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Diakaridia Sangare, Agnes Chartier, Mario Moscosa-Santillan, Iskender Gökalp, Stéphane Bostyn. Kinetic studies of hydrothermal carbonization of avocado stone and analysis of the polycyclic aromatic hydrocarbon contents in the hydrochars produced. *Fuel*, 2022, 316, pp.123163. 10.1016/j.fuel.2022.123163 . hal-03812199

**HAL Id: hal-03812199**

**<https://cnrs.hal.science/hal-03812199v1>**

Submitted on 22 Jul 2024

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1                    **Kinetic Studies of Hydrothermal Carbonization of Avocado Stone and**  
2                    **Analysis of the Polycyclic Aromatic Hydrocarbon Contents in the Hydrochars Produced.**

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14  
15                    **Abstract:**

16                    Model-free and model-fitting kinetic approaches were used to investigate the hydrothermal  
17                    carbonization (HTC) of avocado stone. The total solid mass yield was used to estimate the  
18                    kinetic parameters and reaction mechanism. The results obtained show that the HTC process for  
19                    avocado stones could be divided into four temperature zones. Up to 160 °C, the initial induction  
20                    period where the reaction rate is relatively slow. The second zone (160 to 200 °C) corresponds to  
21                    the maximum decomposition rate. The third zone between 200 and 220 °C corresponds to the  
22                    stabilization zone; in this zone, the total solids yield is practically constant, and finally, the  
23                    polymerization zone, between 220 and 250 °C, where an increase in total solid yield was  
24                    observed. The kinetic parameters and reaction mechanism were determined in two temperature  
25                    zones, from 150 to 210 °C and 210 to 250 °C. In the first zone, the decomposition of avocado  
26                    stone during the HTC process followed a random nucleation reaction mechanism (Avrami-  
27                    Erofeev-1) with the activation energy of  $87.84 \pm 3.28$  kJ/mol. In contrast, in the second zone, it  
28                    followed a first-order reaction model, and the activation energy was  $230.96 \pm 28.84$  kJ/mol.  
29                    Analysis of PAHs with gas chromatography-mass spectrometry showed that the number of PAHs  
30                    in the hydrochar increases with an increase in temperature from 190 to 250 °C. The 3-4 rings

31 PAHs were dominant in the hydrochars prepared at temperatures between 230 and 250 °C, while  
32 two rings were largely prevalent in the hydrochar obtained at low temperatures.

33

34 **Keywords:** Avocado stone; hydrothermal carbonization; Kinetic model; PAHs

## 35 **1 INTRODUCTION**

36 The increasing demand for energy and the rapid depletion of fossil fuels are the reasons for  
37 the need to find new sources of energy, sustainable technologies, or processes that are  
38 environmentally friendly. This problem has inspired researchers to study and develop more  
39 efficient and reliable tools to exploit biomass as a source of renewable energy. The  
40 thermochemical conversion processes of biomass have better industrial prospects for biomass  
41 valorization since the process conditions can be optimized to maximize gas, liquid, and solid  
42 yields [1]. Among thermochemical processes, hydrothermal carbonization (HTC) of biomasses  
43 (agro-industrial, forestry, and urban waste) has received widespread attention in recent years  
44 because of its efficiency and convenience [2, 3]. HTC technology is based on a thermochemical  
45 conversion process by which it converts organic material into carbonized material (hydrochar),  
46 liquid (bio-oil mixed with water), and small fractions of gases. The HTC process is performed in  
47 the temperature range of 180-250°C, during which biomass is submerged in water and is heated  
48 under autogenous saturated vapor pressure between 10 and 40 bars and residence time ranging  
49 from a few minutes up to several hours [4]. Under these process conditions, water exhibits a  
50 behavior similar to that of an organic solvent owing to changes in its polarity and dielectric  
51 constant and acts as a catalyst for the conversion of biomass through hydrolysis, dehydration,  
52 decarboxylation, aromatization, condensation, and polymerization [5]. Through the HTC  
53 process, researchers have investigated distinct types of biomass, tomato waste [6], sugarcane  
54 bagasse [7], olive pomace [4], corn cob [8], and olive stones [9]. Most of these biomasses are  
55 agro-industrial wastes. Avocado stones is some of the most massive agro-industrial wastes  
56 generated in Mexico.

57 The avocado is one of the most frequently consumed fruits in the world. Mexico is globally the  
58 leading avocado producing country, with more than 45% (~2.18 million tons/year) of the total  
59 production in 2020 [10]. Products derived from avocados include ice cream, drinks, and

60 guacamole being the most marketed product [11]. There are also examples of avocado oil  
61 production, which is of a quality similar to olive oil [12]. Avocado processing generates an  
62 enormous amount of waste, particularly the skin and seed or stone. The stone represents 15.0–  
63 16.0% of the fruit weight [13]. A significant amount (~170,000 tons/year) of avocado production  
64 is guacamole, and this represents more than 25,000 tons of waste per year [14].

65 The technology of the HTC process of waste to form hydrochar and bio-oil has been is the focus  
66 in recent years [6, 8, 9]. During the HTC process, hydrochar formation can be carried out in two  
67 reaction pathways. The formation can proceed from the reaction of the solid-solid pathway  
68 known as primary hydrochar (P-HC), in which hydrochar maintains the original structural  
69 elements and morphology of the parent biomass matrix; and the hydrochar formation can be  
70 carried out from aqueous phase degradation of the biomass followed by polymerization of the  
71 organic molecules into a solid phase, called secondary hydrochar (S-HC). This secondary  
72 hydrochar is extractable with organic solvents [15]. This S-HC is a sequential result of  
73 hydrolysis, dehydration, and isomerization during HTC to produce furfurals and their  
74 derivatives. The furfurans and their derivatives polymerize as microspheres, these microspheres  
75 can be further carbonized by dehydration reactions, resulting in an amorphous solid that is  
76 soluble in organic solvents [15]. Although, Paksung et al.[16] reported that it is not easy to  
77 distinguish analytically between P-HC and S-HC; because both appear as a single solid mass of  
78 char.

79 The main product of HTC is hydrochar, a solid material 55-74% rich in carbon, is the stable, a  
80 lignite-like material which is characterized by a high heating value (21.1–30.6 MJ/kg) [4] and its  
81 physical, chemical, and mechanical properties make it susceptible to different uses. Hydrochar  
82 can thus be used directly as a solid fuel that can be burned for energy or produce syngas. Most  
83 recently, the hydrochar has also been applied as an additive agent for soil amendment [17, 18].  
84 The hydrochar has proved to be a favorable soil of amendment, increased cation extraction  
85 capacity, and reduced solid bulk density [19]. However, for the soil use of hydrochars,  
86 contaminants such as heavy metals and polycyclic aromatic hydrocarbons (PAHs), in hydrochars  
87 are of significant concerns.

88 Peng et al. [17] reported a significant increase of PAHs in the hydrochar of municipal solid  
89 waste, with the increase in temperature of HTC between 160°C and 240°C. The formation of

90 PAHs from biomass is -a multi-step process. The S-HC formation during the hydrothermal  
91 carbonization of biomass leads to increased PAHs formation and their retention in the primary  
92 hydrochar [20, 21].

93 Biomass decomposition by HTC is dominated by chemical reactions similar to pyrolysis;  
94 however, the HTC process is initiated by hydrolysis, leading to biomass decomposition  
95 temperatures lower than those of pyrolysis [23]. The HTC reaction mechanisms complexity has  
96 led some authors to develop lumped kinetics models to describe it [24]. For simplification, the  
97 authors have used the biomass components model, such as cellulose, hemicellulose, and lignin.  
98 For example, Reza et al. [25] determined the activation energy of cellulose and hemicellulose in  
99 the temperature range between 200 and 260°C. They reported that cellulose degradation is  
100 described by a first-order rate constant with an activation energy  $73\pm 6$  kJ/mol, and hemicellulose  
101 degradation has an activation energy of  $30\pm 12$  kJ/mol. For the same operating conditions (200-  
102 260°C), Killer et al. [26] reported activation energy values equal to 61 kJ/mol and 127 kJ/mol for  
103 hemicellulose and cellulose, respectively. On the other hand, Liu and Balasubramanian [27]  
104 considered the HTC process as a first-order reaction and estimated the activation energy for  
105 coconut fibers (67.5 kJ/mol) and eucalyptus leaves (59.2 kJ/mol). Recently Pecchi et al. [28]  
106 reported  $E_a$  values of 139.16 and 161.68 kJ/mol and reaction orders of about 2.68 and 2.46, for  
107 digestate and sludge, respectively, using Differential Scanning Calorimetry. As can be seen,  
108 different approaches have been used to determine the kinetic parameters during the HTC process  
109 of the biomass. However, researchers have used conventional methods in only a few studies to  
110 determine kinetic parameters. Methods based on thermal analysis, such as thermogravimetric  
111 analysis, have been widely used in the literature to study biomass decomposition kinetics. They  
112 are high-precision methods that can be used for the quantitative examination of processes as well  
113 as for estimating useful kinetic parameters for various thermal decomposition reactions. Since  
114 thermogravimetric analysis is a technique based on mass loss or conversion as a function of  
115 temperature and time during thermochemical conversion, a similar analogy can be used for the  
116 HTC process based on the hydrochar mass yield as a function of temperature and reaction time.

117 For this reason, this research - focuses on the determination of the kinetic parameters that  
118 described the hydrothermal carbonization process of the avocado stone, using the thermal  
119 analysis technique in an open-loop controller system. The biomass's HTC behavior was studied  
120 using the total solid mass yield or hydrochar yield produced at different temperatures and times.

121 The kinetic predictions were made by using the Model-Free Method, such as FWO, KAS, and  
 122 Friedman and the Model-Fitting Methods were used to determine the most appropriate kinetic  
 123 model mechanism of HTC reactions. In addition, a qualitative analysis of the hydrochars  
 124 produced was performed to determine the structure of polycyclic aromatic hydrocarbons (PAHs).

## 125 2 MATERIALS AND METHODS

### 126 2.1 Feedstock

127 In this study, avocado stones (AS) of the *Hass* variety from Michoacán (Mexico) were used. In  
 128 general, an AS has a moisture content between 65 and 75% [29], which is ideal for HTC.  
 129 Initially, an AS was cut and dried in a stove at 80 °C for storage; subsequently, it was ground to  
 130 obtain a particle size between 0.5 and 1mm. **Table 1** contains the physical and chemical  
 131 characteristics associated with the raw AS. The details of the determination of these parameters  
 132 were explained in our previous study [30].

133 **Table 1.** Proximate, ultimate, extractive, hemicellulose, cellulose, lignin analysis, and higher heating  
 134 value characteristics of AS

Proximate analysis (%)	
MC	3.2±0.4
VM	72.5±1.7
FC <sup>a</sup>	22.4±1.0
Ash	1.9±0.6
Ultimate analysis (%)	
Carbon	46.1±0.2
Hydrogen	6.4±0.1
Nitrogen	0.02 ± 0.0
Sulphur	nd
Oxygen <sup>a</sup>	47.9±0.9
Extractives (%)	3.6±0.4
Hemicellulose (%)	76.4±0.3
Cellulose <sup>a</sup> (%)	3.0±0.3
Lignin (%)	17.0±0.3
<b>HHV(MJ/kg)</b>	<b>18.6±0.2</b>

MC: moisture content; VM: volatile matter; FC: fixed carbon; nd: not detected; <sup>a</sup>:by difference

### 135 2.2 HTC Reactor Description and Experimental Procedure

136 The detailed descriptions of the experimental procedures can be found in our previous studies  
 137 [31]. Briefly, the HTC experiments were carried out in the stirred autoclave reactor (Top  
 138 Industrie, France) with an internal volume of 300 mL suitable for a pressure of 100 bars. This  
 139 stirred autoclave reactor consisted of a reactor vessel and a cylindrical capping vessel. The

140 capping vessel included a central connection for a magnetic stirrer (max. 1500rpm, 50 W) and  
141 connections for measuring pressure, monitoring temperatures, and releasing the gases. For each  
142 HTC run,  $18.65 \pm 0.05$  g of dry sample were loaded into the reactor together with  $186.5 \pm 1.5$  g of  
143 deionized water, with a biomass-to-water ratio (AS/W) equal to 1/10 (w/w). Before starting the  
144 heating program, the residual air inside the reactor was removed using a vacuum pump to a  
145 pressure of less than 40 mbar. The reactor was heated from room temperature to setpoint  
146 temperature at different powers supplied in the reactor 160, 200, and 240 W; these represent  
147 overall average heating rate of 1.5, 2.0, and 2.8 °C/min, respectively. The setpoint temperature  
148 was varied from 150 °C to 250 °C. For powers of 160 and 240 W, the setpoint temperatures were  
149 150, 170, 190, 210, 230 and 250 °C, while for power of 200 W the setpoint temperatures were  
150 150 to 250 °C with a 10 °C increase. The setpoint temperatures of 150, 190, and 250 °C were  
151 carried out in triplicate; allowing to define an error less than 1.5% in all cases. During the  
152 experiment, the reactor was stirred at 550 rpm. After the reactor reaches the setpoint temperature,  
153 it was immediately cooled down, and this took 5 to 10 minutes to cool it down by immersing it in  
154 a 5 °C water bath. After cooling the reactor, the system pressure was noted, the reactor was  
155 opened, the liquid and solids were separated with a Whatman filter paper with a pore size of 11  
156 microns, and the solid was weighed after drying at 105 °C for 24 hours in the stove. The  
157 hydrochar yield or total solid yield ( $Y_{HC}$ ) was determined through the **Eq.( 1)**:

$$Y_{HC} = \frac{m_{HC}}{m_{bio}} \cdot 100 \quad (1)$$

158 Where  $m_{HC}$  is the mass of total solid (on a dry base), and  $m_{bio}$  is the raw biomass mass (on a dry  
159 base). The derivative hydrochar yield ( $DY_{HC}$ ) is the first-order derivative of  $Y_{HC}$  with respect to  
160 time. From this approach, it is possible to determine the maximum temperature decomposition of  
161 biomass. The  $DY_{HC}$  was determined through the **Eq.( 2)**:

$$DY_{HC} = \frac{\Delta Y_{HC}}{\Delta t} \quad (2)$$

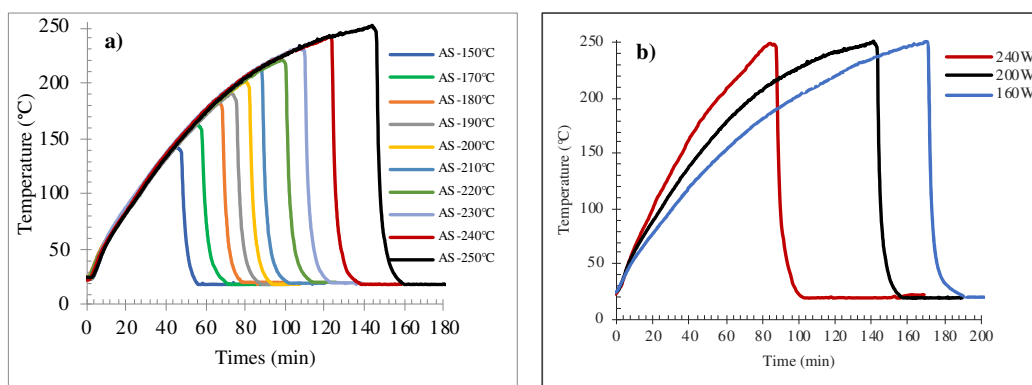
162 Where  $DY_{HC}$  is derivative hydrochar yield (%/min),  $\Delta Y_{HC}$  is the difference between  $Y_{HC}$  from  
163 one setpoint temperature to another, and  $\Delta t$  is the time variation (min) between setpoint  
164 temperatures.

### 165 **2.3 HTC reactor heat-up and reaction time**

166 In reality, the constant temperature during HTC is not correct in batch autoclave reactors because  
167 there are different step of heating: i) a heating time, ii) a holding time temperature, and finally,

168 iii) a cooling time. In many publications in the literature, the definition of reaction time is not  
169 standardized. Often, HTC reaction time starts to be counted when the set HTC temperature is  
170 reached [4] while in some other cases [32] includes heat-up time. The heat-up time may be  
171 neglected only if it is very rapid as it could be the case when the HTC is performed in batch  
172 micro-reactors. In this study, an open-loop system was used, where the power supplied to the  
173 furnace of the reactor is controlled (i.e., constant in each experiment), and we consider the  
174 reaction time of the HTC is the heat-up time until the setpoint temperature is reached.

175 **Fig. 1** shows the different heating time profiles established for different setpoint temperatures at  
176 200 W electrical power (**Fig. 1a**) and for the different electrical powers used (**Fig. 1b**). In this  
177 case, holding time temperature and cooling time was not considered because when the setpoint  
178 temperature was reached, the reactor was cold down from setpoint temperature to room  
179 temperature; it took 5 to10 minutes to cool it down by immersing it in a 5°C water bath.



180  
181 **Fig. 1:** Temperature trends vs. time of hydrothermal tests, (a) conducted at 200W to set-point  
182 temperature, (b) different powers (heating rate) from ambient temperature to 250 °C.

#### 183 184 **2.4 Secondary hydrochar extraction and GC–MS analyzer**

185 Extraction of S-HC was performed with toluene (100%) as the extraction solvent in a Soxhlet  
186 extractor. Toluene is a good solvent for the extraction of tar, such as PAHs, in hydrochar [33].

187 For each extraction, about 2 g of hydrochar and 250 mL toluene were placed in the Soxhlet  
188 extractor for 36 h. After this time, the solution was concentrated by a rotary evaporator to obtain  
189 25 mL volume. The S-HC composition was detected using a GC–MS analyzer. The analysis was  
190 carried out by two different methods and columns to detect aliphatic and PAHs compounds.

191 Aliphatic compounds were detected on a Trace Ultra-ISQ gas chromatograph single quadrupole  
192 mass spectrometer (Thermo Scientific, Villebon Sur Yvette, France) equipped with a



193 programmed temperature vaporizing injector (PTV) and a 2 mm diameter. Thermo PTV liner  
194 was used. A DB35ms column (30 m length, 0.25 mm internal diameter, and 0.25  $\mu\text{m}$  film  
195 thickness) was installed in the GC oven. Initially the temperature of the GC oven was set at 80  
196  $^{\circ}\text{C}$  for 2 min followed by a 10  $^{\circ}\text{C}/\text{min}$  ramp to 200  $^{\circ}\text{C}$  and a 15  $^{\circ}\text{C}/\text{min}$  ramp to 320  $^{\circ}\text{C}$  with a 5  
197 min hold. For the data acquisition using the Electron Impact (EI) mode, the transfer line  
198 temperature and the ion source were held at 315  $^{\circ}\text{C}$  and 250  $^{\circ}\text{C}$ , respectively. A mass range ( $m/z$   
199 50–300 amu with a dwell time of 0.2s) was scanned in full scan acquisition. In order to detect  
200 PAHs, the extracted liquid was diluted 50 times in dichloromethane. The PAHs were detected on  
201 a Trace Ultra gas chromatography coupled with a quadrupole mass spectrometer. A DB17ms  
202 Agilent column (30 m length, 0.32 mm internal diameter, and 0.25  $\mu\text{m}$  film thickness) was  
203 installed in the GC oven. Initially, the temperature of the GC oven was set at 40  $^{\circ}\text{C}$  for 7 min  
204 followed by a 20  $^{\circ}\text{C}/\text{min}$  ramp to 75  $^{\circ}\text{C}$ , and it was held on for 15 minutes and then a 20  $^{\circ}\text{C}/\text{min}$   
205 ramp to 200  $^{\circ}\text{C}$  for 8 minutes, and finally a 10  $^{\circ}\text{C}/\text{min}$  ramp to 220  $^{\circ}\text{C}$ , and it was held on for 55  
206 minutes. For the data acquisition using the Electron Impact (EI) mode, both the temperature of  
207 the transfer line and the ion source was held at 200  $^{\circ}\text{C}$ . The temperature for the inlet injector was  
208 fixed at 300  $^{\circ}\text{C}$  for attaining a well-vaporization of the sample, and a spitless liner was installed.  
209 A mass range ( $m/z$ ) of 50–300 amu was scanned, that is, in full scan acquisition.

## 210 **2.5 Kinetic models and mechanisms of the HTC process of biomass**

211 A model is a theoretical and mathematical description of what occurs experimentally. This study  
212 will analyze the kinetic models that can describe the kinetic reaction of the HTC process of the  
213 biomass, based only on the formation of hydrochar (evolution of the solid phase). The overall  
214 reaction of the biomass in the HTC process is presented in the following reaction:



215 The mass yield of the solid or hydrochar produced during HTC for time ( $d\alpha/dt$ ), depends on the  
216 rate of reaction constants, which are influenced by temperature [ $k(T)$ ] and reaction model [ $f(\alpha)$ ],  
217 expressed as:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (4)$$

218 where  $k(T)$  is the reaction rate constant depending on the temperature,  $f(\alpha)$  is the function of  $\alpha$ ,  
219 and  $\alpha$  is the conversion or weight loss rate that can be calculated with the following equation:

$$\alpha = \frac{m_{\text{bio}} - m_{\text{HC}_T}}{m_{\text{bio}} - m_{\text{HC}_\infty}} \quad (5)$$

220 where  $m_{\text{bio}}$  (g), is the initial weight of the sample,  $m_{\text{HC}_T}$  (g) is the weight of the sample at a  
 221 given temperature and time, and  $m_{\text{HC}_\infty}$  (g) is the final sample weight. The solid conversion rate  
 222 ( $d\alpha/dt$ ) can be expressed as:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = k(T) \cdot f(\alpha) \quad (6)$$

223 where  $\beta$  is the heating rate or the rate of temperature change ( $dT/dt$ , K/min).

224 The kinetic parameters were determined using two HTC temperature zones (150-210 °C and  
 225 210-250 °C). For each temperature range, the biomass samples were subjected to three heating  
 226 powers (160, 200 and 240 W). These powers correspond to different average value of  $\beta$   
 227 depending on the temperature zone. In the first zone, the  $\beta$  values corresponding to the powers  
 228 were 1.8, 2.3 and 3 °C/min, while in the second zone the  $\beta$  values were 0.7, 1.25 and 1.8 °C/min.  
 229 The continuous decrease of  $\beta$  value for the duration of the experiment at the same power is due  
 230 to heat loss. However, for each power in the given temperature range, the value of  $\beta$  can be  
 231 considered constant. As shown in **Fig. 1**, the temperature profile as a function of time at 150-210  
 232 °C; and 210-250 °C, can be considered as straight lines with  $R^2 > 0.983$  for each.

233 The  $k(T)$  can be described according to the Arrhenius equation:

$$k(T) = A \cdot e^{\frac{-E\alpha}{RT}} \quad (7)$$

234 where  $A$  ( $\text{min}^{-1}$ ) refers to the pre-exponential factor, and  $E\alpha$  (J/mol) is the apparent activation  
 235 energy,  $T$  (K) represent the absolute temperature, and  $R$  universal gas constant (8.314 J/  
 236 ( $\text{mol} \cdot \text{K}$ )), respectively. Substituting Eq. (7) into (6) gives the following equation:

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = A \cdot e^{\frac{-E\alpha}{RT}} \cdot f(\alpha) \quad (8)$$

237 The integral form of  $f(\alpha)$  can be obtained after integrating Eq. (8) with respect to temperature.

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{\frac{-E\alpha}{RT}} dT \quad (9)$$

238 where  $g(\alpha)$  is the integrated reaction model, and some common forms of  $f(\alpha)$  and  $g(\alpha)$  for solid-  
 239 state reactions are described in **Table 2**.

240 **Table 2:** Expressions for functions  $f(\alpha)$  and  $g(\alpha)$  of some reaction models to describe thermal  
 241 decomposition solid state reactions [34]

Symbols	Reaction models	Differential form $f(\alpha)$	Integral form $g(\alpha)$
		Reaction order models	

R1	First order	$1 - \alpha$	$-\ln(1 - \alpha)$
R2	Second order	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$
R3	Third order	$(1 - \alpha)^3$	$[(1 - \alpha)^{-2} - 1]/2$
R4	One and half order	$(1 - \alpha)^{3/2}$	$[(1 - \alpha)^{-1/2} - 1]$
Diffusion models			
D1	1D diffusion	$1/2\alpha$	$\alpha^2$
D2	2D diffusion-Valensi	$[-\ln(1 - \alpha)]^{-1}$	$(1 - \alpha)\ln(1 - \alpha) + \alpha$
D3	3D diffusion-Jander	$(1 - \alpha)^{3/2}/[1 - (1 - \alpha)^{1/3}]$	$[1 - (1 - \alpha)^{1/3}]^2$
D4	3D diffusion-Ginstling	$(3/2)/[(1 - \alpha)^{-1/3} - 1]$	$1 - 2\alpha/3 - (1 - \alpha)^{2/3}$
Power law nucleation Models			
P1	Power law (1)	$(2/3)\alpha^{-1/2}$	$\alpha^{3/2}$
P2	Power law (2)	$2\alpha^{1/2}$	$\alpha^{1/2}$
P3	Power law (3)	$3\alpha^{2/3}$	$\alpha^{1/3}$
P4	Power law (4)	$4\alpha^{3/4}$	$\alpha^{1/4}$
Random nucleation and subsequent growth Models			
A1	Avrami-Erofeev (1)	$(3/2)(1 - \alpha)[- \ln(1 - \alpha)]^{1/3}$	$[- \ln(1 - \alpha)]^{2/3}$
A2	Avrami-Erofeev (2)	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	$[- \ln(1 - \alpha)]^{1/2}$
A3	Avrami-Erofeev (3)	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	$[- \ln(1 - \alpha)]^{1/3}$
A4	Avrami-Erofeev (4)	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	$[- \ln(1 - \alpha)]^{1/4}$
A5	Random nucleation (1)	$(1 - \alpha)^2$	$1/(1 - \alpha)$
A6	Random nucleation (2)	$(1 - \alpha)^3/2$	$1/(1 - \alpha)^2$
Geometrical contraction models			
F1	Contracting area	$2(1 - \alpha)^{1/3}$	$1 - (1 - \alpha)^{1/2}$
F2	Contracting volume	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$

242 The kinetics of thermal reactions in solids has been widely studied in the literature [34]. There  
 243 are two main methods to determine the kinetic parameters, the model-free methods, and the  
 244 model-fitting method.

### 245 2.5.1 Model-free method

246 The model-free method has been used in the pyrolysis, gasification, and combustion kinetic  
 247 model and allows the kinetic parameters to be calculated as a function of the degree of  
 248 conversion. Different methods have been used, such as the differential method proposed by  
 249 Friedman and the integral methods, such as the FWO method and KAS method [46-48].

250 *Friedman method:* The Friedman method is the most common differential isoconversion method  
 251 for determining activation energy as a function of conversion  $\alpha$ , and it is given in the following  
 252 equation:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta \frac{d\alpha}{dt}\right) = \ln[A_\alpha f(\alpha)] - \frac{E\alpha}{RT} \quad (10)$$

253  $E_a$  can be obtained from the slope of the fit line drawn between  $\ln\left(\beta \frac{d\alpha}{dt}\right)$  versus  $\frac{1}{T}$ .

254 *FWO method:* This method is derived from the integral isoconversional method. The method  
 255 uses the linear Doyle's approximation for the estimation of temperature integral [35], and it is  
 256 given in the following equation:

$$\ln \beta = \ln \frac{AE\alpha}{Rg(\alpha)} - 5.331 - 1.052 \frac{E\alpha}{RT} \quad (11)$$

257 Plots of  $\ln \beta$  vs.  $1/T$ , at fixed value of conversion help in evaluating the activation energy from  
 258 the slope of straight-line plot.

259 *KAS method:* The KAS method is based on the Coats–Redfern approximation and it is given in  
 260 the following equation:

$$\ln \frac{\beta}{T^2} = \ln \frac{AR}{E\alpha g(\alpha)} - \frac{E\alpha}{RT} \quad (12)$$

261 For a constant value of  $\alpha$ , the activation energy  $E\alpha$  can be obtained from the plot of  $\ln \frac{\beta}{T^2}$  against  
 262  $\frac{1}{T}$  with  $-E\alpha/R$  as the slope.

263 Several solid-state kinetic models have been discussed in the literature, and many different  
 264 reaction mechanisms have been proposed to describe solid-state reactions, some of which are  
 265 listed in **Table 2**. The models can be expressed in a differential form  $f(\alpha)$  and an integral form  
 266  $g(\alpha)$ . The most used reaction mechanisms are described below.

### 267 2.5.2 Model-fitting methods

268 Model-fitting methods are commonly applied because the kinetic parameters can be determined  
 269 and provide information about possible reaction mechanism models. The Coats-Redfern method,  
 270 the most popular form of model-fitting, proposed in 1964 [36], uses Taylor's series approach by  
 271 limiting the number of terms in the series. The Taylor series expansion form can be given as:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{-\frac{E\alpha}{RT}} dT = \frac{AE\alpha}{\beta R} \int_x^\infty \frac{e^{-x}}{x^2} dx \quad (13)$$

$$g(\alpha) = \frac{AE\alpha}{\beta R} \int_x^\infty \frac{e^{-x}}{x^2} dx \cong \frac{AE\alpha}{\beta R} \left[ \frac{e^{-x}}{x^2} \left( 1 - \frac{2!}{x} + \frac{3!}{x^2} - \frac{4!}{x^3} + \dots \right) \right] \quad (14)$$

$$\frac{AE\alpha}{\beta R} \left[ \frac{e^{-x}}{x^2} \left( 1 - \frac{2!}{x} + \frac{3!}{x^2} - \frac{4!}{x^3} + \dots \right) \right] = \frac{AE\alpha}{\beta R} p(x) \quad (15)$$

272 where  $x$  is equal to  $\frac{E\alpha}{RT}$ , the  $p(x)$  is the temperature integral and it has no analytical solution.

273 Therefore, **Eq. (15)** can only be solved using either numerical integration or approximation to  
 274 deal with the complex integral. By introducing an approximation  $p(x) = x^{-2}e^{-x}$  ( $20 \leq x \leq 50$ ) into  
 275 **Eq. (14)**, the relationship between heating rate and inverse temperature becomes:

$$g(\alpha) = \frac{ART^2}{\beta E\alpha} \left( 1 - \frac{2RT}{E\alpha} \right) e^{-\frac{E\alpha}{RT}} \quad (16)$$

276 Taking the natural logarithm of both sides of **Eq. (16)**.

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{\beta E\alpha} \left(1 - \frac{2RT}{E\alpha}\right) - \frac{E\alpha}{RT} \quad (17)$$

277 Since  $2RT/E\alpha \ll 1$ , the equation can be converted into

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{\beta E\alpha} - \frac{E\alpha}{RT} \quad (18)$$

278 For a fixed  $\beta$  and proposed reaction mechanism  $g(\alpha)$ , plotting  $\ln \frac{g(\alpha)}{T^2}$  versus  $\frac{1}{T}$  gives a straight  
 279 line. The equations corresponding to  $g(\alpha)$  are presented in **Table 2**. The slope  $-E\alpha/R$  and  
 280 intercept  $\ln \frac{AR}{\beta E\alpha}$  can be used to determine  $E\alpha$  and  $A$ , respectively [37].

### 281 **2.5.3 Kinetic reaction mechanism models**

282 All kinetic reaction mechanism models used in this study are presented in **Table 2**. Most solids  
 283 contain different defects, weak points that can initiate physical and chemical changes during their  
 284 reaction. These defects play an essential role when nucleation is the limiting step in a reaction  
 285 [38]. If the reaction involves random nucleation followed by the growth of nuclei of a defined  
 286 dimensionality, the Avrami-Erofeev equation can be derived and applied; in some cases, the  
 287 nucleation rate follows the power law [37, 39]. In other cases, the solid-state reactions, are  
 288 controlled by diffusion of the reagents or products. This situation is not common because the  
 289 mass transfer in the solid-state is slower [39, 40]; however, in HTC processes, where one of the  
 290 most important reactions is hydrolysis [23, 41], which modifies the biomass structure, the  
 291 diffusion of water into the pores of the biomass particles can control the reaction mechanisms.  
 292 This phenomenon was explained by Reza et al. [42]. Some solid-state reactions involve two or  
 293 more substances, where phase boundaries are formed between the reagents and the products. In  
 294 this case, the advance in the phase boundary thus formed determines that reaction rate [38].  
 295 When the advancement of the phase boundary is one-dimensional, a reaction of zero-order is  
 296 obtained; if the phase boundary is two-dimensional the contracting area models is generated and  
 297 if the phase boundary is three-dimensional, the contracting volume is obtained [43]; these  
 298 models are based on the assumption of spherical solid particles. Finally, the kinetics of the solid-  
 299 state reaction can be controlled by the order of the reaction. These models are the simplest as  
 300 they are similar to those used in homogenous kinetics [24, 44]. Often, first and second-order  
 301 reactions are used. Higher-order reactions are rarely used and difficult to interpret in solid-state  
 302 reactions [38].

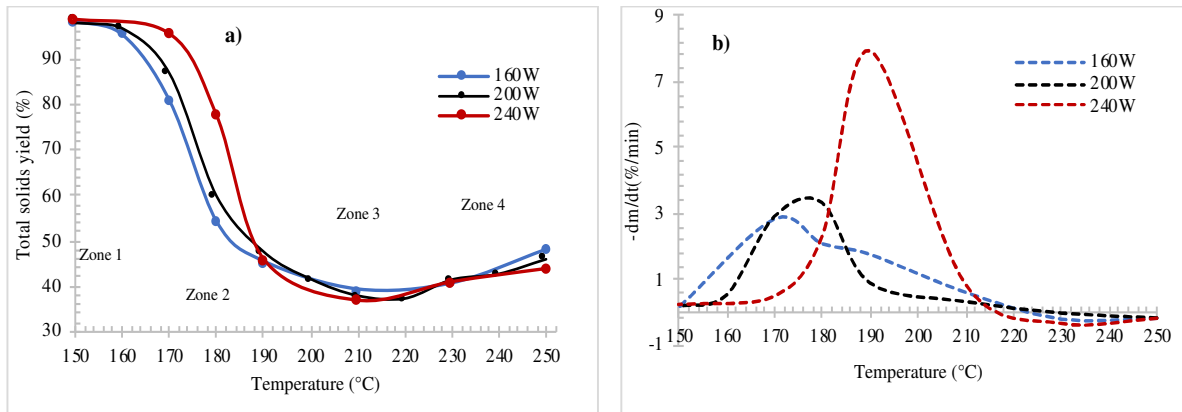
### 303 3 RESULTS AND DISCUSSION

#### 304 3.1 Mass yield and derivative mass yield analysis

305 The  $Y_{HC}$  and  $DY_{HC}$  curves of the AS at different powers applied in the reactor corresponding to  
306 different heating rates are shown in **Fig. 2a**. The evolution with the temperature at different  
307 heating rates of  $Y_{HC}$  is calculated based on the **Eq.( 1)** at different temperatures. Four distinct  
308 zones can be identified in the **Fig. 2a**. Up to 160 °C, initial induction period is observed in which  
309 the reaction rate is quite slow (first zone). In this period, the energy in the reaction medium is not  
310 high enough to reach activation energy. The reaction starts in the second zone, at a temperature  
311 of ~160 °C; in this zone, the maximum rate of biomass decomposition is observed, and it is  
312 finished at approximately 200 °C.

313 This decrease in mass yield is due to decomposition reactions of biomasses, such as hydrolysis,  
314 dehydration, decarboxylation, and so forth [41]. The hydrolysis breaks down the biomass  
315 chemical structure through cleavage of ester and ether bonds of bio-macromolecules with water  
316 molecules. This process creates (oligo-) saccharides and fragments of lignin that enter the liquid  
317 phase [45, 46] thus reducing the total solid yield, as shown in **Fig. 2a**. The hydrolyzed products  
318 can degrade into furfurals, particularly 5-hydroxymethylfurfural, aldehyde, erythrose, and with  
319 undergo dehydration and decarboxylation [47]. Dehydration removes water from the biomass  
320 matrix without changing its chemical constitution, evidenced by the increased carbon contents  
321 and decreased oxygen contents. Decarboxylation involves the degradation of hemicellulose and  
322 cellulose; these materials can degrade into monomers, such as acetic acid, formic acid, lactic  
323 acid, and furfurals further degrade into  $CO_2$  and  $H_2O$  [42]. The decarboxylation reaction removes  
324 carboxyl and carbonyl groups. Carboxyl and carbonyl groups rapidly degrade above 150-180 °C,  
325 yielding  $CO_2$ , and  $CO$ , respectively [48]. All these reactions mentioned above are decomposition  
326 reactions, causing a decrease in the total solid yield and increasing the liquid and gas production.  
327 The low decomposition temperature of this biomass can be related to its high content of  
328 hemicellulose (76.4%) or biomolecules with solubilities similar to that of hemicellulose. Other  
329 reaction mechanisms of HTC are aromatization and polymerization. HTC increases the  
330 production of aromatics from intermediates products formed during hydrolysis [42]. Moreover,  
331 lignin is composed of many aromatic compounds polymerized by various linkages. Hydrochar  
332 produced during HTC is a cross-linked polymer and has similar properties to lignin, so

333 hydrochar is almost impossible to distinguish from the unreacted lignin fraction. Also, a  
334 polymer, such as cellulose and hemicellulose can be converted into a cross-linked polymer  
335 similar to lignin [49, 50].



336

337 **Fig. 2:** Evolution with temperature, a) the total solids yield ( $Y_{HC}$ ), b) and derivative of total solids yield  
338 ( $DY_{HC}$ ) at different power (160, 200 and 240W).

339 The stability of the aromatic structures is a basic element in the hydrochar formation. This  
340 stability is observed in zone 3, between 200 and 220 °C, as shown in **Fig. 2a**. The intermediates  
341 of unsaturated compounds such as aldehydes, furfural, and 5-HMF produced from dehydration  
342 and decarboxylation reactions are highly reactive. These monomers are followed by  
343 condensation, polymerization, and aromatization to form S-HC [5, 42]. The S-HC formation  
344 increases the total solid yield, as shown in zone 4 in **Fig. 2a**, between 220 and 250 °C. Similar  
345 increases of the total solid yield were observed by Yang et al. [51] during the cellulose  
346 carbonization at a temperature above 275 °C. The inclusion of a stirrer in the reactor helps obtain  
347 a uniform biomass/water mixture inside the reactor, avoiding concentration or temperature  
348 gradients inside the reactor; this may increase the reaction mechanisms in the HTC process. The  
349 increased reaction mechanism can lead to rapid polymerization of the intermediates of  
350 unsaturated compounds produced from dehydration and decarboxylation.

351 The heating rate is an essential factor during the thermochemical conversion process of biomass  
352 since it affects the process through a heat transfer and mass transfer through the biomass  
353 particles. In the **Fig. 2**, the  $Y_{HC}$  and  $DY_{HC}$  are represented at various heating rates. However,

354  $DY_{HC}$  curve (**Fig. 2b**) became sharper as the heating rate increased. Higher heating rates  
355 significantly enhanced total solid yield loss rates than those by the lower heating rates.

356 **Fig. 2b** shows that the peaks of  $DY_{HC}$  curves slightly shifted to the right as the heating rate  
357 increased this can be explained by the fact that the gradient temperature of a particle and  
358 distribution of temperature was smaller at low heating rates. The maximum decomposition peaks  
359 were observed of 174, 182, and 189 °C for a power of 160, 200, and 240 W, respectively.

### 360 **3.2 Secondary hydrochar analysis.**

361 The condensation, polymerization, and aromatization reactions form secondary hydrochar on the  
362 surface of the primary hydrochar. This secondary hydrochar is derived from the decomposition  
363 of hemicellulose, and cellulose, followed by polymerization of intermediates product into  
364 amorphous carbonaceous compounds during HTC. The increase in temperature and time of HTC  
365 gradually increases the amorphous carbon, such as aliphatic and aromatic groups on the surface  
366 of the primary hydrochar [52]. The condensation of amorphous carbon on the primary hydrochar  
367 surface during HTC results in the retention of PAHs [20]. This secondary hydrochar was  
368 extracted from the total solids produced at 190, 210, 230, and 250 °C at a heating power of 1.5  
369 °C/min by extracting Soxhlet with toluene (100%). Extraction was also done with raw biomass.  
370 The amount extracted in the hydrochar structures and the raw biomass is presented in **Table 3**. It  
371 was noteworthy to note that a significant increase in secondary hydrochar removed in total  
372 solids produced was observed when the temperature was above 190 °C; this explains the increase  
373 in total solid yield or total hydrochar as explained in **section 3.1, Fig. 2**. The analyses of liquid  
374 solutions of secondary hydrochar and biomass extractive compounds show different aliphatic  
375 and PAHs compounds.

376 **Table 3:** The secondary hydrochar removed in total solids yield at different HTC temperatures.

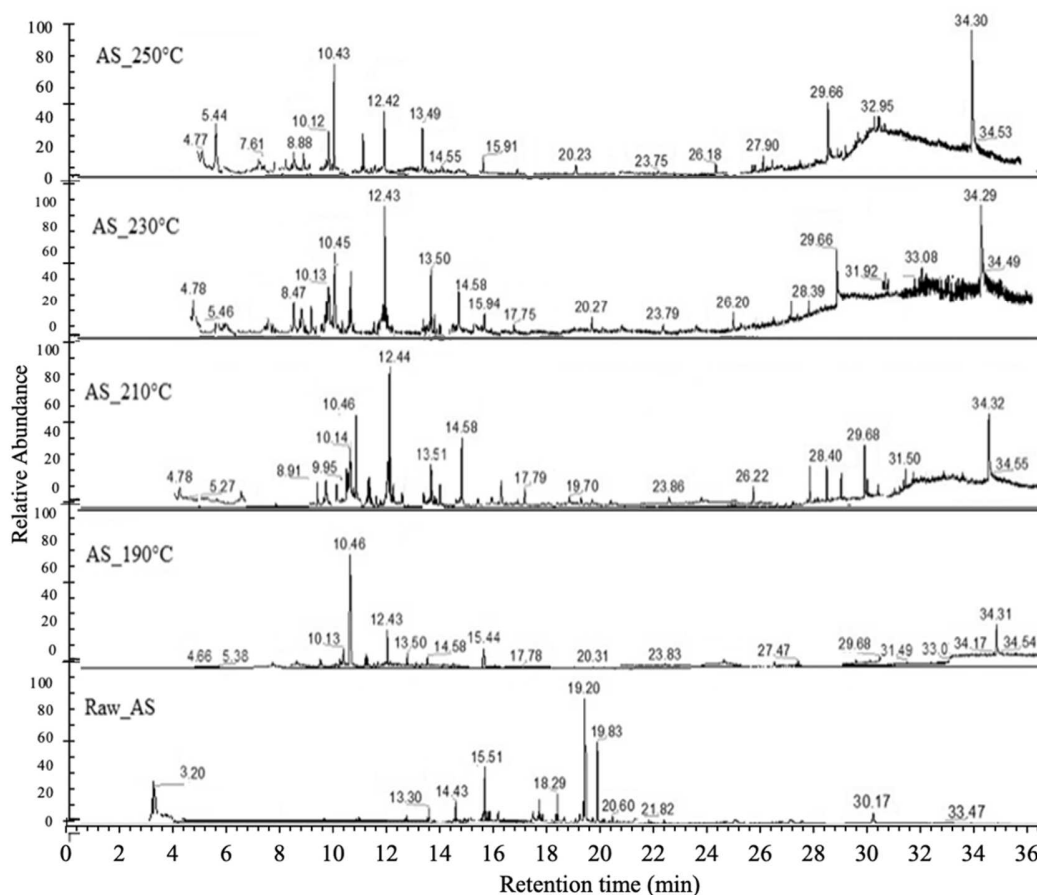
HTC-Temperature	Extracted secondary hydrochar. (wt.%)
AS_250°C	19.01
AS_230°C	13.86
AS_210°C	10.05
AS_190°C	5.48
Raw_AS	3.80



377 **3.2.1 Aliphatic content analysis**

378 The long-chain aliphatic hydrocarbons that were found are shown in **Fig. 3**. During HTC, a  
379 series of reactions of the coalification occurred. The oxygenated hydrocarbons are initially  
380 converted to aliphatic (alkanes, olefins) and aromatics compounds and then transformed to  
381 higher hydrocarbons and larger PAHs with a further increase in temperature [17]. The high  
382 molecular weight hydrocarbons, which were found in the S-HC solution, include long chain  
383 alkanes, such as tetradecane (RT  $\approx$ 8.9min), pentadecane (RT  $\approx$ 10.1min), hexadecane (RT  $\approx$   
384 11.3min), heptadecane (RT  $\approx$  12.4min), octadecane (RT  $\approx$  13.5min), and eicosane (RT  $\approx$   
385 14.6min). The signal of these aliphatic compounds increases with increasing temperature, and it  
386 was not detected in the S-HC solution removed from the raw biomass.

387 The main olefin of high molecular weight detected was 9-octadecenoic acid (oleic acid), an 18-  
388 carbon monounsaturated fatty acid (RT  $\approx$  34.3min). Also, it was detected 9-octadecenamide  
389 (RT $\approx$  29.7min), an amide derived from oleic fatty acid. All these compounds were detected in all  
390 the hydrochars produced. The intensity of the peaks increases, with the increase of the  
391 temperature, they confirm the formation of tars on the hydrochar structure. The condensation of  
392 these aliphatic compounds on hydrochar surface results in retention of PAHs [20]. Unlike the  
393 hydrochar produced, the components that were detected in the raw biomass extractable were  
394 mainly fatty acids, such as stearic acid (RT  $\approx$  19.20min) and (11E)-11-octadecenoic acid (RT $\approx$   
395 19.83min).

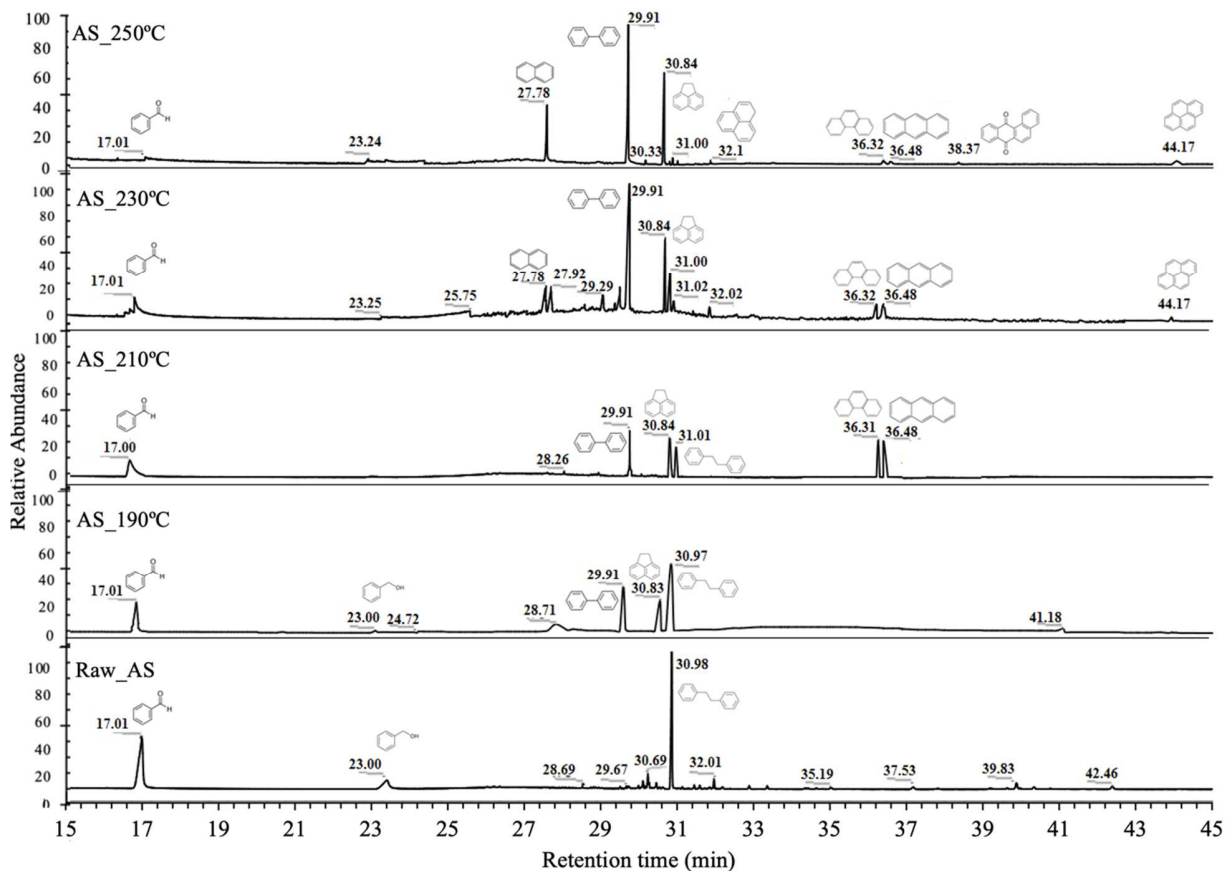


396

397 **Fig. 3:** The main aliphatic compounds detected in secondary hydrochar solution removed in the hydrochar  
 398 structure and raw AS.

### 399 3.2.2 PAHs content analysis.

400 The chromatogram of total PAHs in hydrochar and raw AS are presented in **Fig. 4**. The results  
 401 showed that total PAHs in the hydrochars were higher than those in raw AS. The PAHs detected  
 402 in the raw biomass was bibenzyl (RT $\approx$  30.98min), the simplest PAHs (2 rings). The peak with a  
 403 retention time of 17 and 23min are benzaldehyde and Benzyl alcohol, respectively. The number  
 404 of PAHs detected in the hydrochars increases with increasing temperature; this may be explained  
 405 by polymerization and aromatization reactions during the HTC process. At the lower temperature  
 406 of HTC (190°C and 210°C), the PAHs detected were mainly 2-3 rings.



407  
 408 **Fig. 4:** The main PAHs compounds detected in secondary hydrochar solution removed in the hydrochar  
 409 structure and raw AS.

410 The 2-ring were biphenyl, bibenzyl, and naphthalene with the retention time of 29.91, 31 and  
 411 27.78min respectively. The PAHs with 3 rings detected were acenaphthene, phenanthrene, and  
 412 anthracene with retention times 30.84, 36.32, and 36.48min, respectively. In addition to the fact  
 413 that all these mentioned PAHs were detected at a high temperature of HTC (230 and 250 °C),  
 414 other PAHs were detected, such as 4-methyl biphenyl, acenaphthene, cis-stilbene, 1H-phenalene,  
 415 and pyrene, with the retention time of 30.33, 31.07, 31.22 32.1, and 44.17 min respectively. At a  
 416 temperature of 250°C, another 4-ring oxygenated PAHs was detected, such as 7,12-  
 417 dihydrobenzo[a]anthracene, with the retention time of 38.37min. At low temperatures, the  
 418 biomass was subjected to initial hydrolysis, dehydration, and depolymerization reaction [47],  
 419 which led to a decrease in total PAHs because the polymerization and aromatization reaction  
 420 have not started.. The intermediates unsaturated compounds produced from dehydration and  
 421 decarboxylation promoted PAHs formation with increasing temperature by aromatization and

422 polymerization reactions, so increasing the PAHs rings formed. The hydrochars obtained at  
 423 temperatures from 190 to 210 °C, biphenyl and bibenzyl (2 rings) were dominant while  
 424 phenanthrene, Anthracene, and Pyrene were most prevalent at high HTC temperature (230 - 250  
 425 °C).

### 426 3.3 Kinetic analysis results

427 Thermal analysis methods are currently used to determine the reactivities and mechanisms of  
 428 thermal reactions of solids. Estimation of kinetic parameters involves activation energy and pre-  
 429 exponential factor. This study proposes different model-free methods, such as FWO, KAS, and  
 430 Friedman to determine AS kinetic parameters during HTC. Although model-free methods can  
 431 reliably estimate the kinetic parameters, the information obtained is limited, It do not allow to  
 432 define the reaction mechanism unlike model-fitting methods [53].

#### 433 3.3.1 Model-free method

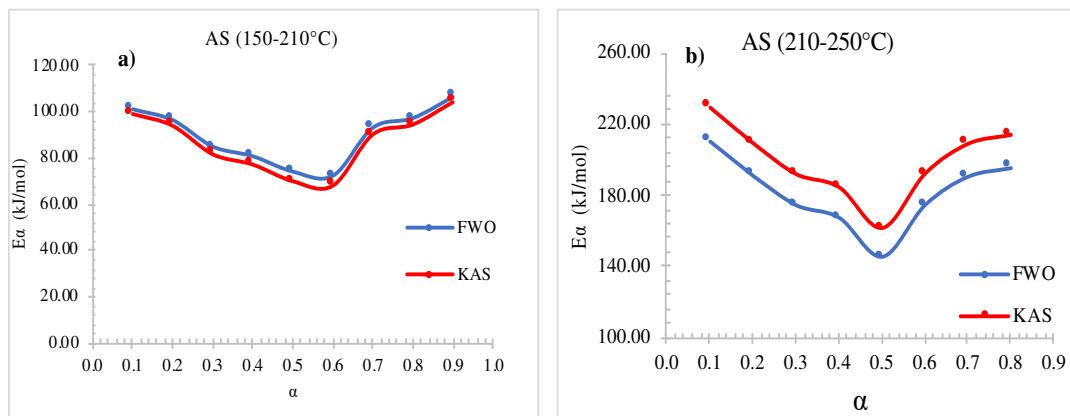
434 In this study, model-free methods first analyzed the kinetics of the HTC of AS. Starting from **Eq.**  
 435 ( 5) and applying above mentioned isoconversional methods. The activation energy ( $E\alpha$ ), pre-  
 436 exponential factor (A), and linear correlation coefficient ( $R^2$ ) at various conversion rates of 0.1–  
 437 0.9 were calculated using the FWO, KAS, and Friedman methods. The calculated average values  
 438 of  $E\alpha$ , A, and  $R^2$  are shown in **Table 4**. These parameters were calculated in two zones of HTC  
 439 temperature. The first zone corresponds to the decrease in the  $Y_{HC}$  between 150 and 210 °C, and  
 440 the second zone corresponds to the increase of the  $Y_{HC}$  from 210 to 250 °C where appears  
 441 formation of heavy PAHs

442 **Table 4:** Kinetic parameters of AS determined by the model-free kinetics methods.

Temperature (°C)	FWO			KAS			Friedman		
	$E\alpha$ (kJ/mol)	A (min <sup>-1</sup> )	$R^2$	$E\alpha$ (kJ/mol)	A (min <sup>-1</sup> )	$R^2$	$E\alpha$ (kJ/mol)	A (min <sup>-1</sup> )	$R^2$
150-210	89.61±12.19	7.55x10 <sup>9</sup>	0.982	86.79±12.82	3.39x10 <sup>9</sup>	0.979	73.81±35.47	2.24x10 <sup>12</sup>	0.630
210-250	181.28±20.13	78x10 <sup>-19</sup>	0.909	199.12±21.16	1.38x10 <sup>-19</sup>	0.916	223.27±31.56	2.49x10 <sup>-6</sup>	0.801

443 As shown in **Table 4**, the  $E\alpha$  values obtained for the integral methods (FWO and KAS) are  
 444 similar and show the best fit correlation coefficient ( $R^2$ ) compared to the differential method  
 445 (Friedman). The Friedman method requires derivative conversion data, which would lead to  
 446 being numerically unstable and noise-sensitive [54]. For this reason, in general, the integral  
 447 methods show the best-fit correlation coefficient values than the differential method.

448 In the first zone, the HTC temperatures were between 150 and 210 °C. The average  $E_a$  values  
 449 were  $89.61 \pm 12.19$  kJ/mol,  $86.79 \pm 12.82$  kJ/mol. The small differences observed in  $E_a$  values  
 450 obtained using KAS and FWO can be assigned to the different approximations of the  
 451 temperature integral. In **Fig. 5a**, it can be observed that the values of  $E_a$  are not similar for all  
 452 conversion values, indicating the existence of a complex multi-step mechanism reaction that  
 453 occurs in the biomass HTC process. The progressive variation of  $E_a$  values could correspond to  
 454 competitive or consecutive reactions and the multiphasic biomass conversion. For  $\alpha$  values from  
 455 0.1 to 0.6, a decrease of  $E_a$  from 99 to 68 kJ/mol. However, from 0.6, an increase of  $E_a$  is  
 456 observed; this may be due to the change of the mechanism of chemical reactions. In this range of  
 457 HTC temperature, similar values of  $E_a$  were reported by Killer et al. [26] for cellulose and  
 458 hemicellulose using the nonlinear least-square minimization method. The values obtained were  
 459 61 kJ/mol and 127 kJ/mol for hemicellulose and cellulose. Also, Danso-Boateng et al. [55]  
 460 reported the value of activation energy (77.8 kJ/mol, with pre-exponential factor  $1.5 \times 10^7 \text{ min}^{-1}$ )  
 461 for synthetic feces and 70.4 kJ/mol, with a pre-exponential factor of  $4.0 \times 10^6 \text{ min}^{-1}$  for primary  
 462 sewage sludge.



463  
 464 **Fig. 5:**  $E_a$  values according to the degree of conversion ( $\alpha$ ) for HTC process of (a) 150 to 210 °C and (b)  
 465 150 to 210 °C of HTC temperature according to the FWO and KAS.

466 In the second zone (210 to 250 °C), they corresponded to an increase in  $Y_{HC}$  for AS. The  $E_a$   
 467 values are displayed in **Table 4** and **Fig. 5b**. The values obtained are a similar trend for integral  
 468 methods.

469 As in the previous one, there is also a change in the trend of  $E_a$  showing a complex multi-step  
 470 mechanism reaction. The values of  $E_a$  vary from 145.28 to 210.74 kJ/mol and 245.28 to 229.95

471 kJ/mol for FWO and KAS respectively. As a comparison, the FWO and KAS method was more  
 472 reliably attributed to its higher  $R^2$  values. The high  $E_a$  values obtained in this temperature zone  
 473 are due to the condensation, polymerization, and aromatization reactions. This reaction occurs at  
 474 higher temperatures and reaction times [5]. In this temperature range (205-245 °C), Yang et al.  
 475 [51] reported values of 226.5 kJ/mol of HTC for cellulose.

476 As shown in **Fig. 5**, the different  $E_a$  express different reaction mechanisms. The model-fitting  
 477 methods can explain the different models for each stage of conversion.

### 478 3.3.2 Model-fitting method

479 The model-fitting method applied in this study was the Coats-Redfern method; this method  
 480 enabled the determination of the kinetic parameters, i.e., activation energy and kinetic model  
 481 ( $g(\alpha)$ ). In **Table 5**, the average activation energy of different heating rates is displayed to identify  
 482 the kinetic reaction model of the HTC process for AS. As shown in **Table 5**, the  $E_a$  values  
 483 determined are somewhat mildly variable when changing the reaction model and can be really  
 484 different to the value obtained with model-free method.

485 **Table 5:** Kinetic parameters of AS determined by model-fitting method in HTC process for AS

Model-Symbols	150-210°C		210-250°C	
	$E_{a\text{mean}}$ (kJ/mol)	$R^2_{\text{mean}}$	$E_{a\text{mean}}$ (kJ/mol)	$R^2_{\text{mean}}$
R1	148.84±4.93	0.968	<b>230.96±28.84</b>	<b>0.916</b>
R2	212.95±5.53	0.988	330.30±37.72	0.937
R3	292.87±6.57	0.977	453.89±48.76	0.928
R4	178.58±5.19	0.983	277.12±32.98	0.933
D1	214.92±8.94	0.909	329.16±44.61	0.853
D2	239.39±9.26	0.931	367.69±48.32	0.877
D3	270.92±9.55	0.953	417.00±52.85	0.902
D4	249.74±9.35	0.939	383.89±49.81	0.887
P1	159.32±6.70	0.907	244.76±33.45	0.85
P2	48.12±2.22	0.888	75.96±11.14	0.831
P3	29.59±1.48	0.87	47.83±7.42	0.813
P4	20.32±1.10	0.847	33.76±5.56	0.794
A1	<b>96.73±3.28</b>	<b>0.966</b>	151.16±19.22	0.913
A2	70.68±2.46	0.964	111.26±14.41	0.91
A3	44.63±1.64	0.96	71.36±9.60	0.903
A4	31.60±1.23	0.955	51.41±7.20	0.896
A5	101.75±2.32	0.903	161.50±16.08	0.87

A6	210.98±4.59	0.869	331.44±32.16	0.906
F1	48.12±2.22	0.888	75.96±11.14	0.831
F2	29.59±1.48	0.87	47.83±7.42	0.813

486 The main hypotheses that can explain the inconsistency  $E\alpha$  values between the model-free and  
 487 model-fitting methods are the model-free model assumes that the reaction mechanism is first-  
 488 order. However, there may be different mechanisms during the conversion process. These  
 489 mechanisms can be explained for the model-fitting. Also, to determine the kinetic parameter for  
 490 model-free method, at least three heating rates are required. On the other hand, only one heating  
 491 rate value is necessary for the model-fitting to estimate the kinetic parameters. In most biomass  
 492 thermal degradation works in literature, the chosen kinetic model is the reaction first order  
 493 ( $f(\alpha)=1-\alpha$ ), even if each phase could be described as a different model. In this case, if the mean  
 494 value of  $E\alpha$  for different heating rates at a specified conversion range based upon one particular  
 495 model is closest to the value by the model-free methods, in addition to the high correlation  
 496 coefficients ( $R^2$ ), then this model may dominate the reactions in this range [56, 57].

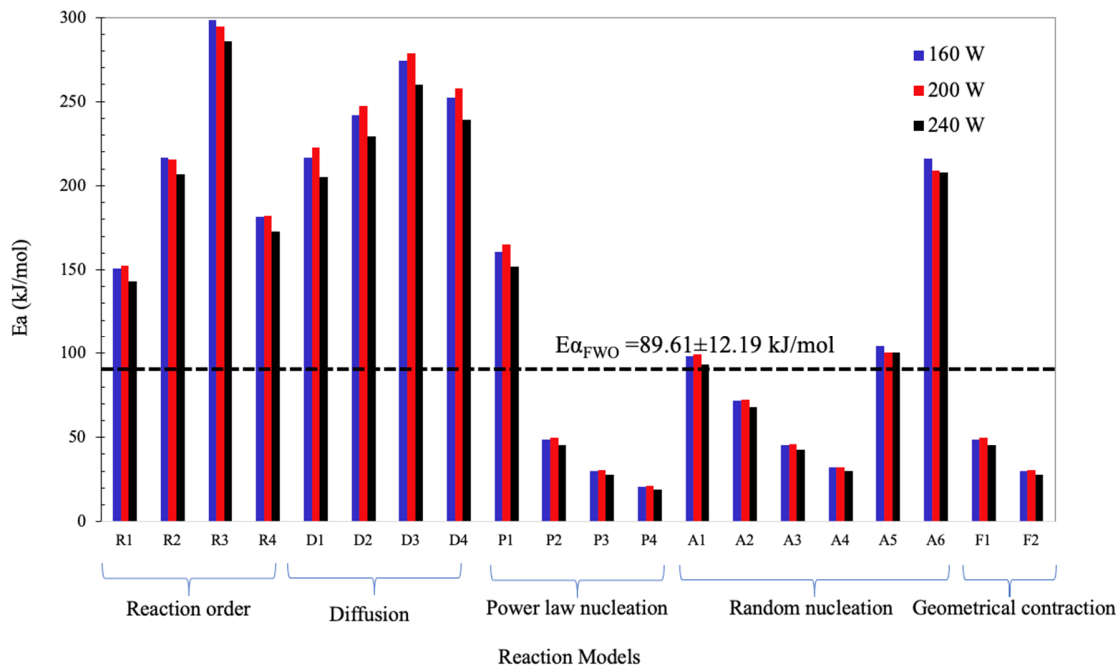
497 The calculated  $E\alpha$  at different heating rates is shown in **Fig. 6** and **Fig. 7**. It can be seen in **Fig. 6**  
 498 that for the reaction order model series, the estimated average value of  $E\alpha$  for the cases of the  
 499 three heating rates varies from 148.8 kJ/mol to 292.87kJ/mol. But none of the estimated average  
 500  $E\alpha$  based upon this series reaction model is close to 89.61 kJ/mol. Although higher correlation  
 501 values are obtained for this model series ( $R^2 > 0.968$ ), the  $E\alpha$  values obtained are much greater  
 502 than those of the free models values.

503 In fact, the reaction model corresponding to Avrami-Erofeev (1) gives a similarity  $E\alpha$  values  
 504 with model-free methods in the temperature between 150 and 210°C indicate that the HTC  
 505 kinetics of AS follows a random nucleation model ( $g(\alpha) = [-\ln(1-\alpha)]^{2/3}$ ). The kinetic  
 506 transformations of Avrami-Erofeev models usually follow a characteristic sigmoidal profile (S-  
 507 shape) where the transformation rates are low at the beginning and the end of the transformation  
 508 but rapid in between; this explains the shape of the curve in **Fig. 2a**. A similar observation was  
 509 reported by Álvarez-Murillo et al. [58] in the HTC process for the cellulose decomposition  
 510 curve.

511 However, in the second zone (210 to 250°C) corresponding to an increase in  $Y_{HC}$ , the best model  
 512 giving the value close to  $E\alpha_{FWO}$  (181.28 kJ/mol) is the first order model (R1) as shown in **Fig. 7**.  
 513 The estimated average value of  $E\alpha$  varies from 199.26 kJ/mol to 255.65 kJ/mol. The first-order

514 reaction model may be the most appropriate model to express the HTC process of AS in this  
 515 temperature range.

516



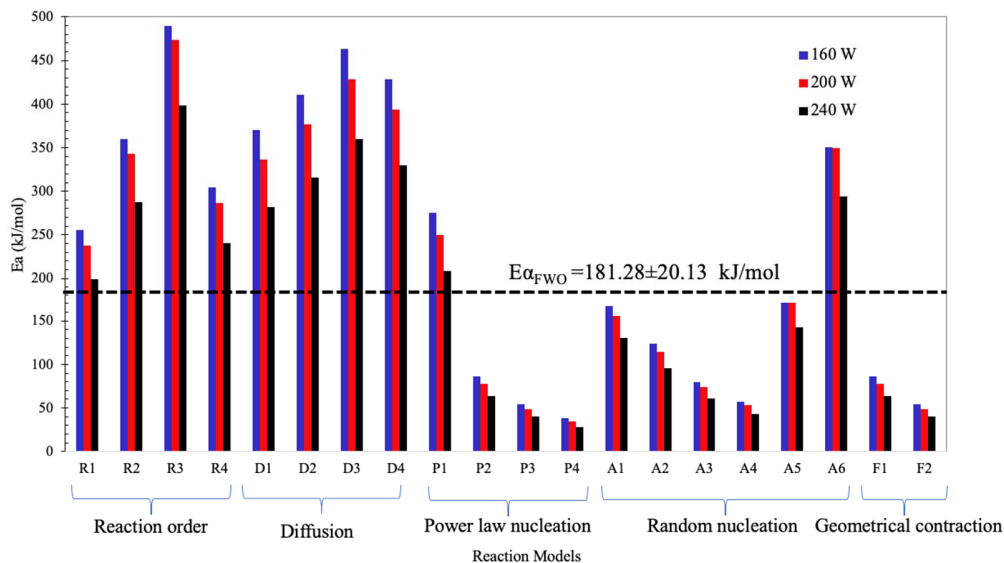
517

518 **Fig. 6:** Comparison of kinetic parameters from model-fitting methods of temperature between 150 and  
 519 210°C

520 Although model-free methods were generally regarded as reliable ones, they can calculate both  
 521  $E\alpha$  and A values. However, this method is based on supposed first-order reaction models, and the  
 522 thermal decomposition can follow different reaction models, which are not necessarily first-order  
 523 model reactions, as demonstrated for AS HTC temperature between 150 and 210 °C. On the  
 524 other hand, model-fitting methods have enabled the determination of the kinetic model ( $g(\alpha)$ ),  
 525 also activation energy ( $E\alpha$ ), but any list of the model-fitting method is certainly incomplete, and  
 526 it is entirely possible that the studied process is not described by any of them [54].

527 Moreover, this method depends on the heating rate and range of conversion. As shown in **Fig. 7**,  
 528  $E\alpha$  values increased with increasing heating rate. This phenomenon is because as the heating rate  
 529 increased, it led to a sharp increase in intermediates reaction rates and lower activation energies.  
 530 Similar results were observed by Mui et al. [59] in the pyrolysis of cellulose, hemicellulose, and  
 531 lignin.





533

534 **Fig. 7:** Comparison of kinetic parameters from model-fitting methods of temperature between 210 and  
535 250°C

536 Consequently, it was recommended that model-fitting methods and model-free methods support  
537 each other to investigate the HTC mechanism. Therefore, according to comparing the model-free  
538 and model-fitting methods' activation energy, the random nucleation (Avrami-Erofeev-1) model  
539 may be considered the most suitable model to characterize the HTC of AS in the range of 150°C  
540 to 210°C. Simultaneously, a temperature between 210 and 250°C follows a first-order reaction  
541 model.

## 542 **Conclusions:**

543 This study is focused on kinetic studies of hydrothermal carbonization of avocado stone, using  
544 different temperature and time conditions. The kinetics of the process was studied using different  
545 models and methods (model-free and model-fitting methods). The following conclusions can be  
546 drawn from the results of the study:

547 According to the analysis of total solids yield, the HTC of the AS can be divided into four main  
548 zones. Initial induction period in the first zone in which the reaction rate is relatively slow (up to  
549 160°C), followed by a maximum loss of total solid yield up to 200°C. The third zone corresponds  
550 to the stabilization zone, dominated by condensation reactions; this stability is observed between  
551 200 and 220°C. The last zone is the increase in the total solid mass yield. The increase of the

552 total solid mass yield between 220 and 250°C is related to the aromatization and polymerization  
553 reactions. This increase was confirmed with the Soxhlet extraction and analysis of the secondary  
554 hydrochars (tars) formed. The increase in temperature of HTC gradually increases the tars  
555 compounds, such as aliphatic and PAHs on the hydrochar.

556 The results of GC–MS analysis of the secondary hydrochar solution indicate that it contains  
557 aliphatic and PAHs components. The aliphatic compounds detected were mainly characterized  
558 by long-chain alkanes and some unsaturated fatty acids. The number and weight of PAHs  
559 increase with the increasing temperature of HTC. The most abundant PAHs were two and three-  
560 ring. However, 4-ring PAHs were detected in low numbers in hydrochars produced at 230 and  
561 250°C.

562 The decomposition of avocado stone during the HTC in temperatures range between 150 and  
563 210°C follows a random nucleation reaction mechanism (Avrami-Erofeev-1) whereas in the  
564 temperature between 210 and 250 follows a first-order reaction model. The average activation  
565 energy estimated for Avrami-Erofeev-1 was  $96.73 \pm 3.28$  kJ/mol. The values obtained from FWO  
566 and KAS are consistent with Avrami-Erofeev-1, where the activation energies are  $89.61 \pm 12.19$   
567 kJ/mol and  $86.79 \pm 12.82$  kJ/mol, respectively. The average activation energy estimated for the  
568 first-order reaction model is  $230.96 \pm 28.84$  kJ/mol. The best values obtained for the model-free  
569 method were between 145-210 kJ/mol and 161-229 kJ/mol for the FWO and KAS methods.  
570 Moreover, the values of activation energies at different conversions have indicated the multi-  
571 reaction scheme's existence during the HTC of avocado stone.

## 572 **Acknowledgments**

573 The authors are grateful to CONACYT (Consejo Nacional de Ciencia y Tecnología de México)  
574 for granting the scholarship No. 659624 for this research. Also, we are grateful to ICARE -  
575 CNRS- France and the Région Centre-Val de Loire for financial support within the INFLUX  
576 project.

577

## 578 **References**

- 579 1. Czernik S, Bridgwater A. Overview of applications of biomass fast pyrolysis oil. *Energy & fuels*  
580 2004; **18**(2): 590-598
- 581 2. Funke A, Ziegler F. Hydrothermal carbonization of biomass: a summary and discussion of  
582 chemical mechanisms for process engineering. *Biofuels, Bioproducts and Biorefining* 2010; **4**(2):  
583 160-177

- 584 3. Kim D, Lee K, Park K Y. Hydrothermal carbonization of anaerobically digested sludge for solid  
585 fuel production and energy recovery. *Fuel* 2014; **130**: 120-125
- 586 4. Missaoui A, Bostyn S, Belandria V, Cagnon B, Sarh B, et al. Hydrothermal carbonization of  
587 dried olive pomace: Energy potential and process performances. *Journal of Analytical and*  
588 *Applied Pyrolysis* 2017
- 589 5. Sevilla M, Fuertes A B. The production of carbon materials by hydrothermal carbonization of  
590 cellulose. *Carbon* 2009; **47**(9): 2281-2289
- 591 6. Sabio E, Álvarez-Murillo A, Román S, Ledesma B. Conversion of tomato-peel waste into solid  
592 fuel by hydrothermal carbonization: Influence of the processing variables. *Waste management*  
593 2016; **47**: 122-132
- 594 7. Chen W-H, Ye S-C, Sheen H-K. Hydrothermal carbonization of sugarcane bagasse via wet  
595 torrefaction in association with microwave heating. *Bioresource technology* 2012; **118**: 195-203
- 596 8. Zhang L, Liu S, Wang B, Wang Q, Yang G, et al. Effect of residence time on hydrothermal  
597 carbonization of corn cob residual. *BioResources* 2015; **10**(3): 3979-3986
- 598 9. Álvarez-Murillo A, Román S, Ledesma B, Sabio E. Study of variables in energy densification of  
599 olive stone by hydrothermal carbonization. *Journal of Analytical and Applied Pyrolysis* 2015;  
600 **113**: 307-314
- 601 10. Alves B. Fresh avocado production in Mexico from 2013/14 to 2019/20. 2020; Available from:  
602 <https://www.statista.com/statistics/591329/mexico-fresh-avocado-production/>
- 603 11. Perea-Moreno A-J, Aguilera-Ureña M-J, Manzano-Agugliaro F. Fuel properties of avocado stone.  
604 *Fuel* 2016; **186**: 358-364
- 605 12. Salgado J M, Danieli F, Regitano-D'Arce M A B, Frias A, Mansi D N. The Avocado Oil (persea  
606 Americana Mill) As A Raw Material For The Food Industry [o óleo De Abacate (persea  
607 Americana Mill) Como Matéria-prima Para A Indústria Alimentícia]. *Ciencia e Tecnologia de*  
608 *Alimentos* 2008
- 609 13. Rodríguez-Sánchez D G, Pacheco A, García-Cruz M I, Gutiérrez-Urbe J A, Benavides-Lozano J  
610 A, et al. Isolation and structure elucidation of avocado seed (*Persea americana*) lipid derivatives  
611 that inhibit *Clostridium sporogenes* endospore germination. *Journal of agricultural and food*  
612 *chemistry* 2013; **61**(30): 7403-7411
- 613 14. McLeod L, Flores D. USDA-Foreign-Agricultural-Service (2017) Mexico Avocado Annual. 2017  
614 [cited 2020 25/10]; Available from: <https://www.fas.usda.gov/data/mexico-avocado-annual-2>
- 615 15. Lucian M, Volpe M, Gao L, Piro G, Goldfarb J L, et al. Impact of hydrothermal carbonization  
616 conditions on the formation of hydrochars and secondary chars from the organic fraction of  
617 municipal solid waste. *Fuel* 2018; **233**: 257-268
- 618 16. Paksung N, Pfersich J, Arauzo P J, Jung D, Kruse A. Structural effects of cellulose on hydrolysis  
619 and carbonization behavior during hydrothermal treatment. *ACS omega* 2020; **5**(21): 12210-  
620 12223
- 621 17. Peng N, Li Y, Liu T, Lang Q, Gai C, et al. Polycyclic aromatic hydrocarbons and toxic heavy  
622 metals in municipal solid waste and corresponding hydrochars. *Energy & Fuels* 2017; **31**(2):  
623 1665-1671
- 624 18. Wang L, Li A, Chang Y. Hydrothermal treatment coupled with mechanical expression at  
625 increased temperature for excess sludge dewatering: Heavy metals, volatile organic compounds  
626 and combustion characteristics of hydrochar. *Chemical Engineering Journal* 2016; **297**: 1-10

- 627 19. Malghani S, Gleixner G, Trumbore S E. Chars produced by slow pyrolysis and hydrothermal  
628 carbonization vary in carbon sequestration potential and greenhouse gases emissions. *Soil*  
629 *Biology and Biochemistry* 2013; **62**: 137-146
- 630 20. Al-Wabel M I, Rafique M I, Ahmad M, Ahmad M, Hussain A, et al. Pyrolytic and hydrothermal  
631 carbonization of date palm leaflets: Characteristics and ecotoxicological effects on seed  
632 germination of lettuce. *Saudi journal of biological sciences* 2019; **26**(4): 665-672
- 633 21. Wang T, Zhai Y, Zhu Y, Li C, Zeng G. A review of the hydrothermal carbonization of biomass  
634 waste for hydrochar formation: Process conditions, fundamentals, and physicochemical  
635 properties. *Renewable and Sustainable Energy Reviews* 2018; **90**: 223-247
- 636 22. Zeng X, Ueki Y, Yoshiie R, Naruse I, Wang F, et al. Recent progress in tar removal by char and  
637 the applications: A comprehensive analysis. *Carbon Resources Conversion* 2020; **3**: 1-18.
- 638 23. Kambo H S, Dutta A. A comparative review of biochar and hydrochar in terms of production,  
639 physico-chemical properties and applications. *Renewable and Sustainable Energy Reviews* 2015;  
640 **45**: 359-378
- 641 24. Ischia G, Fiori L. Hydrothermal Carbonization of Organic Waste and Biomass: A Review on  
642 Process, Reactor, and Plant Modeling. *Waste and Biomass Valorization* 2021; **12**(6): 2797-2824
- 643 25. Reza M T, Yan W, Uddin M H, Lynam J G, Hoekman S K, et al. Reaction kinetics of  
644 hydrothermal carbonization of loblolly pine. *Bioresource technology* 2013; **139**: 161-169
- 645 26. Keiller B G, Muhlack R, Burton R A, van Eyk P J. Biochemical Compositional Analysis and  
646 Kinetic Modeling of Hydrothermal Carbonization of Australian Saltbush. *Energy & Fuels* 2019;  
647 **33**(12): 12469-12479
- 648 27. Liu Z, Balasubramanian R. Hydrothermal carbonization of waste biomass for energy generation.  
649 *Procedia Environmental Sciences* 2012; **16**: 159-166
- 650 28. Pecchi M, Patuzzi F, Benedetti V, Di Maggio R, Baratieri M. Kinetic analysis of hydrothermal  
651 carbonization using high-pressure differential scanning calorimetry applied to biomass. *Applied*  
652 *Energy* 2020; **265**: 114810
- 653 29. Ceballos A M, Montoya S. Evaluación química de la fibra en semilla, pulpa y cáscara de tres  
654 variedades de aguacate. *Biotecnología en el sector agropecuario y agroindustrial* 2013; **11**(1):  
655 103-112
- 656 30. Sangare D, Missaoui A, Bostyn S, Belandria V, Moscosa-Santillan M, et al. Modeling of Agave  
657 Salmiana bagasse conversion by hydrothermal carbonization (HTC) for solid fuel combustion  
658 using surface response methodology. *aimspress energy* 2020; **8**(4): 538-562
- 659 31. Sangare D, Bostyn S, Moscosa-Santillan M, Gökalp I. Hydrodynamics, heat transfer and kinetics  
660 reaction of CFD modeling of a batch stirred reactor under hydrothermal carbonization conditions.  
661 *Energy* 2020: 119635
- 662 32. Román S, Libra J, Berge N, Sabio E, Ro K, et al. Hydrothermal carbonization: modeling, final  
663 properties design and applications: a review. *Energies* 2018; **11**(1): 216
- 664 33. Hilber I, Blum F, Leifeld J, Schmidt H-P, Bucheli T D. Quantitative determination of PAHs in  
665 biochar: a prerequisite to ensure its quality and safe application. *Journal of agricultural and food*  
666 *chemistry* 2012; **60**(12): 3042-3050
- 667 34. Mumbach G D, Alves J L F, da Silva J C G, Di Domenico M, de Sena R F, et al. Pyrolysis of  
668 cocoa shell and its bioenergy potential: evaluating the kinetic triplet, thermodynamic parameters,  
669 and evolved gas analysis using TGA-FTIR. *Biomass Conversion and Biorefinery* 2020: 1-17

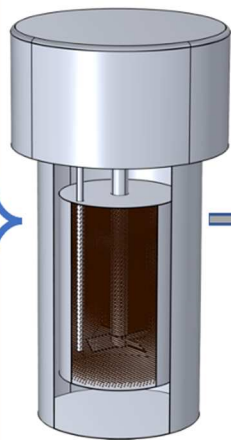
- 670 35. Doyle C D. Kinetic analysis of thermogravimetric data. *Journal of applied polymer science* 1961;  
671 5(15): 285-292
- 672 36. Coats A, Redfern J. Kinetic parameters from thermogravimetric data. *Nature* 1964; **201**(4914):  
673 68-69
- 674 37. Yao Z, Yu S, Su W, Wu W, Tang J, et al. Kinetic studies on the pyrolysis of plastic waste using a  
675 combination of model-fitting and model-free methods. *Waste Management & Research* 2020;  
676 **38**(1\_suppl): 77-85
- 677 38. Qiu Y, Chen Y, Zhang G G, Yu L, Mantri R V, Developing solid oral dosage forms:  
678 pharmaceutical theory and practice, in *Book Developing solid oral dosage forms: pharmaceutical*  
679 *theory and practice*. 2016, Academic press
- 680 39. Khawam A, Flanagan D R. Solid-state kinetic models: basics and mathematical fundamentals.  
681 *The journal of physical chemistry B* 2006; **110**(35): 17315-17328
- 682 40. Brown M E, Dollimore D, Galwey A K, Reactions in the solid state, in *Book Reactions in the*  
683 *solid state*. 1980, Elsevier
- 684 41. Volpe M, Goldfarb J L, Fiori L. Hydrothermal carbonization of *Opuntia ficus-indica* cladodes:  
685 Role of process parameters on hydrochar properties. *Bioresource technology* 2018; **247**: 310-318
- 686 42. Reza M T, Uddin M H, Lynam J G, Hoekman S K, Coronella C J. Hydrothermal carbonization of  
687 loblolly pine: reaction chemistry and water balance. *Biomass Conversion and Biorefinery* 2014;  
688 **4**(4): 311-321
- 689 43. Galwey A K, Brown M E, Thermal decomposition of ionic solids: chemical properties and  
690 reactivities of ionic crystalline phases, in *Book Thermal decomposition of ionic solids: chemical*  
691 *properties and reactivities of ionic crystalline phases*. 1999, Elsevier
- 692 44. Khawam A. Application of solid-state kinetics to desolvation reactions. *The journal of physical*  
693 *chemistry B* 2007; **210**(37): 1520-1545
- 694 45. Fang J, Zhan L, Ok Y S, Gao B. Minireview of potential applications of hydrochar derived from  
695 hydrothermal carbonization of biomass. *Journal of Industrial and Engineering Chemistry* 2018;  
696 **57**: 15-21
- 697 46. Gao P, Zhou Y, Meng F, Zhang Y, Liu Z, et al. Preparation and characterization of hydrochar  
698 from waste eucalyptus bark by hydrothermal carbonization. *Energy* 2016; **97**: 238-245
- 699 47. Krylova A Y, Zaitchenko V. Hydrothermal carbonization of biomass: a review. *Solid Fuel*  
700 *Chemistry* 2018; **52**(2): 91-103
- 701 48. Peterson A A, Vogel F, Lachance R P, Fröling M, Antal Jr M J, et al. Thermochemical biofuel  
702 production in hydrothermal media: a review of sub-and supercritical water technologies. *Energy*  
703 *& Environmental Science* 2008; **1**(1): 32-65
- 704 49. Reza M T, Upgrading biomass by hydrothermal and chemical conditioning. 2013, University of  
705 Nevada, Reno.
- 706 50. Reza M T, Andert J, Wirth B, Busch D, Pielert J, et al. Hydrothermal carbonization of biomass  
707 for energy and crop production. *Applied Bioenergy* 2014; **1**(1): 11-29
- 708 51. Yang W, Shimanouchi T, Wu S, Kimura Y. Investigation of the degradation kinetic parameters  
709 and structure changes of microcrystalline cellulose in subcritical water. *Energy & fuels* 2014;  
710 **28**(11): 6974-6980

- 711 52. Jaruwat D, Udomsap P, Chollacoop N, Fuji M, Eiad-ua A. Effects of hydrothermal temperature  
712 and time of hydrochar from Cattail leaves. in AIP Conference Proceedings. 2018. AIP Publishing  
713 LLC
- 714 53. Ali I, Naqvi S R, Bahadar A. Kinetic analysis of Botryococcus braunii pyrolysis using model-free  
715 and model fitting methods. Fuel 2018; **214**: 369-380
- 716 54. Cai J, Xu D, Dong Z, Yu X, Yang Y, et al. Processing thermogravimetric analysis data for  
717 isoconversional kinetic analysis of lignocellulosic biomass pyrolysis: Case study of corn stalk.  
718 Renewable and Sustainable Energy Reviews 2018; **82**: 2705-2715
- 719 55. Danso-Boateng E, Holdich R, Shama G, Wheatley A D, Sohail M, et al. Kinetics of faecal  
720 biomass hydrothermal carbonisation for hydrochar production. Applied energy 2013; **111**: 351-  
721 357
- 722 56. Chen R, Lu S, Zhang Y, Lo S. Pyrolysis study of waste cable hose with  
723 thermogravimetry/Fourier transform infrared/mass spectrometry analysis. Energy Conversion and  
724 Management 2017; **153**: 83-92
- 725 57. Pan L, Jiang Y, Wang L, Xu W. Kinetic study on the pyrolysis of medium density fiberboard:  
726 Effects of secondary charring reactions. Energies 2018; **11**(9): 2481
- 727 58. Álvarez-Murillo A, Sabio E, Ledesma B, Román S, González-García C. Generation of biofuel  
728 from hydrothermal carbonization of cellulose. Kinetics modelling. Energy 2016; **94**: 600-608
- 729 59. Mui E L, Cheung W, Lee V K, McKay G. Kinetic study on bamboo pyrolysis. Industrial &  
730 engineering chemistry research 2008; **47**(15): 5710-5722
- 731
- 732

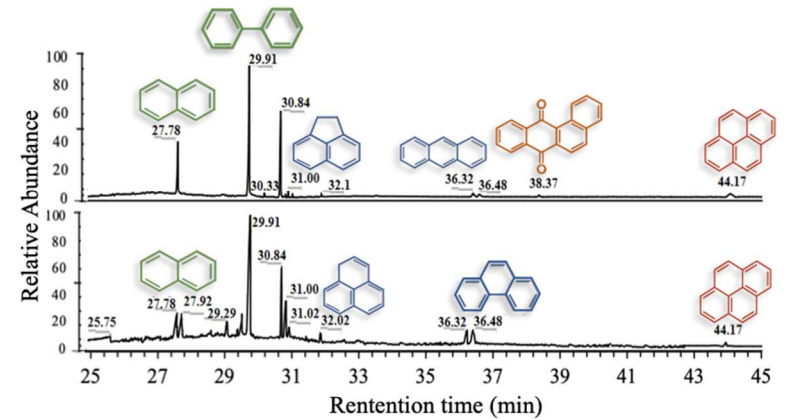
# Graphical abstract



**HTC Reactor**



**Hydrochar**



**PAHs compounds detected in the tar removed in the hydrochar**

