal standard. ^{a,b,c,d,e,f,g} Means within each row with different letters are significantly different ($p < 0.05$), Tukey's test.

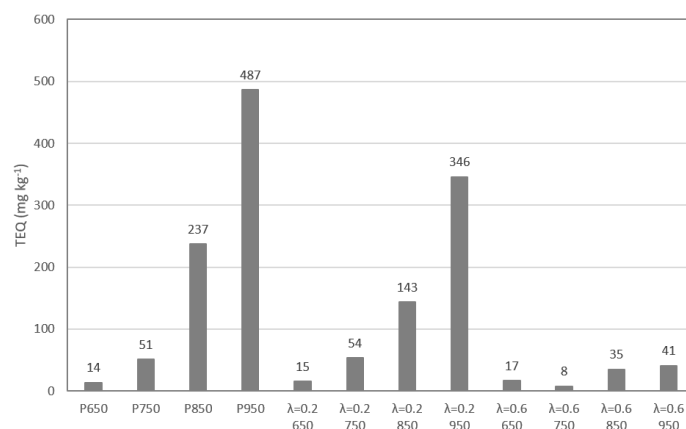


298

299 **Figure 1.** PAH emissions from A) pyrolysis and combustion, with B) $\lambda=0.2$ or C) $\lambda=0.6$,

300 runs at 650, 750, 850 and 950 °C.

301 Using the Toxicity Equivalency Factors (TEF) published previously (Nisbet and LaGoy,
 302 1992) for the 16 individual PAHs, it is possible to determine the equivalent toxicity of a
 303 mixture of PAHs in a specific emission. These values are calculated assuming that
 304 toxicity is additive. Therefore, the total equivalent toxicity (TEQ) of a sample is
 305 calculated by summing the toxic potencies of the individual PAHs, i.e., PAH
 306 concentration x TEF. Results are shown in Figure 2 and vary between 7.75 and 486.52
 307 mg kg sample⁻¹, with the lowest value observed in the thermal decomposition of the
 308 starch/PVA film at 750 °C and $\lambda=0.6$. As a general rule, TEQ values increase with
 309 temperature and decrease with increasing the oxygen content. This is mainly due to the
 310 significant contribution of benzo(a)pyrene, whose yield follows these same trends, to the
 311 toxicity of emissions. Though this compound is not a majority component the emissions,
 312 it has the highest TEF value. For example, when analyzing the most toxic experiment
 313 (pyrolysis at 950 °C), we can estimate that benzo(a)pyrene toxicity represents 68% of the
 314 total toxicity of the emission. It should be remarked that the major PAHs present in the
 315 emission of the studied sample (naphthalene, acenaphthylene, and phenanthrene) have
 316 the lowest TEF values (0.001).



317

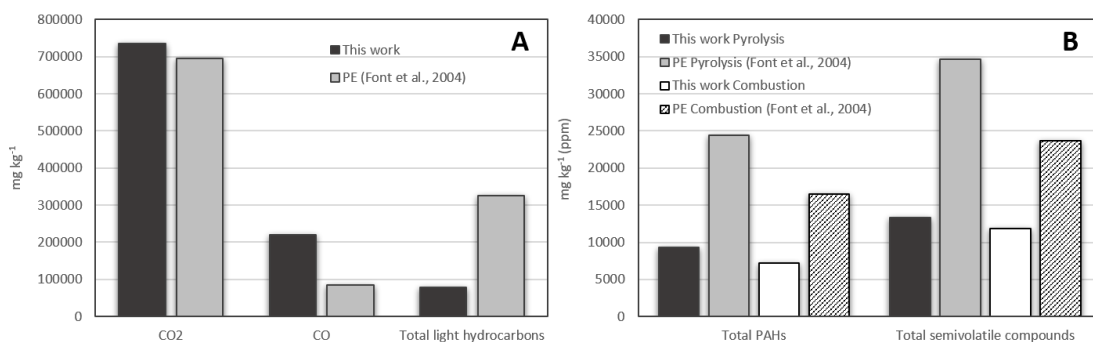
318 **Figure 2.** The TEQ of PAHs in pyrolysis and combustion experiments at 650, 750, 850
 319 and 950 °C.

320

3.3. Comparison of the emissions from other materials

321 As starch/PVA films have been widely synthesized in the last years, with the aim of
322 serving as potential substitutes for PE materials, the comparison between the emissions
323 obtained from the pyrolysis and combustion of both materials represents an interesting
324 approach. For comparison, results obtained with the same equipment and analysis method
325 have been used. In addition, experimental conditions at the same temperature (850 °C)
326 and a similar oxygen ratio ($\lambda \approx 0.2$) have been selected (Font et al., 2004). Firstly, Figure
327 3A shows the gases (CO_2 and CO) and total light hydrocarbon emissions obtained in
328 experiments carried out in similar conditions with both starch/PVA films and PE. As seen,
329 the CO_2 and CO emissions are similar or higher in this work than in combustion runs with
330 PE. However, the total emitted light hydrocarbons are considerably lower in this work.
331 This can be a result of different elemental analyses of both samples. While the starch/PVA
332 films contained 44.7% oxygen, the PE examined had no oxygen. This fact could promote
333 a higher formation of CO_2 and CO in the starch/PVA samples during combustion
334 experiments, hence, contributing to a lower emission of light hydrocarbons, which is
335 more benign from an environmental point of view.

336



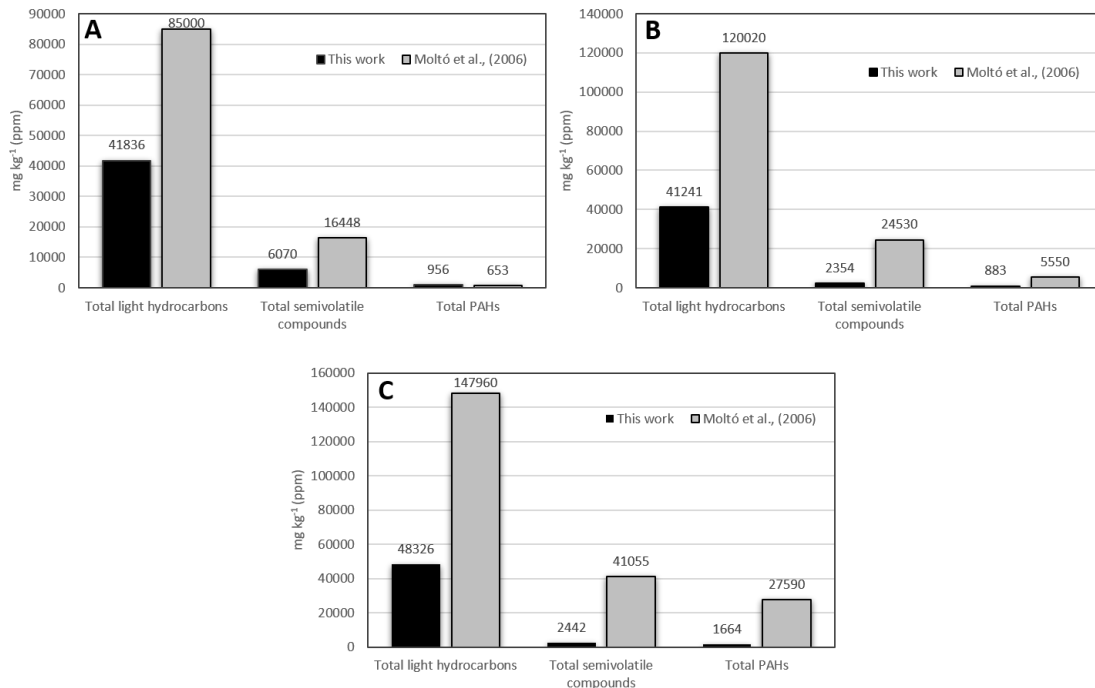
337 **Figure 3.** A) Emissions of gases (CO_2 and CO) and light hydrocarbons in combustion
338 experiments ($\lambda \approx 0.2$) at 850 °C with starch/PVA films and PE (Font et al., 2004). B)
339 Emissions of PAHs and total semivolatiles compounds (including PAHs) in pyrolysis and

340 combustion experiments ($\lambda \approx 0.2$) at 850 °C with starch/PVA films and PE (Font et al.,
341 2004).

342 Figure 3B shows the comparison of PAHs and total semivolatile compounds emitted in
343 pyrolysis and combustion experiments ($\lambda \approx 0.2$) when starch/PVA films and PE (Font et
344 al., 2004) are used. Interestingly, the formation of these compounds is considerably lower
345 in both combustion and pyrolysis experiments with starch/PVA samples than in the case
346 of PE. Specifically, the total semivolatile compounds emitted after pyrolysis and
347 combustion of starch/PVA samples represent only the 38 and 50%, respectively, of those
348 emitted with PE. This is indicative of the lower potential toxicity in terms of pollutants
349 formed from the samples studied in this work. Therefore, these results constitute another
350 interesting advantage for the successive replacement of conventional petroleum-based
351 plastics with starch-based polymers.

352 Apart from PE, comparison with the emissions of other conventional polymers with
353 similar oxygen content, such as polyesters, can be more representative. In previous work
354 from our group (Moltó et al., 2006), the organic compounds produced in the pyrolysis
355 and combustion of used polyester fabrics (oxygen content = 32.4%) were analyzed. Due
356 to the differences between the experimental conditions used in this work and in Moltó et
357 al. (2006), we only can establish an accurate comparison with the emission values
358 obtained during pyrolysis experiments at 650 °C and combustion experiments at 750 and
359 950 °C. The comparison is given in Figure 4. As seen, in all three cases, the total light
360 hydrocarbons and the total semivolatile compounds emitted are considerably higher in
361 the pyrolysis and combustion of polyester than in the pyrolysis and combustion of the
362 biodegradable starch/PVA films. The total PAHs are also higher, except in pyrolysis
363 experiments where the value is similar for both wastes. Therefore, we can conclude that
364 the emissions produced from the pyrolysis and combustion of starch/PVA films are lower

365 than those produced from polyesters fabrics when measurements are completed with the
 366 same equipment and at very similar temperatures and oxygen ratios, even when the
 367 oxygen content of the waste is on the same order of magnitude.



368

369 **Figure 4.** Emissions of total light hydrocarbons, total semivolatile compounds, and total
 370 PAHs in A) pyrolysis experiments at 650 °C, B) combustion experiments ($\lambda \approx 0.6$) at 750
 371 °C, and C) combustion experiments ($\lambda \approx 0.6$) at 950 °C, obtained with starch/PVA films
 372 (this work) and polyester (Moltó et al., 2006).

373 Another comparison of the organic compounds produced during thermal decomposition
 374 can be made with cotton fabrics (Moltó et al., 2005), which can be considered biomass
 375 according to their origin and have similar composition to starch. The oxygen content of
 376 the cotton fabrics used was 47.5%, which is very similar to the oxygen content for the
 377 starch/PVA films. In addition, the net calorific value of the cotton fabrics (17100 kJ kg⁻¹)
 378 ¹⁾ is almost the same as the sample studied in this work (17177 kJ kg⁻¹). Taking into
 379 account the oxygen ratio used for the experiments with cotton, a comparison can be

380 established between the emission values obtained for both wastes in combustion
381 experiments at 750 °C and $\lambda \approx 0.6$. The yields obtained for the emission of CO and CO₂
382 with cotton fabrics were 365000 and 821800 mg kg⁻¹, respectively. In the case of the
383 starch/PVA films, the yield of CO was considerably lower (72427 mg kg⁻¹), while CO₂
384 was considerably higher (1678933 mg kg⁻¹). The difference between these results could
385 be due to the different crystallinities of each waste. Starch/PVA films are mainly
386 amorphous because of the plasticization process of the polymers (starch and PVA), and
387 cotton is mainly composed of cellulose, which is a highly crystalline polymer. The
388 accessibility of oxygen in a crystalline structure, such as cellulose, is usually lower than
389 that observed in more amorphous materials. Hence, the oxidation of starch/PVA films is
390 faster, giving higher CO₂ yields. In addition, according to Zhang et al. (2017), higher
391 crystallinity leads to higher thermal stability. With respect to the yield of total PAHs, both
392 materials reached similar values (880–890 mg kg⁻¹). Probably, the formation of PAHs
393 and other pollutants under oxygen-rich conditions will be very small, as expected with
394 the cotton fabrics. Therefore, despite the similar oxygen content and nature of both
395 sources, the combustion of the starch/PVA films is better because of the lower CO yield
396 and similar PAH emissions.

397 **4. Conclusions**

398 This study evaluated the pollutant emissions from the thermal decomposition of
399 starch/PVA films under different conditions. Experiments were carried out at 650, 750,
400 850 and 950 °C and under three different atmospheres (pyrolysis, $\lambda=0.2$, and $\lambda=0.6$).
401 Comparing with PE and polyester, the yields of total light hydrocarbons and total
402 semivolatile compounds emitted were considerably lower in the case of the starch/PVA
403 films. Specifically, the total semivolatile compounds emitted after pyrolysis and
404 combustion of starch/PVA samples represent only 38 and 50%, respectively, of those

405 emitted with PE. Methane was the main light hydrocarbon emitted in all runs. The total
406 light hydrocarbons in emissions were considerably higher in pyrolysis experiments than
407 in combustion experiments due to the presence of oxygen in the atmosphere for
408 combustion runs contributes to the oxidation of light hydrocarbons giving higher CO₂
409 yields. Naphthalene was the most abundant PAH formed in the thermal degradation of
410 the starch/PVA films due to its low boiling point and high stability. Additionally, the PAH
411 yield was considerably higher in experiments with low oxygen content (pyrolysis and
412 combustion at $\lambda=0.2$) than in the combustion runs with $\lambda=0.6$. These results demonstrated
413 the lower potential toxicity in terms of pollutant formation from the starch/PVA films
414 compared to the conventional polymers studied (Font et al., 2004; Moltó et al., 2006).
415 Therefore, these results constitute another interesting advantage for the partial
416 replacement of these conventional polymers with starch-based polymers.

417 **Acknowledgements**

418 This work was partially supported from the European Commission (FEDER/ERDF) and
419 the Spanish MINECO (Ref. CTQ2016-78246-R and CTQ2016-76608-R). M.G.
420 Montalbán acknowledges support from MINECO (Juan de la Cierva-Formación contract,
421 Ref. FJCI-2016-28081).

422

423 **References**

- 424 Aracil, I., Font, R., Conesa, J.A., 2005. Semivolatile and volatile compounds from the
425 pyrolysis and combustion of polyvinyl chloride. *J. Anal. Appl. Pyrolysis* 74, 465–
426 478. <https://doi.org/10.1016/J.JAAP.2004.09.008>
- 427 Cano, A.I., Cháfer, M., Chiralt, A., González-Martínez, C., 2016. Biodegradation
428 behavior of starch-PVA films as affected by the incorporation of different
429 antimicrobials. *Polym. Degrad. Stab.* 132, 11–20.

430 <https://doi.org/10.1016/J.POLYMDEGRADSTAB.2016.04.014>

431 Chien, Y.C., Liang, C., Liu, S.H., Yang, S.H., 2010. Combustion kinetics and emission
432 characteristics of polycyclic aromatic hydrocarbons from polylactic acid
433 combustion. *J. Air Waste Manag. Assoc.* 60, 849–855.
434 <https://doi.org/10.3155/1047-3289.60.7.849>

435 Conesa, J.A., Egea, S., Moltó, J., Ortuño, N., Font, R., 2013. Decomposition of two
436 types of electric wires considering the effect of the metal in the production of
437 pollutants. *Chemosphere* 91, 118–123.
438 <https://doi.org/10.1016/j.chemosphere.2012.11.014>

439 Conesa, J.A., Font, R., Fullana, A., Martín-Gullón, I., Aracil, I., Gálvez, A., Moltó, J.,
440 Gómez-Rico, M.F., 2009. Comparison between emissions from the pyrolysis and
441 combustion of different wastes. *J. Anal. Appl. Pyrolysis* 84, 95–102.
442 <https://doi.org/10.1016/J.JAAP.2008.11.022>

443 Directive 2019/904/EU of the European Parliament and of the Council of 5 June 2019
444 on the reduction of the impact of certain plastic products on the environment. In:
445 European Commission, European Commission (Eds.), *Official Journal of the*
446 *European Union*, Brussels.

447 Domene-López, D., Delgado-Marín, J.J., García-Quesada, J.C., Martín-Gullón, I.,
448 Montalbán, M.G., 2020. Electroconductive starch/multi-walled carbon nanotube
449 films plasticized by 1-ethyl-3-methylimidazolium acetate. *Carbohydr. Polym.* 229,
450 115545. <https://doi.org/10.1016/J.CARBPOL.2019.115545>

451 Domene-López, D., García-Quesada, J.C., Martín-Gullón, I., Montalbán, M.G., 2019a.
452 Influence of starch composition and molecular weight on physicochemical
453 properties of biodegradable films. *Polymers* 11(7), 1084.

454 Domene-López, D., Delgado-Marín, J.J., Martín-Gullón, I., García-Quesada, J.C.,
455 Montalbán, M.G., 2019b. Comparative study on properties of starch films obtained
456 from potato, corn and wheat using 1-ethyl-3-methylimidazolium acetate as
457 plasticizer. *Int. J. Biol. Macromol.* 135, 845–854.
458 <https://doi.org/10.1016/J.IJBIOMAC.2019.06.004>

459 Domene-López, D., Guillén, M.M., Martín-Gullón, I., García-Quesada, J.C.,
460 Montalbán, M.G., 2018. Study of the behavior of biodegradable starch/polyvinyl
461 alcohol/rosin blends. *Carbohydr. Polym.* 202, 299–305.
462 <https://doi.org/10.1016/J.CARBPOL.2018.08.137>

463 EPA, 2007a. Method 3545A. Pressurized Fluid Extraction (PFE). United States
464 Environmental Protection Agency, Washington, DC.

465 EPA, 2007b. Method 8270D. Semivolatile Organic Compounds by GC/MS. United
466 States Environmental Protection Agency, Washington, DC.

467 Font, R., Aracil, I., Fullana, A., Conesa, J.A., 2004. Semivolatile and volatile
468 compounds in combustion of polyethylene. *Chemosphere* 57, 615–627.
469 <https://doi.org/10.1016/J.CHEMOSPHERE.2004.06.020>

470 Font, R., Aracil, I., Fullana, A., Martín-Gullón, I., Conesa, J.A., 2003. Semivolatile
471 compounds in pyrolysis of polyethylene. *J. Anal. Appl. Pyrolysis* 68–69, 599–611.
472 [https://doi.org/https://doi.org/10.1016/S0165-2370\(03\)00038-X](https://doi.org/https://doi.org/10.1016/S0165-2370(03)00038-X)

473 Handbook for Air Toxics Emission Inventory Development, Volume I: Stationary
474 Sources. In: US EPA, US EPA (Ed.), EPA-454/B-98-002. United States
475 Environmental Protection Agency, Office of Air Quality Planning and Standards
476 (1998).

477 Ishigaki, T., Kawagoshi, Y., Ike, M., Fujita, M., 1999. Biodegradation of a polyvinyl
478 alcohol-starch blend plastic film. *World J. Microbiol. Biotechnol.* 15, 321–327.
479 <https://doi.org/10.1023/A:1008919218289>

480 Mastral, F., Esperanza, E., García, P., Juste, M., 2002. Pyrolysis of high-density
481 polyethylene in a fluidised bed reactor. Influence of the temperature and residence
482 time. *J. Anal. Appl. Pyrolysis* 63, 1–15. [https://doi.org/10.1016/S0165-](https://doi.org/10.1016/S0165-2370(01)00137-1)
483 [2370\(01\)00137-1](https://doi.org/10.1016/S0165-2370(01)00137-1)

484 Moltó, J., Font, R., Conesa, J.A., 2006. Study of the organic compounds produced in the
485 pyrolysis and combustion of used polyester fabrics. *Energy & Fuels* 20, 1951–
486 1958. <https://doi.org/10.1021/ef060205e>

487 Moltó, J., Conesa, J.A., Font, R., Martín-Gullón, I., 2005. Organic compounds produced
488 during the thermal decomposition of cotton fabrics. *Environ. Sci. Technol.* 39,
489 5141–5147. <https://doi.org/10.1021/es0482435>

490 Nisbet, I.C.T., LaGoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic
491 aromatic hydrocarbons (PAHs). *Regul. Toxicol. Pharmacol.* 16, 290–300.
492 [https://doi.org/10.1016/0273-2300\(92\)90009-X](https://doi.org/10.1016/0273-2300(92)90009-X)

493 Ortuño, N., Conesa, J.A., Moltó, J., Font, R., 2014a. Pollutant emissions during
494 pyrolysis and combustion of waste printed circuit boards, before and after metal
495 removal. *Sci. Total Environ.* 499, 27–35.
496 <https://doi.org/10.1016/j.scitotenv.2014.08.039>

497 Ortuño, N., Moltó, J., Conesa, J.A., Font, R., 2014b. Formation of brominated
498 pollutants during the pyrolysis and combustion of tetrabromobisphenol A at
499 different temperatures. *Environ. Pollut.* 191, 31–37.
500 <https://doi.org/10.1016/j.envpol.2014.04.006>

501 Rotival, C., Renacco, E., Arfi, C., Pauli, A.M., Pastor, J., 1994. Gases emitted during
502 thermal decomposition of a polypropylene film and a polyurethane adhesive. *J.*
503 *Therm. Anal.* 41, 1519–1527. <https://doi.org/10.1007/BF02549949>

504 Shi, R., Bi, J., Zhang, Z., Zhu, A., Chen, D., Zhou, X., Zhang, L., Tian, W., 2008. The
505 effect of citric acid on the structural properties and cytotoxicity of the polyvinyl
506 alcohol/starch films when molding at high temperature. *Carbohydr. Polym.* 74,
507 763–770. <https://doi.org/10.1016/j.carbpol.2008.04.045>

508 Soler, A., Conesa, J.A., Iñiguez, M.E., Ortuño, N., 2018. Pollutant formation in the
509 pyrolysis and combustion of materials combining biomass and e-waste. *Sci. Total*
510 *Environ.* 622–623, 1258–1264. <https://doi.org/10.1016/j.scitotenv.2017.12.068>

511 Tak, H.-Y., Yun, Y.-H., Lee, C.-M., Yoon, S.-D., 2019. Sulindac imprinted mungbean
512 starch/PVA biomaterial films as a transdermal drug delivery patch. *Carbohydr.*
513 *Polym.* 208, 261–268. <https://doi.org/10.1016/J.CARBPOL.2018.12.076>

514 Tang, X., Alavi, S., 2011. Recent advances in starch, polyvinyl alcohol based polymer
515 blends, nanocomposites and their biodegradability. *Carbohydr. Polym.* 85, 7–16.
516 <https://doi.org/10.1016/J.CARBPOL.2011.01.030>

517 Thomas, S., Ledesma, E.B., Wornat, M.J., 2007. The effects of oxygen on the yields of
518 the thermal decomposition products of catechol under pyrolysis and fuel-rich
519 oxidation conditions. *Fuel* 86, 2581–2595.
520 <https://doi.org/10.1016/J.FUEL.2007.02.003>

521 Wang, Z., Wang, J., Richter, H., Howard, J.B., Carlson, J., Levendis, Y.A., 2003.
522 Comparative study on polycyclic aromatic hydrocarbons, light hydrocarbons,
523 carbon monoxide, and particulate emissions from the combustion of polyethylene,
524 polystyrene, and poly(vinyl chloride). *Energy & Fuels* 17, 999–1013.

525 <https://doi.org/10.1021/ef020269z>

526 Zhang, Z., Zhu, M., Zhang, D., 2017. Pyrolysis characteristics of cellulose isolated from
527 selected biomass feedstocks using a thermogravimetric analyser. Energy Procedia
528 142, 636–641. <https://doi.org/10.1016/J.EGYPRO.2017.12.105>

529

530

531

532

533

534

535

536

537

538

539

540

541

542

543

544