

# 1 Microwave heating as a novel route for obtaining carbon precursors from anthracene oil

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## 11 Abstract

12 This work describes a novel route for the preparation of pitches by oxidative polymerization of  
13 an industrial anthracene oil (AO) in a microwave semi-pilot equipment consisting in a multi-  
14 mode applicator having a 2.45 GHz magnetron with variable microwave power. The  
15 experimental five variables of microwave heating of AO air-blowing range between 320-380 °C  
16 (temperature), 0.2 - 3.9 °C min<sup>-1</sup> (heating rate), 1.5 - 5 h (soaking time), 16 - 20.5 % (air/AO  
17 ratio ) and 200 - 1500 g (initial weight). Their effect on the overall microwave air-blowing  
18 process is evaluated by means of a statistical analysis. A detailed characterization of the pitches  
19 has been carried out in terms of ultimate analysis, softening point, solubility parameters (toluene  
20 insolubles (TI) and quinoline insolubles (QI)) and thermogravimetric analysis. The experiments  
21 were also carried out by using conventional heating for comparative purposes. The detailed study  
22 of the electric energy consumption of the overall microwave treatment allows estimating a  
23 significant electric energy saving of about 20 % when compared to conventional heating thus  
24 representing an excellent result in the production of carbon precursors.

25 **Keywords:** microwave heating, conventional heating, anthracene oil-based pitches, oxidative  
26 polymerization, carbon precursor, energy consumption

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29

## 30 **1. Introduction**

31 Anthracene oil (AO) is a tar fraction that distils between 250 and 370 °C. This fraction mainly  
32 consists of polycyclic aromatic hydrocarbons (PAHs) of 3-5 rings, which can be transformed  
33 into a pitch by oxidative thermal condensation [1,2]. The conversion of AO into pitch is  
34 performed by conventionally thermal treatment in the presence of air (or oxygen) by using a  
35 traditional electrical device (e.g. reactor, autoclave, etc.). Briefly, the oxidative thermal  
36 condensation consists on the reaction of PAHs with oxygen, forming free radicals able to react  
37 among them giving rise to larger PAHs [3]. These polymerization reactions take place by the  
38 input of energy provided by thermal heating, which in turn is supplied by the above mentioned  
39 electrical device. However, this energy could be provided in other ways.

40 Microwave heating is an unconventional heating alternative, based on conversion of  
41 electromagnetic (EM) energy into heat depending on the type of interaction with the targeted  
42 materials. Furthermore, the heating of a material in microwave field depends on its dielectric and  
43 magnetic properties as the electric and magnetic fields interact with the material during  
44 irradiation [4].

45 Several advantages can be cited when using microwaves as the heating source: (1) localized  
46 heating allowing higher heating rates and shorter processing times; (2) selective heating with  
47 smaller heat loss; (3) possibility of energy saving, once it is used to directly heat the reaction  
48 mass; (4) possibility of using a commercially available and relatively compact device; (5)  
49 switching speed to start and stop; (6) precise process control, as the most of the available  
50 equipments allow the monitoring of different experimental parameters [5,6].

51 A microwave oven is mainly composed of a microwave source (magnetron which is used to  
52 generate long microwaves) with the power supply and control, connected to a transmission line  
53 (waveguide for higher power, coaxial cables for lower power), transmitting electromagnetic  
54 energy into a metallic cavity (commonly called applicator) into which the reactor is inserted [7].  
55 The geometry of the cavity can adopt various forms, depending on the process to be carried  
56 out. When the microwaves are injected into the cavity, the metal walls generate reflections of  
57 well-known phenomenon of interference, characterized by the low field strength alternating with  
58 high-intensity positions.

59 The main difference between conventional and microwave heating is the way in which heat is  
60 generated. In conventional processing, energy is transferred to the material through convection,  
61 conduction and radiation of heat from its surface [8]. In contrast, further studies have showed

62 that microwave energy is led directly to the material through molecular interactions with the  
63 electromagnetic waves being transformed into heat inside the particles by dipole rotation and  
64 ionic conduction. The main benefit of using microwave heating is that the treatment time can be  
65 considerably reduced, which in many cases also represents a reduction in the energy  
66 consumption. The uniqueness of the microwave treatment is to process materials with selective  
67 energy, higher rate, uniform heating of any absorbing microwave material and energy  
68 conservation [9-12]. There are a wide range of microwave equipments for different chemical or  
69 biochemical applications, including single or multiple-mode microwave cavity, with temperature  
70 measurement devices including K-type metallic thermocouples, pyrometers, with flux of  
71 different gases and electronic balance.

72 In the last 65 years, the unconventional processing of materials by microwave heating become  
73 popular due to potential advantages over the conventional techniques. Since its first application  
74 for cooking [13], microwaves have been used for many purposes, including chemical synthesis  
75 of organic and inorganic substances, industrial processes, biosciences, food industry and  
76 environmental treatments among others [14-24].

77 Recently, microwave energy has been widely used in a large number of applications and  
78 different processing levels from laboratory to industrial scale. There are publications which  
79 describe the use of microwaves for carbonization of different carbon precursors [9,25,26],  
80 activation and regeneration trials [27-29] as well as for the modification of the surface chemistry  
81 of activated carbon fibers [23] having positive influence on the characteristics of the final  
82 products [30,31]. In addition, the production of micro-mesoporous activated carbons for high  
83 performance supercapacitors [32-34], graphene oxide-carbon nanotube composites as negative  
84 electrode materials for lithium ion batteries [35-37], graphitic carbon [38,39] and nitrogen-doped  
85 hollow carbon spheres with high monodispersity [40] have been also reported.

86 This paper reports on the preparation of pitches by the air-blowing of an industrial AO. As a  
87 novelty, the process was performed in a semi-pilot microwave equipment and the effect of the  
88 experimental variables on the properties of the AO-based pitches obtained has been studied.  
89 Moreover, a detailed characterization of selected microwave-derived AO pitches has been  
90 carried out in order to compare them with AO pitches prepared by conventional thermal heating.  
91 Of particular interest has been the detailed study of the energy consumption of the overall  
92 microwave treatment which allows estimating a significant energy saving when compared to  
93 conventional heating thus representing an excellent result in the production of carbon precursors.

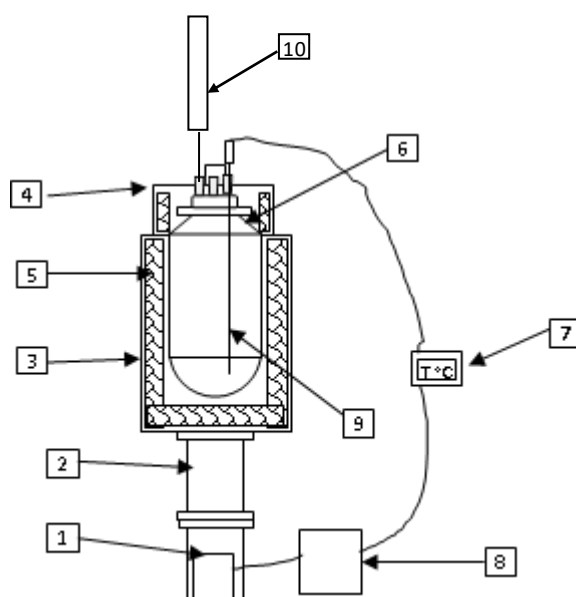
94 **2. Experimental**

95 **2.1 Raw material**

96 A commercial anthracene oil (AO) supplied by Industrial Química del Nalón S.A (Asturias,  
97 Spain), was used as raw material.

98  
99 **2.2 Oxidative polymerization of anthracene oil by microwave heating**

100 Oxidative polymerization of AO was carried out in a specifically designed microwave equipment  
101 (Fig. 1). It mainly consists on a multi-mode applicator having a quartz reactor with a total  
102 capacity of 2000 mL. At the top there is a lid with three necks: one for air cooled reflux  
103 condenser, one for thermocuple, and one for a glass tube (3 mm in diameter) which assured  
104 air/inert gas inlet into the sample, and thus allowed the continuously sample mixing by gas  
105 bubbling. Since the dielectric constant and the penetration depth of microwaves into the reaction  
106 mass of AO were not determined, this equipment was also equipped with an impedance tuner,  
107 devices for measuring direct microwave power ( $P_{\text{direct}}$ ) and reflected microwave power ( $P_{\text{reflected}}$ ),  
108 water load or sliding short circuit, an infrared temperature sensor and a microwave-power  
109 controller system. Multi-mode applicator was chosen because electric field has a known  
110 configuration and AO can be placed in its maximum field of the microwave. In order to prevent  
111 evaporation of low weight AO components, an air-cooled reflux condenser was placed on the top  
112 of the quartz reactor.



121 *Fig. 1. Schematic diagram of the multi-mode experimental microwave reactor (1. Microwave*  
122 *generator, 2. Waveguide; 3. Applicator; 4. Lid; 5. Thermal insulation; 6. Quartz reactor; 7.*  
123 *Temperature controler; 8. Power controller system; 9. Thermocouple, 10. Condenser system).*

124 Each run was defined by five different technological variables summarized in Table 1. In a  
125 typical run, the desired amount of AO was placed in the microwave oven. AO was heated from  
126 room temperature to the desired final temperature (320-380 °C) with the selected heating rate.  
127 For this purpose, 2.45 GHz frequency was used. Once reached the final temperature, the system  
128 was maintained for the desired soaking time. Once the reaction was finished the system was  
129 allowed to cool down to room temperature. From all the pitches obtained, three were selected for  
130 further characterization, labelled as MWP-71, MWP-92 and MWP-221 in correspondence with  
131 their softening points (see Supporting Information (SI) for details).

132  
133 *Table 1. Operational ranges of the technological variables used in the oxydative polymerization*  
134 *of anthracene oil (AO) in a microwave semi-pilot equipment.*

135

<b>Technological variables</b>	<b>Limit Min.</b>	<b>Limit Max.</b>
Maximum temperature of the treatment (T <sub>Max</sub> , °C)	320	380
Heating rate (°C min <sup>-1</sup> )	0.2	3.9
Soaking time (h)	1.5	5
Air /AO ratio <sup>1</sup> (%)	16	20.5
Initial weight (g)	200	1500

136 <sup>1</sup>*Air/AO ratio (%) = ratio of air intake to the AO amount*

### 137 **2.3 Statistical analysis**

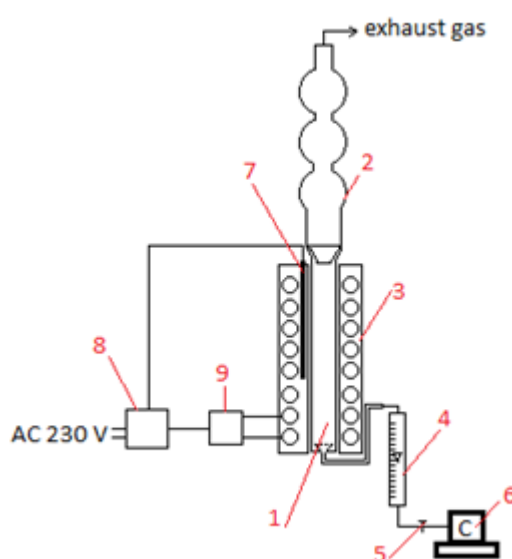
138 A multiple regression linear analysis was conducted to estimate the oxidative polymerization of  
139 AO by microwave heating using the Statgraphics software. The five technological factors were  
140 used as variables. As responses, the pitch yield and its toluene insoluble content (TI) were  
141 selected. The experimental desing was achieved by means of an aleatory selection of twelve (12)  
142 runs in which the operiational variables were fixed (see S.I., for details).

143 The adjustment was optimized via the Cochran-Orcutt model which allowed since least square  
144 lower regression coefficients [41].

### 145 **2.4 Oxidative polymerization of anthracene oil by conventional thermal treatment**

146 For comparative purposes AO was also treated by conventional heating, using an electrical oven  
147 (Fig. 2). In brief, the experimental device consists on a laboratory oven of 1,500 W which works  
148 up to 800 °C via an auto-transformer able to ensure variations between 0 and 220 V under a  
149 maximum current intensity of 8.5 A. On the route command an electric panel was inserted, on  
150 which the values of electrical load and temperature can be tracked simultaneously.

151 The parameters used for conventional oxidative thermal treatment of 200 g of AO were: a  
152 reaction temperature of 340 °C; air/AO ratio of 27% , a heating rate of 2 °C min<sup>-1</sup> and a soaking  
153 time of 2 h. Under these conditions, TTP-140 was obtained (name in reference to the softening  
154 point of that pitch).



155 *Fig. 2. Schematic diagram for conventional oxidative thermal treatment of anthracene oil by*  
156 *electrical heating (1. Reactor; 2. Cooler condenser; 3. Electrical oven; 4. Flow meter; 5. Valve;*  
157 *6. Air pump; 7. Thermocouple; 8. Temperature reader and control system; 9. Autotransformer).*  
158

## 159 **2.5 Characterization of the pitches**

### 160 **2.5.1 Elemental analysis**

161 The carbon and hydrogen content of the samples was determined by elemental analysis with a  
162 LECO-CHNS-932 microanalyzer. The oxygen content was ascertained directly using a LECO-  
163 VTF-900 furnace coupled to the microanalyzer. The analyses were performed using 1 mg of  
164 ground sample. The results were quoted from an average of the values of four determinations. In  
165 all cases, the experimental error was < 0.5 % of the absolute value.

### 167 **2.5.2 Softening point**

168 The softening point (SP) of the pitches was determined using a Mettler Toledo instrument  
169 adopting the ASTM D-3104-97 Standard.

170

### 171 ***2.5.3 Solubility parameters***

172 The solubility of the samples in toluene (determined as toluene insoluble fraction, TI) and  
173 quinoline (determined as the quinoline insoluble fraction, QI) was determined according to  
174 Pechiney B-16 (series PT-7/79 of STPTC) Standard and ASTM D2318-16 Standard,  
175 respectively.

176

### 177 ***2.5.4 Thermogravimetric analysis***

178 Thermogravimetric analyses (TG/DTG) were carried out in a thermobalance TA Instruments  
179 SDT 2960, using 15-20 mg of sample (particle size < 0.4 mm) placed in a platinum crucible and  
180 heating at 10 °C min<sup>-1</sup> to 1000 °C in a nitrogen flow of 100 mL min<sup>-1</sup>.

181

## 182 **3. Results and discussion**

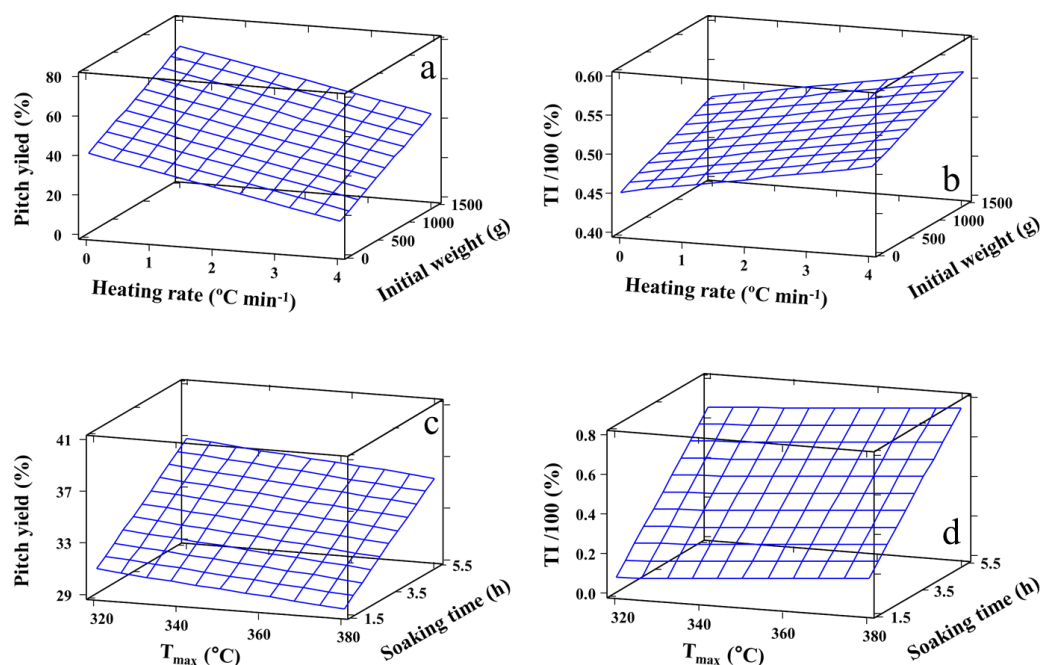
183

### 184 ***3.1 Oxidative polymerization of anthracene oil by microwave heating***

185 AO was polymerized by using the microwave device depicted in Fig. 1. After setting the  
186 working temperature, the heating process was conducted by means of a monophasic auto  
187 transformer. This allowed controlling magnetron tension involved in assuring microwave power.  
188 A graduated increase of the microwave power prevented AO overheating. The device was  
189 designed to optimize the five technological variables more relevant for the process (i.e.  
190 maximum temperature of the treatment, heating rate, soaking time at maximum temperature,  
191 air/AO ratio and initial weight of AO) which operate in the ranges summarized in Table 1. To  
192 estimate the complex effects of the five factors at the same time on the overall microwave air-  
193 blowing process, a statistical analysis of multiple regression was carried out in the range of  
194 factor studied [41]. Two properties of the pitches were selected as responses for this analysis.  
195 These are the yield of the pitch after the experiment, which is the main factor defining the overall  
196 yield of the preparation procedure, and the toluene insoluble content of each pitch (TI, %), which  
197 is a measurement of the intrinsic properties of the pitch, in this case, of the polymerization  
198 degree of its components [42-44].

199 The fiability of the statistical empirical model for each response is shown in Equations (I) and  
200 (II). The coefficient of determination,  $R^2$ , was 0.816 for pitch yield and 0.812 for TI (see SI for  
201 details).

202 Additionally, the model equations were evaluated by the F-test ANOVA. The analysis of  
203 variance (ANOVA), with Prob > F\* of 0.0019 for pitch yield and of 0.0021 for TI (both values  
204 < 0.05) confirms the significance of the methodology applied. The results summarizing the  
205 significance of the variables are depicted in SI for details. This analysis also indicate the  
206 significant microwave technology features which mostly affect each response studied. These are  
207 the initial weight of AO loaded in the microwave reactor, the air flow and the heating rate used  
208 for pitch yield (%) and only the initial weight and the air flow for TI (%). It should be noted that  
209 the critical effect caused by the initial weight in the microwave reactor can be understood by  
210 considering a resonant cavity in the microwave field. The variation of the amount of AO  
211 subjected to radiation involves a change in shape of the electric field which ensures the heating.  
212 In addition, by increasing the thickness of the sample located in the electric field, an increase in  
213 the number of polar oriented molecules is expected, thus enhancing the probability of efficient  
214 collisions favorable to the development of chemical reactions among AO components [45,46].  
215 On the other hand, the air flow controlles the (vapor/liquid) level at equilibrium which should be  
216 maintained for all runs thus limiting the ratio to be used.



217  
218 *Fig. 3. Response surface plots showing the effect of a,b) heating rate and initial AO weight at*  
219 *fixed conditions of T<sub>max</sub> of 360 °C, air/AO ratio 20.5% and soaking time of 4 h for pitch yield (a)*



220 *and toluene insolubles (b); c,d)  $T_{max}$  and soak time at fixed conditions of heating rate of 2.5 °C*  
221 *min<sup>-1</sup>, air/AO ratio 20.5% and 400 g of AO loading for pitch yield (c) and toluene insolubles (d).*

222  
223 It is possible to easily visualize the estimated effect of the two factors mainly affecting each  
224 response by means of the corresponding 3D response surface plots. To construct the plots the  
225 other three factors must be fixed. As an example, and considering the factors most affecting the  
226 variables previously discussed, Fig. 3a and 3b shows the variations of pitch yield and TI,  
227 respectively, with the heating rate and the initial weight at the conditions arbitrary fixed at  $T_{max}$   
228 of 360 °C, air/AO ratio 20.5% and soaking time of 4 h. Results indicate that, at these conditions,  
229 higher AO loadings in the microwave reactor increase both the pitch yield and the TI content,  
230 which confirms the previous assumptions. The effects are however less pronounced in the case  
231 of TI. The results also indicate that an increment in the air flow increases the pitch yield but  
232 contributes to decrease the toluene insoluble content. This opposite tendency could be related  
233 with the complexity of the polymerization mechanism of the AO components with air that could  
234 produce an initial aggregation of cross-linked molecules but with no great increase of their  
235 overall molecular weight [1].

236 The variation of the pitch yield (Fig. 3c) and TI (Fig. 3d) with the  $T_{max}$  and soaking time (two of  
237 the known factors affecting the polymerization process itself) were also investigated for an  
238 arbitrary fixed conditions of heating rate of 2.5 °C min<sup>-1</sup>, air/AO ratio 20.5% and 400 g of AO  
239 loading. At these conditions it is observed that the pitch yield decreases with the  $T_{max}$  applied  
240 while rapidly increases at higher soaking times. This tendency is expected considering that  
241 longer reaction times favour the polymerization of the AO components. On the other hand,  
242 higher temperatures could also favour polymerization, but it also favours the elimination of  
243 larger volatiles with the overall tendency observed. This seems to be corroborated analysing the  
244 TI content for the same conditions (Fig. 3d) showing that an increment of both, the  $T_{max}$  and  
245 soaking time increases the TI content (ascribed to highly polymerized pitch) [42-44].

246

### 247 **3.2 Properties of the microwave and thermally treated pitches**

248 It is also important to determine wheather the properties of the microwave-based anthracene oil  
249 pitches obtained by this new technology are comparable to the standard AO pitch obtained by  
250 conventional hetaing.

251 The pitches under study were characterized by means of elemental analysis, quinoline insoluble  
252 content and softening point (Table 2).

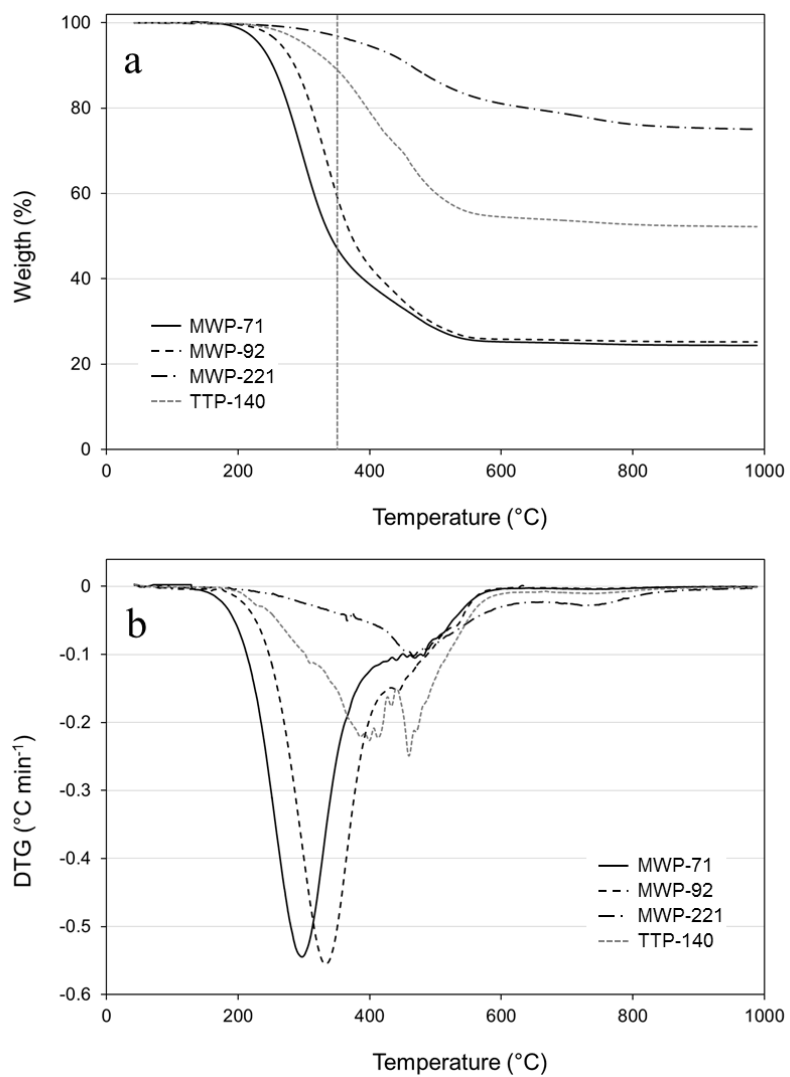
253 *Table 2. Processing conditions used for the preparation of pitches by microwave heating (MWP-*  
 254 *Series) and conventional thermal treatment (TTP-Series) and pitch characteristics.*

Sample	Processing conditions			Pitch characteristics						
	Air/AO ratio (%)	T <sup>1</sup> (°C)	t <sub>r</sub> <sup>2</sup> (h)	O <sup>3</sup>	H <sup>4</sup>	C/O <sup>5</sup>	C/H <sup>6</sup>	TI <sup>7</sup>	QI <sup>8</sup>	SP <sup>9</sup>
AO	-	-	-	0.9	5.6	136.4	1.4	0.0	0.0	-
MWP-71	20.5	320	3.5	2.5	4.7	57.8	1.6	17.6	0.0	71
MWP-92	18.7	360	2.5	2.0	4.7	64.3	1.6	14.0	0.0	92
MWP-221	16.0	380	4.0	1.3	3.7	91.3	2.0	60.7	24.0	221
TTP-140	27.0	340	2.0	2.9	4.0	42.1	1.9	58.9	14.2	140

255 <sup>1</sup> Reaction temperature, <sup>2</sup> Soaking time, <sup>3</sup> Oxygen content (wt.%), <sup>4</sup> Hydrogen content (wt.%), <sup>5</sup> Carbon/oxygen  
 256 atomic ratio, <sup>6</sup> Carbon/hydrogen atomic ratio, <sup>7</sup> Toluene insoluble content (wt.%), <sup>8</sup> Quinoline insoluble content  
 257 (wt.%), <sup>9</sup> Softening point (°C)

259 In general terms, pitches with the highest softening points (MWP-221 and TTP-140) exhibit  
 260 higher QI and TI contents as a consequence of their higher polymerization degree. This is not the  
 261 case of pitches with lower softening point since the TI content in MWP-92 (14.0 wt.%) is lower  
 262 than in MWP-71 (17.6 wt.%). This fact can be, however, explained by considering competitive  
 263 AO oxydation/polymerization mechanisms taking place at those milder experimental conditions  
 264 (i.e. lower temperature of thermal treatment and lower soaking time).

265 When comparing the O content in the microwave-based pitches series, it is observed that an  
 266 increase in the softening point (which was also obtained via higher temperatures) is accompanied  
 267 by a decrease of their O content (from 2.5 wt.% of O in MWP-71 to 1.3 wt.% in MWP-221.  
 268 What is more, the pitch obtained by conventional heating, exhibit the highest O content (2.9  
 269 wt.%) despite having an intermediate softening point of 140 °C. This clearly highlights that the  
 270 microwave technology developed herein allows the preparation of polymerized anthracene oil  
 271 based pitches incorporating a low amount of oxygen in its composition.



272

273

*Fig. 4. TG (a) and DTG (b) curves of pitches MWP-71, MWP-92, MWP-221 and TTP-140.*

274

275

Table 3. Thermogravimetric parameters of the pitches.

Sample	T <sub>i</sub> <sup>1</sup>	T <sub>max1</sub> <sup>2</sup>	R <sub>350</sub> <sup>3</sup>	R <sub>1000</sub> <sup>4</sup>
MWP-71	196	297	47.2	24.4
MWP-92	222	333	59.5	25.2
MWP-221	273	400/460 <sup>5</sup>	96.9	75.0
TTP-140	239	400/460 <sup>5</sup>	89.1	52.2

<sup>1</sup> Temperature of initial weight loss (°C), <sup>2</sup> Temperature of maximum rate of weight loss (°C), <sup>3</sup> Carbonaceous residue at 350 °C (wt. %), <sup>4</sup> Carbonaceous residue at 1000 °C (wt. %), <sup>5</sup> multiples temperatures of maximum rate of weight loss

276

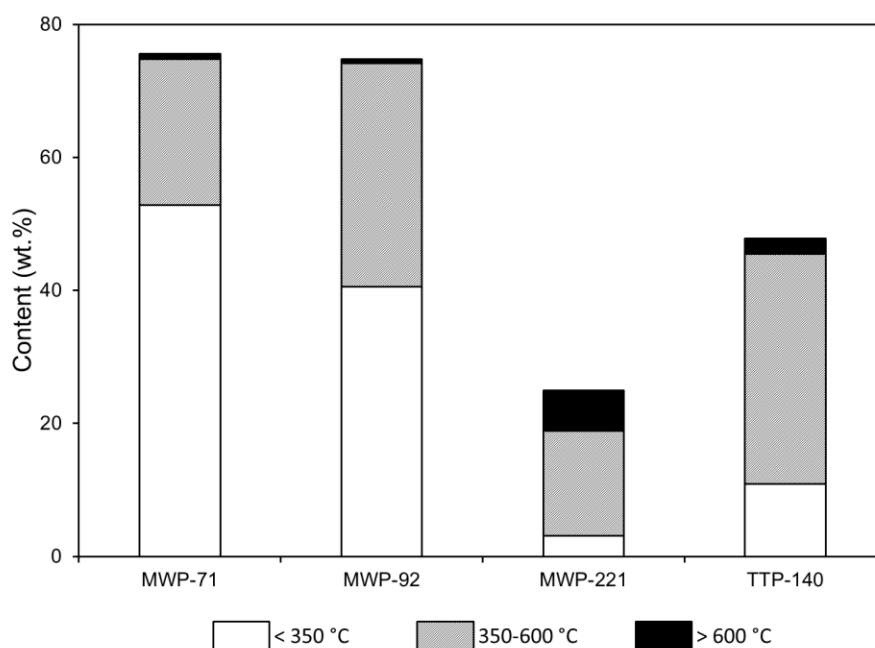
277 The pyrolysis behavior of the pitches, studied by thermogravimetric analysis, is mainly  
 278 determined by their characteristics, which in turn are governed by the polymerization degree.  
 279 The thermogravimetric results of the pitches under study are depicted in Fig. 4 and Table 3. A  
 280 detailed quantification of weight loss by temperature ranges is summarized in Fig. 5.

281 For all the pitches, the initial temperature of weight loss (Fig. 4a) and the maximum temperature  
 282 of weigh loss rate (T<sub>i</sub> and T<sub>max</sub> respectively, Table 3) increase at higher softening point of the  
 283 pitches, as an indication of the direct relation of the softening point of the pitch with its  
 284 polymerization degree.

285 Interestingly, MWP-71 and MWP-92 show a temperature of initial weight loss at 196 and 222  
 286 °C, respectively, and a temperature of maximum rate of weight loss centered at 297 and 333 °C,  
 287 respectively. A thermogravimetric parameter of special relevance for determining the  
 288 polymerization degree in AO is R<sub>350</sub>. This parameter is defined as the residue left by the sample  
 289 at 350 °C, which is zero in the case of AO [1]. The value of this parameter in AO-based pitches  
 290 can be directly related with the amount of raw material (i.e. anthracene oil) that has been  
 291 polymerized.

292 For MWP-71 and MWP-92 this parameter reaches values of 47.2 and 59.5 wt. %, respectively  
 293 and increases up to 89.1 % for TTP-140 and 96.9 % for MWP-221. This seems to reflect that the  
 294 volatile content of these pitches has a great influence in their softening point.

295



296  
 297 *Fig. 5. Variation of weight loss in the temperature range of < 350 °C, 350-600 °C and > 600 °C,*  
 298 *determined by thermogravimetric analysis for microwave- based pitches MWP-71, MWP-92 and*  
 299 *MWP-221, and conventionally heated pitch TTP-140.*

300  
 301 However, not all the polymerized AO components are consolidated during the subsequent  
 302 carbonization. In a second temperature range, between 350 – 600 °C, the weight loss is mainly  
 303 due to AO components that, even having being polymerized, are distilled once their boiling point  
 304 is reached due to their thermal instability (Fig. 5). Thus, although the polymerization degree of  
 305 MWP-92 is greater than that of MWP-71 (lower weight loss below 350 °C, Fig. 5), the thermal  
 306 stability of their polymerized components is lower (higher weight loss in the temperature range  
 307 of 350 – 600 °C, Fig. 5) and it is only MWP-221 that the weight loss in this region decreases.  
 308 The small molecules generated as a consequence of the complex reactions that take place during  
 309 the thermal treatment in this temperature range (e.g. cracking, condensation, etc.) are also  
 310 removed. It is only above 600 °C, once the pitches have been progressed generating a solid green  
 311 coke, that the weight loss is mainly attributed to the removal of small molecules related to the  
 312 multiple reactions that take place at this high temperature (e.g., isomerizations, molecular  
 313 rearrangements, etc.). In this region, low softening point pitches lose similar amount of weight ~  
 314 1 wt.% (Fig. 5). In contrast, MWP-221 loses a 5.7 wt. %. This result suggests that, in all cases,  
 315 the oxidative treatment has caused a certain cross-linking between AO components and,  
 316 consequently, some small molecules are removed due to the reactions that take place when the  
 317 sample is already a solid (green coke). Moreover, the carbonaceous residue at 1000 °C for MWP-

318 221 (75 wt. %) evidence that in this pitch the degree of polymerization and the capacity of  
319 consolidation of the polymerized components is much greater than in the two previous ones.

320 It is important to remark that the pitch obtained by conventional thermal treatment (TTP-140)  
321 exhibits somehow an intermediate behaviour between MWP-92 and MWP-221 (pitches with  
322 intermediate softening points). It seems therefore that despite a different polymerization  
323 mechanism could be established at early stages of the AO polymerization, i.e. by using milder  
324 microwave reaction conditions, the use of more severe reaction conditions in the microwave  
325 oven minimizes the differences in the properties of the pitches obtained with respect to those  
326 obtained by conventional thermal treatment.

327

### 328 ***3.3 Electric energy consumption during microwave and conventional heating***

329 Of particular importance is to evaluate the electric energy consumption of the AO  
330 polymerization which, in turn, will determine the feasibility of the microwave technology  
331 developed herein to produce AO-based pitches in competitive conditions to those required by  
332 using conventional heating. The study approached two thermal ranges, below 290 °C and over  
333 290 °C.

334 This temperature was selected as the threshold during the microwave studies, as, before the  
335 oxidative treatment, a distillation step was performed at 290 °C in order to reduce the influence  
336 of light fractions during the microwave heating behavior of AO. The data of Table 4 come from  
337 the measurements made in the laboratory trials.

338

Table. 4. Electric energy consumption for oxidative polymerization of AO in microwave and conventional heating

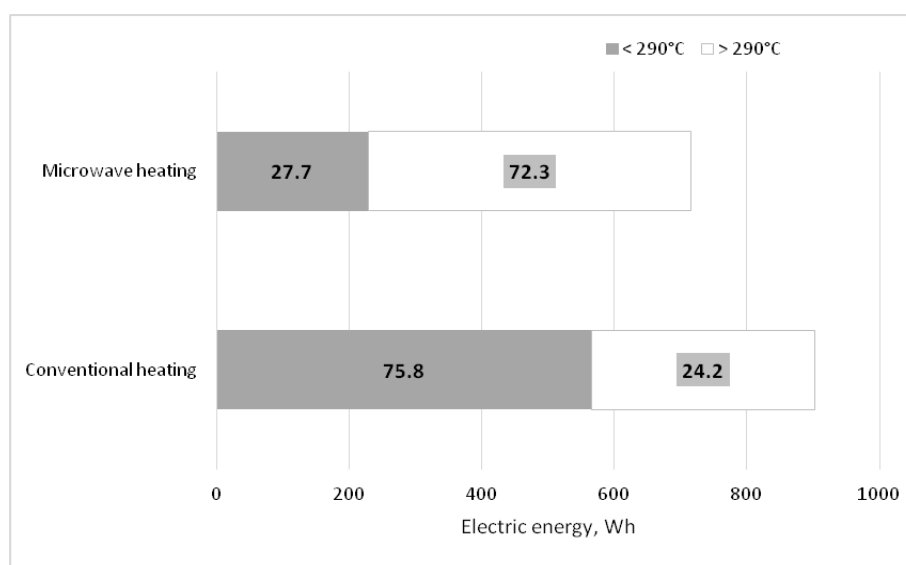
Characteristic	Unit	Microwave-based pitches			Conventional-based pitch	
		MWP-71	MWP-92	MWP-221	TTP-140	
AO amount	g	200	400	200	200	
Electric energy consumption on thermal stages	< 290°C	Wh	247.4	267.5	204.6	2825.3
	> 290°C	Wh	833	553	534	902
Total electric energy consumption	Wh	1080.4	820.5	738.6	3727.3	
Percent of electric energy consumption on thermal stages	< 290°C	%	22.9	32.6	27.7	75.8
	> 290°C	%	77.1	67.4	72.3	24.2
Microwave power density	W/g	3.8	2.2	3.2	-	
Electric power consumption on thermal stages	< 290°C	W	192.4	148.6	181.8	1284.2
	> 290°C	W	151.4	158	133.5	180.4

340  
 341 Considering the concept of microwave power density, the average values for this parameter  
 342 were: 3.8, 2.2 and 3.2 W/g for pitches MWP-71, MWP-92 and MWP-221, respectively. As  
 343 heating from room temperature to 290 °C was performed with a low percent of electric energy  
 344 consumption (27.7 %) the most of the electric energy consumption of the process was assigned  
 345 to the polymerisation stages of the AO over 290 °C (72.3 %). Therefore, calculations of electric  
 346 energy consumption were made on each processing step related to chemical changes. As a result,  
 347 when processing 100 g of each AO sample the average electric power consumptions calculated  
 348 were of 151.4, 158.0 and 133.5 W under the experimental procedures followed for obtaining  
 349 MWP-71, MWP-92 and MWP-140, respectively.

350 Although at a laboratory stage, these results present a proof of concept according to which the  
 351 heating in microwave field provides benefits regarding the time of heat treatment and electric  
 352 energy consumption. The average value of 147.6 W of electric power consumption in case of  
 353 experiments carried out by microwave heating shows a decrease of about 20 % compared to the  
 354 electric power consumption of 180.4 W for conventional heating (Fig. 6).

355 The experiments also confirmed the basic principles of microwave heating. Thus, energy is  
 356 conducted directly to materials through molecular interactions and electromagnetic waves which  
 357 are transformed into heat inside the particles, requiring a lower electric energy consumption of  
 358 only 27.7 % of the total electric energy in the preliminary phase of AO heating, up to the  
 359 reaction temperature (290 °C). During conventional heating according to which energy is  
 360 transferred to material through convection, conduction and radiation of heat from its surface,  
 361 75.8 % of the total electric energy is consumed in the preliminary phase of heating up to the  
 362 reaction temperature (290 °C) and the rest of 24.2 % is used during polymerisation stages of AO  
 363 (Fig. 6).

364



365

366

367 *Fig. 6. Assessment of the total percent of electric energy consumption on thermal stages*  
 368 *in case of microwave and conventional heating*

369

370 Of course, this assessment is a preliminary one as between the conventional and microwave  
 371 heating occur differences in the heating rate and the processes can not be currently compared  
 372 step by step.

373

#### 374 **4. Conclusions**

375

376 In this study, a microwave device was developed in order to perform, for the first time, the air-  
 377 blowing polymerization of AO.



378 The statistical analysis of the technological variables controlling the overall process reveals that  
379 two are the most important factors affecting the microwave heating: the initial weight of AO  
380 introduced, which has an influence on the shape of the electric field and in the number of polar  
381 oriented molecules, and the air flow used, which controls the vapor/liquid level at equilibrium  
382 and should be maintained for all runs thus limiting the ratio to be used in the oven and the air  
383 flow.

384 A detailed analysis of the pitches properties allowed to determine that by controlling the  
385 experimental parameters during the microwave treatment, such properties, in terms of softening  
386 point or toluene insoluble content can be easily modulated. This is due to modifications of the  
387 mechanism involved, particularly at early stages of the polymerization reactions (milder  
388 experimental conditions). The properties of the microwave-based pitches are in any case in the  
389 range of those observed for pitches obtained by conventional thermal heating. This allows  
390 ensuring that the microwave technology developed herein is an attractive alternative to  
391 conventional thermal treatment for the air blowing of AO.

392 The analysis of the electric energy consumption of the overall process points out the benefits of  
393 the microwave technology when compared to the polymerization of AO by means of  
394 conventional thermal treatment. In this regard, this technology provides a significant electric  
395 energy saving, of about 20 %, thus representing an excellent result in the production of carbon  
396 precursors.

397

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514

515 **SUPPORTING INFORMATION**

516 **Microwave heating as a novel route for obtaining carbon precursors from anthracene oil**

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527  
528 **1- *Statistical analysis of oxidative polymerization of anthracene oil by microwave heating***

529 A regression analysis was conducted to estimate the oxidative polymerization of anthracene oil by  
530 microwave heating.

531 As variables we used maximum temperature of the treatment ( $T_{max}$ ), heating rate, soaking time at  
532 maximum temperature (soaking time), air flow (measured as a percentage of air in a nitrogen  
533 flow) and initial weight of AO (Initial weight). As responses we used the pitch residue after the  
534 reaction (pitch yield) and the toluene insoluble content (TI). The experimental design was  
535 achieved by means of a aleatory selection of 12 runs in which the operational variables were  
536 fixed as summarized in Table S1. The adjustment was optimized via the Cochran-Orcutt model  
537 which allowed least square lower regression coefficients.

543 *Table S1. Technological variables involved in the Anthracene oil (AO) polymerization in*  
 544 *microwave semi-pilot equipment.*

545

Run	Technological parameters /variables				
	T <sub>max</sub> °C	Heating rate, °C min <sup>-1</sup>	Soaking time, h	Air flow, %	Initial Weight g
1	320	3.9	2.5	20.5	1468
2		2.6	3		1120
3	320	2.6	3.5	20.5	215
4	350	2.5	1.5	20.5	200
5		0.2	3	20.5	836
6		2.6	3		
7	350	2.6	3	27	300
8		2.5	4		
9		2.5	5		
10	355	2.7	2	20.5	1329
11	360	2.5	2.5	18.7	415
12	380	2.7	4	16	253

546  
 547 The obtained empirical models for each response are shown in Equations S1 and S2. The  
 548 coefficient of determination, R<sup>2</sup>, was 0.816 for pitch yield and 0.812 for TI.

549  
 550 **Pitch Yield (%)** = 0.25246 – 0.000263084×T<sub>max</sub> – 0.061988×Heating rate + 0.0150787×Soaking  
 551 time + 0.00957137×Air flow + 0.000182847×Initial weight. **(Eq. S1)**

552 **TI (%)** = 0.124829 + 0.00156019×T<sub>max</sub> + 0.0141441×Heating rate + 0.147289× Soaking time –  
 553 0.0392213×Air flow + 0.0000353341×Initial weight **(Eq. S2)**

554  
 555 The model equations were evaluated by the F-test ANOVA. The results summarizing the  
 556 significance of the variables are depicted in Table S2.

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567 Table S2. Analysis of variance (ANOVA) for the regression model

Factor	Residue yield ( $R^2 = 0.816$ )					TI ( $R^2 = 0.812$ )				
	Standard Error			Prob>F*		Standard Error			Prob>F*	
T <sub>max</sub>	0.00107393			0.8114		0.893479			0.8917	
HR	0.0158273			0.0029		0.00231722			0.5160	
ST	0.0132935			0.2831		0.0290747			0.6371	
AF	0.00291796			0.0083		0.0277995			0.0003	
Initial	0.0000319886			0.0002		0.00967778			0.0023	
Source	SS	DF	Ms	F-value	Prob>F*	SS	DF	Ms	F-value	Prob>F*
Model	0.122156	5	0.0244313	8.86	0.0019	0.503947	5	0.100789	8.63	0.0021
Residue	0.0275593	10	0.00275593			0.11673	10	0.011673		
Total (Corr.)	0.149716	15				0.620677	15			

568 \*Significant at Prob>F less than 0.05.

569



570 **Highlights**

- 571 - Novel route of anthracene oil-based pitches preparation in microwave heating
- 572 - Detailed characterization of pitches including the thermogravimetric analysis
- 573 - Microwave air-blowing process evaluated by means of a statistical analysis
- 574 - Evaluation of energy benefits of microwave heating when compared to conventional one
- 575