Influence of temperature on the char produced through solar pyrolysis of Agave Angustifolia leaves

Influencia de la temperatura en el carbón producido mediante pirólisis solar de hojas de Agave Angustifolia

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Abstract

The coupling of concentrated solar technologies and thermochemical biomass conversion is a promising alternative because there is an improvement on the process efficiency and a reduction of the environmental impact related to the use of fossil fuels for heat process. Therefore, the use of solar pyrolysis of agro-industrial wastes into fuels results attractive due to the biomass versatility to be transformed in a variety of products. In the present work, leaves of agave *Angustifolia* were used as raw material to performed the solar pyrolysis in the IER-UNAM solar furnace (Mexico) to produce amorphous carbon. The experiments were performed in a borosilicate reactor at different temperatures (450-1550 °C), with an average heating rate of 30 °C/min and 60 min of residence time. The main results show a variety of yields in the char produced from 28-14%, and conversion up to 85%. In addition, according to the temperature range, the amorphous chars produced may be suitable for energy storage in symmetric supercapacitors as carbon electrodes.

Resumen

El acoplamiento de tecnologías de concentración solar y los procesos termoquímicos de conversión de biomasa son una alternativa prometedora, debido al mejoramiento de la eficiencia del proceso y reducción del impacto medioambiental asociado al uso de combustibles fósiles para la generación de calor de proceso. Por ello, el uso de pirólisis solar de desechos agroindustriales hacia combustibles resulta atractiva debido a la versatilidad de la biomasa para ser convertida en una variedad de productos. En el presente trabajo, hojas de agave *Angustifolia* fueron usadas como materia prima para llevar a cabo la pirólisis solar en el horno solar del IER-UNAM (México) para la producción de carbón amorfo. Los experimentos se realizaron a diferentes temperaturas (450-1550 °C), con una rampa de calentamiento promedio de 30 °C/min y 60 min de tiempo de residencia. Los resultados principales muestran una variedad en los rendimientos de 28-14 % y una conversión de hasta 85%. Adicionalmente, de acuerdo al rango de temperatura analizado, la producción de carbones amorfos puede ser adecuada para su uso como electrodos en supercapacitores simétricos, para el almacenamiento de energía.

Keywords: Solar pyrolysis, carbon materials, thermochemical biomass conversion, solar reactor.

1. INTRODUCTION

The employment of biomass is required in order to reach a sustainable future [1]. One of the main interests associated to the use of biomass is the low cost, versatility, and minor environmental impact [2]. Biomass presents the ability to be transformed into different products, such as liquid, gas or solid fuels, trough thermochemical biomass conversion process [3]. Pyrolysis is a well-known process, it can be classified into a low temperature and high temperature process. At low temperature (450 °C), the process is also known as “carbonization” and the target is to obtain high char yields. Meanwhile, at higher temperature, the process receives the name of pyrolysis (up to 2000 °C) [3].

One drawback of conventional pyrolysis is that uses energy from non-renewable sources, which is an environmental concern. Therefore, the use of concentrated solar technologies (CST) to provide the process energy has emerged as an attractive option to reduce the greenhouse gas emissions. Moreover, the use of CST can add some benefits to the process, such as improvement of the energy conversion efficiency, gas pollutants reduction and, finally that the solar energy is chemically stored as fuels [4]. Moreover, solar and conventional heating pyrolysis have been focused mainly in analyzing the optimal operational parameters that lead to higher bio-oil yields and quality, along with higher H_2 production, which lets the char formation as a product less attractive [4–7]heating rate and argon flow rate on products distribution, gas LHV (lower heating value.

Mescal industry is a booming sector in Mexico, which is based on the fermentation and distillation of many species of agave. In 2022, the mezcal industry produced around 8 million of litters [8] and the increasing consumption suggest its continuous expanding. However, after cooking, the agave leaves and the solid product (known as bagasse) ends in the landfill or burned without controlled conditions, in both scenarios it represents an environmental concern. Therefore, in the present work the use of leaves of agave *Angustifolia* as biomass is proposed to performed solar pyrolysis with the aim of produce an amorphous carbon that can be addressable to other applications.

2. METHODOLOGY

2.1. Experimental setup

Fibers of agave *Angustifolia* leaves were provided by a local mescal industry located in Oaxaca. The fibers were previously dried at sun until constant weight to remove moisture excess and to avoid any further decomposition during storage. The pyrolysis experiments were performed in the IER-UNAM horizontal solar furnace (thermal power up to 25 kW in the focal point with an average solar flux density of 5000 kW/m^2). The reactor consisted in a spherical form made of borosilicate of 25 L. Approximately 9-11 g were added in a crucible made of high purity Al_2O_3, and then placed inside the reactor at the focal zone. This arrangement allowed a direct contact of the sample with concentrated solar energy, which lets to reach higher temperatures. An inert atmosphere was achieved by continuously injecting Ar at a rate of 5 NL/min as sweeping gas. Moreover, the continuous addition of Ar permitted to evacuate the gas formation and reduces the tar deposition in the reactor walls, which complicates the transmissivity of solar beams as a result of the tar particles that block the radiation.

The reaction temperature was measured in the crucible by using 5 type-K thermocouples, as presented in Fig. 1.

Where m_{char} is the solid residue mass got after solar pyrolysis, and is the biomass added to the reactor.

2.2. Analytical Methods

The elemental composition (CHNS) was determined using an elemental analyzer (Thermo Scientific, 2000 CHNS), the oxygen content was calculated by difference. Thermogravimetric analysis (TGA) were performed in balance (Q500-TA Intruments). Experiments were carried out in oxygen and nitrogen atmosphere with samples around 15 mg to calculate the proximate analysis. For the crystalline structure a X-RAY Diffractometer d/max 2200 Rigaku was used. The surface morphology and energy dispersive spectroscopy (EDS) was observed through a scanning electron microscopy provided by Hitachi S-5500.

3. RESULTS

3.1. Raw material characterization

Table 1 presents the proximate analysis of agave *Angustifolia* leaves, where it can be observed that initial biomass has low humidity content and high volatile matter.

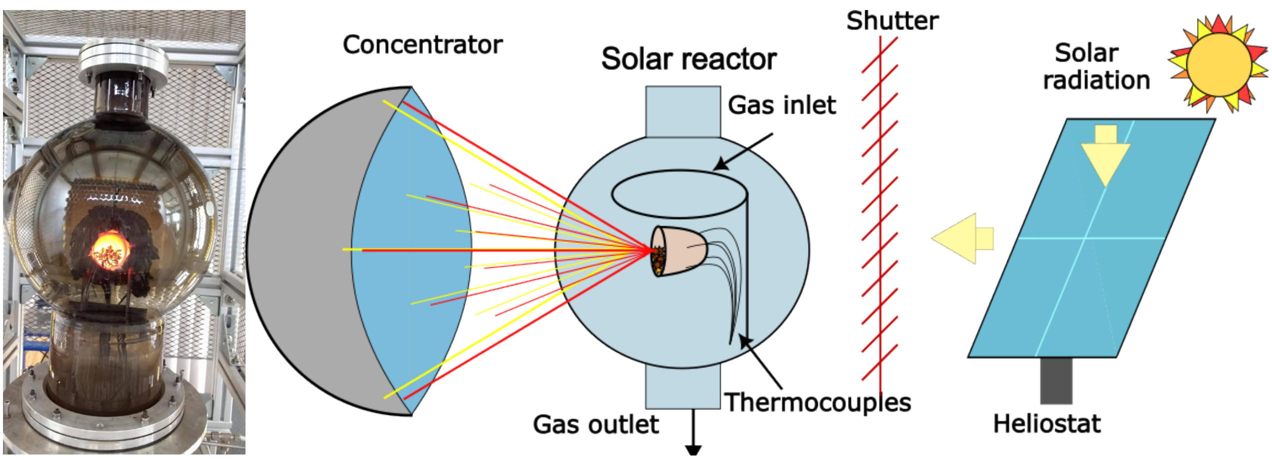


Figure 1. a) Photograph of the solar reactor and b) sketch of the concentrated solar technology "solar furnace" and reactor.

Figura 1. a) Fotografía del reactor solar en el horno solar del IER-UNAM y b) esquema de la tecnología de concentración solar "horno solar" y del reactor.

Experiments were carried out at different temperatures (450, 600, 800, 900, 1100, 1400 and 1550 ºC), an average heating rate of 30 °C/min and 60 min of residence time once the target temperature was reached. Temperatures and heating rates were controlled by regulating the aperture of the shutter placed between the heliostat and the solar concentrator (Fig. 1).

Char yield (Y_{char}) was calculated by a gravimetric equation, according to Eq. 1. On the other hand, the conversion was estimated by Eq. 2.

$$Y_{char}(\%) = \frac{m_{char}}{m_{Bagasse}} \times 100(1)$$

$$Conversion(\%) = \frac{m_{Bagasse} - m_{char}}{m_{Bagasse}} \times 100(2)$$

On the other hand, by energy dispersive spectroscopy was observed the presence of other elements such as Ca, K, Si, Mg and P. This is interesting since some elements present in the ashes (Ca, Na, K, Mg, Si, Ti and Al) can have a significant role in nanomaterials through doping. Other micro-elements (Cu, Fe, Mn, Mo and Zn) also found in biomasses are attractive in thermochemical conversion process as a result of its catalytic effect [9].

In addition, as can be seen in Table 2 the initial biomass is rich in carbon an oxygen content, with minor quantities of nitrogen and sulfur, elements considered as undesired, as a result of the NOx and SOx that can produce during the combustion of the fuels. Likewise, CHNS-O composition of agave leaves are similar to other lignocellulosic biomasses, such as wood [10].

Table 1. Proximate analysis and EDS of the ashes.
Tabla 1. Análisis próximo y EDS de las cenizas.

Component	Composition (wt. %)	Ash element	Composition (wt. %)
Moisture	5.7	O	46.5
Volatile matter	71.04	Ca	22.7
Fixed carbon	13.96	K	17.4
Ashes	9.3	Si	0.4
C	6.7	Mg	2.8
S	1	P	2.5

Table 2. Composición elemental de la biomasa inicial y de los carbones producidos por pirólisis solar a diferentes temperaturas, a una tasa de calentamiento de 30 ºC/min y 60 min de tiempo de residencia.
Tabla 2. Elemental composition of the raw biomass and char produced from solar pyrolysis at different temperatures, 30 ºC/min and 60 min of residence time.

T (°C)	Y_{char} (%)	Conv. (%)	C (wt.%)	H (wt.%)	O (wt.%)	N (wt.%)	S (wt.%)
Biomass	-	-	43.2	5.9	50	0.9	-
450	28.4	71.5	71.1	1.9	26.9	-	0.1
600	26.3	73.7	73.7	1.3	24.9	-	0.1
800	24	76	74.9	0.8	24	-	0.3
900	23.8	76.2	75.9	0.8	23.1	-	0.2
1100	21.4	78.6	79.4	0.5	19.8	-	0.3
1400	19.3	80.6	83.8	0.2	15.8	-	0.2
1550	14.2	85.8	84	0.2	15.6	-	0.2

3.2. Effect of temperature on the char yield

Many operational parameters impact the products distribution in pyrolysis, among them are temperature, heating rate, sweeping gas, biomass and pressure. However, temperature is one of the most analyzed parameters and considered as primary [11,12]. In Table 2 are reported the char yields as function of temperature during solar pyrolysis. It can be observed that there is a linear trend over the char yield, as temperature increased the char production is reduced, this can be ascribed mainly for two reasons: Pyrolysis is a well-known process able to produce liquid products, where the maximal bio-oil yields are reached in the temperature range of 400-550 °C, then starts to decrease. At superior temperatures (up to 1600 ºC), the gas yields are improved, and species like H_2 and CO, and in minor proportion CH_4, CO_2 and C_2H_6 are the result of tar cracking into lighter compounds [11].

3.3. Effect of temperature on the chemical composition

The chemical composition of the different chars obtained by solar pyrolysis can be observed in Table 2, where it can be noted that as temperature rises the carbon content increases and oxygen decreases, from 71-84 and 26-15 wt.%, respectively, due to the gas production [13]. Similar results have been previously reported [12], where the increment in carbon content on the char is related to the graphitization on the char structure. Meanwhile, the hydrogen and oxygen variation are related to the cracking of weaker bonds of the biomass structure [14]. Another way to compare the chemical composition is through Van Krevelen diagram (Fig. 2), where the different chars are compared. It can be noted that as temperature increases, the O/C ratio decreases, along with the H/C ratio, according to Cai *et* al. [15], the direction that follow chars in Van Krevelen diagram can suggest dominant dehydration reactions during the thermal biomass degradation, as consequence of the reduction on oxygen and hydrogen content.

This path on the direction that solar chars show in the Van Krevelen diagram suggest that one of the more suitable applications, rather than combustion fuel, it would be in the field of absorption and energy storage, since the elemental composition of the solar chars is comparable with other works that employ biomass-derived chars, such as nanodiamond or amorphous carbon as electrode for electrochemical implementation [16–18].

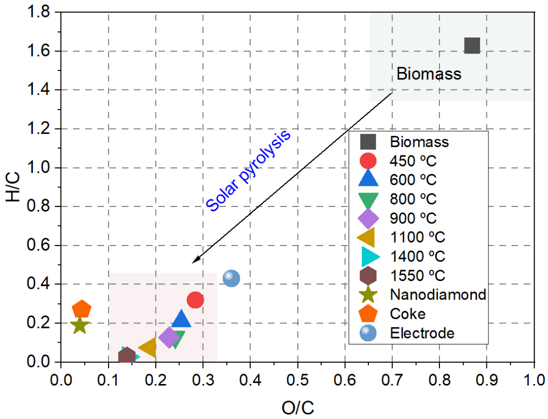
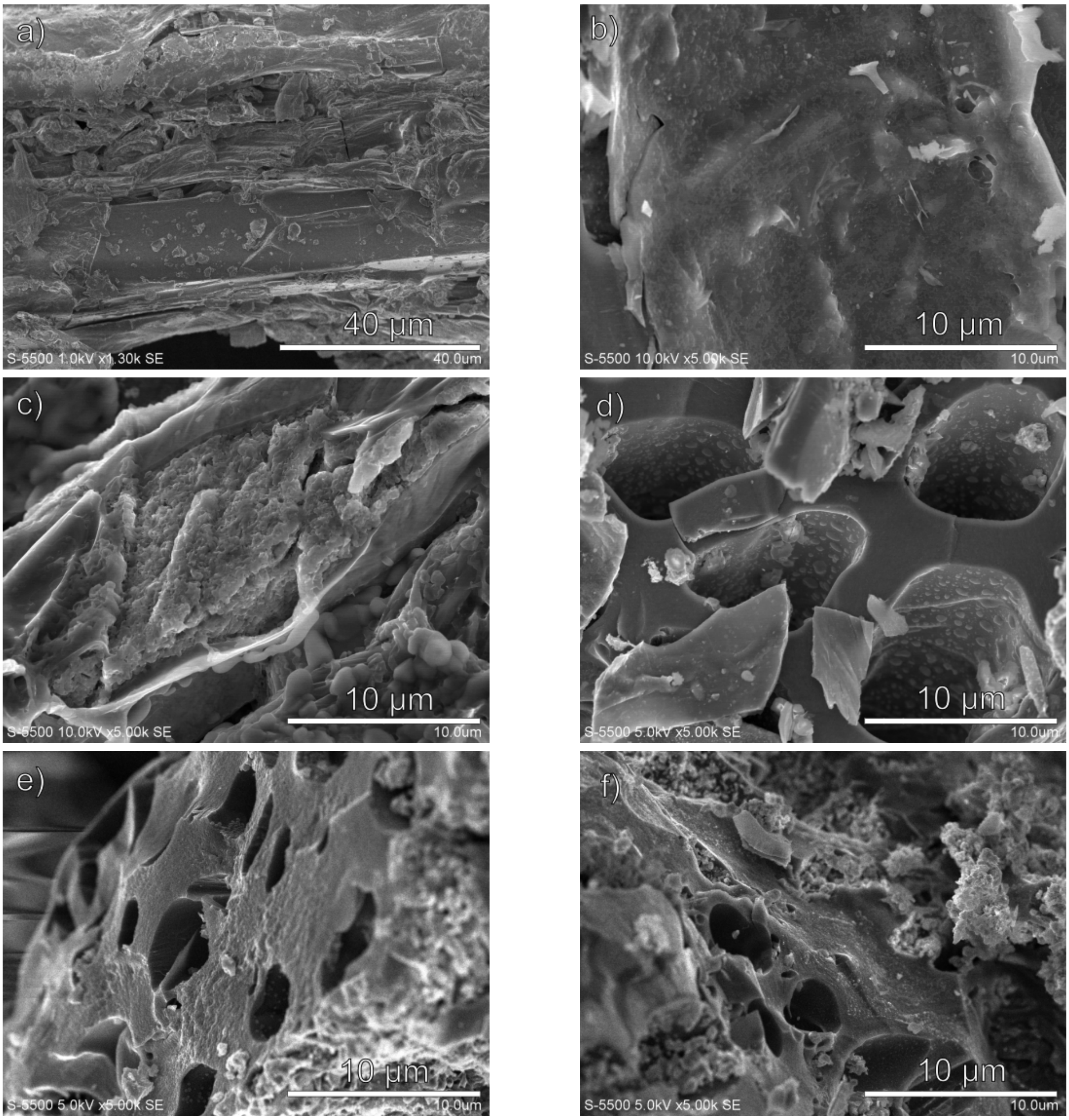


Figure 2. Van Krevelen diagram of the different chars from solar pyrolysis.

Figura 2. Diagrama Van Krevelen de los diferentes carbones producidos por pirólisis solar.

3.4. Effect of temperature on the char's surface

In Fig. 3 it can be seen the surface structure of the initial agave leaves fibers (Fig. 3a), where it seems to be formed of multiple fibers. After being pyrolyzed at 450 ºC (Fig. 3b), the surface structure of the char reveals more defined fibers which could be related to the breaking of lignocellulosic structure. After 600 ºC (Fig. 3c), the external structure of the above-mentioned fibers is broken down and starts to decompose. Eventually, at superior temperatures of 800 ºC (Fig. 3d), it comes more evident a porous structure on the char´s surface, this phenomenon is also observed at further temperatures (900 and 1100 ºC) in Figs. 3e and 3f. At the temperature of 1400 ºC it was not observed the same porous distribution (Fig. 3g), but its presence at 1550 ºC confirms that a porous structure in the chars is maintained at temperatures above 1500 ºC (Fig. 3h).



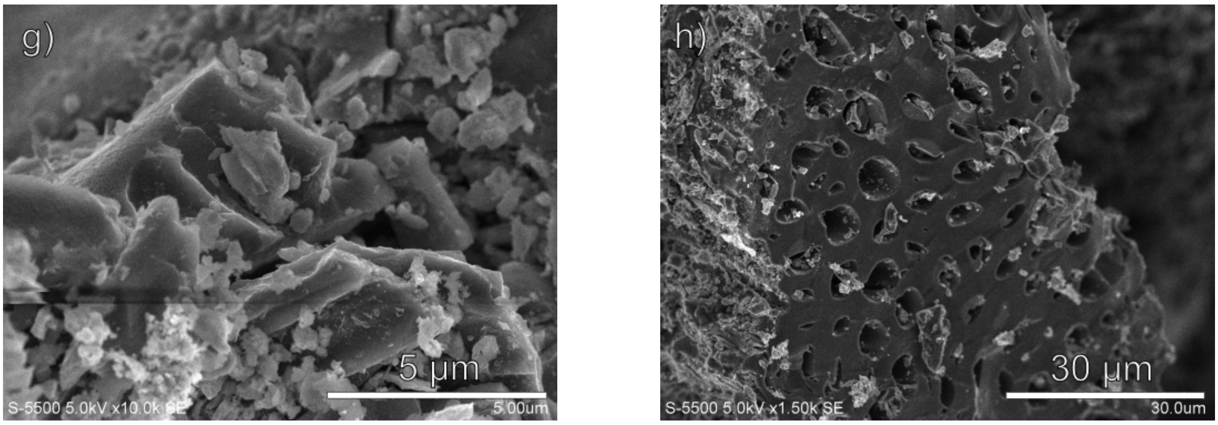


Figure 3. SEM images of the a) agave leave fibers, b) char at 450ºC, c) 600ºC, d) 800ºC, e) 900ºC, f) 1100ºC, g) 1400ºC and h) 1550ºC.

Figura 3. Micrografías de la a) hoja de agave, b) carbón a 450ºC, c) 600ºC, d) 800ºC, e) 900ºC, f) 1100ºC, g) 1400ºC and h) 1550ºC.

3.5. XRD analysis

The initial crystalline structure obtained by XRD (Fig. 4) of the agave leaves fibers showed a component rich in carbon, calcium an oxygen, known as whewellite ($C_2CaO_4H_2O$), and representative of lignocellulosic biomasses. After being pyrolyzed the chars showed different compounds as temperature increased. At 450 ºC, the whewellite is transformed into calcite ($CaCO_3$) and portlandite ($Ca(OH)_2$), dominant compounds in the solar char up to 800 ºC, at higher temperatures calcite is decomposed into CO_2 and calcium oxide (CaO). On the other hand, the portlandite is expected to react in the range of temperature of 420-520 ºC to be transformed into CaO and H_2O. However, it has been reported that this reaction follows a reversible mechanism [13].

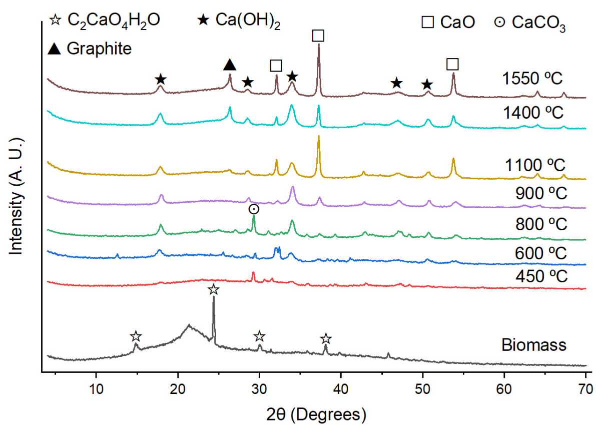


Figure 4. XRD curves of the initial biomass and the chars at different temperatures.

Figura 4. Difractogramas de la biomasa inicial y de los carbones a diferentes temperaturas.

Applications of solar pyrolysis char

Solar pyrolysis of industrial wastes can be successfully produced by using concentrated solar technologies, in this direction, depending on the desired product the operational parameters can be addressed into favor bio-oils, char of gas fuel. The purpose of the present work was to produce amorphous char without physical or chemical activation in a wide range of temperature and to analyze its main chemical and physical characteristics. Therefore, according to the range temperature analyzed (450-1550 °C), some of the chars produced can be possible candidates to be used as electrodes in symmetric supercapacitors due to chemical composition and superficial porous structure, however, these materials need a further analysis [16].

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REFERENCES

[1] M. Saleem, Possibility of utilizing agriculture biomass as a renewable and sustainable future energy source, Heliyon. 8 (2022) e08905. *https://doi.org/10.1016/J.HELIYON.2022.E08905*.

[2] A. Demirbas, Political, economic and environmental impacts of biofuels: A review, Appl. Energy. 86 (2009). *https://doi.org/10.1016/j.apenergy.2009.04.036*.

[3] A. Ayala-Cortés, P. Arcelus-Arrillaga, M. Millan, C.A. Arancibia-Bulnes, P.J. Valadés-Pelayo, H.I. Villafán-Vidales, Solar integrated hydrothermal processes: A review, Renew. Sustain. Energy Rev. 139 (2021). *https://doi.org/10.1016/j.rser.2020.110575*.

[4] K. Zeng, D. Gauthier, J. Lu, G. Flamant, Parametric study and process optimization for solar pyrolysis of beech wood, Energy Convers. Manag. 106 (2015) 987–998. *https://doi.org/10.1016/j.enconman.2015.10.039*.

[5] R. Serefentse, W. Ruwona, G. Danha, E. Muzenda, A review of the desulphurization methods used for pyrolysis oil, in: Procedia Manuf., Elsevier B.V., 2019: pp. 762–768. *https://doi.org/10.1016/j.promfg.2019.07.013*.

[6] A.R.K. Gollakota, M. Reddy, M.D. Subramanyam, N. Kishore, A review on the upgradation techniques of pyrolysis oil, Renew. Sustain. Energy Rev. 58 (2016) 1543–1568. *https://doi.org/10.1016/j.rser.2015.12.180*.

[7] J.O. Ighalo, K.O. Iwuozor, L.A. Ogunfowora, A. Abdulsalam, F.U. Iwuchukwu, B. Itabana, O.C. Bright, C.A. Igwegbe, Regenerative desulphurisation of pyrolysis oil: A paradigm for the circular economy initiative, J. Environ. Chem. Eng. 9 (2021). *https://doi.org/10.1016/j.jece.2021.106864*.

[8] P.A. Becerra-Lucio, E. Diego-García, K. Guillén-Navarro, Y.J. Peña-Ramírez, Unveiling the Microbial Ecology behind Mezcal: A Spirit Drink with a Growing Global Demand, Fermentation. 8 (2022) 662. *https://doi.org/10.3390/fermentation8110662*.

[9] V.G. Matveeva, L.M. Bronstein, From renewable biomass to nanomaterials: Does biomass origin matter?, Prog. Mater. Sci. 130 (2022). *https://doi.org/10.1016/j.pmatsci.2022.100999*.

[10] K. Zeng, D. Gauthier, J. Soria, G. Mazza, G. Flamant, Solar pyrolysis of carbonaceous feedstocks: A review, Sol. Energy. 156 (2017) 73–92. *https://doi.org/10.1016/J.SOLENER.2017.05.033*.

[11] K. Zeng, D. Gauthier, R. Li, G. Flamant, Solar pyrolysis of beech wood: Effects of pyrolysis parameters on the product distribution and gas product composition, Energy. 93 (2015) 1648–1657. *https://doi.org/10.1016/j.energy.2015.10.008*.

[12] K. Zeng, D.P. Minh, D. Gauthier, E. Weiss-Hortala, A. Nzihou, G. Flamant, The effect of temperature and heating rate on char properties obtained from solar pyrolysis of beech wood, Bioresour. Technol. 182 (2015) 114–119. *https://doi.org/10.1016/J.BIORTECH.2015.01.112*.

[13] A. Ayala-Cortés, D.R. Lobato-Peralta, C.E. Arreola-Ramos, D.C. Martínez-Casillas, D.E. Pacheco-Catalán, A.K. Cuentas-Gallegos, C.A. Arancibia-Bulnes, H.I. Villafán-Vidales, Exploring the influence of solar pyrolysis operation parameters on characteristics of carbon materials, J. Anal. Appl. Pyrolysis. 140 (2019) 290–298. *https://doi.org/10.1016/j.jaap.2019.04.006*.

[14] A. Demirbas, Effects of temperature and particle size on bio-char yield from pyrolysis of agricultural residues, J. Anal. Appl. Pyrolysis. 72 (2004) 243–248. *https://doi.org/10.1016/J.JAAP.2004.07.003*.

[15] J. Cai, B. Li, C. Chen, J. Wang, M. Zhao, K. Zhang, Hydrothermal carbonization of tobacco stalk for fuel application, Bioresour. Technol. 220 (2016) 305–311. *https://doi.org/10.1016/j.biortech.2016.08.098*.

[16] D.R. Lobato-Peralta, D.M. Arias, P.U. Okoye, Polymer superabsorbent from disposable diaper as a sustainable precursor for the development of stable supercapacitor electrode, J. Energy Storage. 40 (2021). *https://doi.org/10.1016/j.est.2021.102760*.

[17] M. Zeiger, N. Jäckel, D. Weingarth, V. Presser, Vacuum or flowing argon: What is the best synthesis atmosphere for nanodiamond-derived carbon onions for supercapacitor electrodes?, Carbon N. Y. 94 (2015) 507–517. *https://doi.org/10.1016/j.carbon.2015.07.028*.

[18] S. Rawat, R.K. Mishra, T. Bhaskar, Biomass derived functional carbon materials for supercapacitor applications, Chemosphere. 286 (2022). *https://doi.org/10.1016/j.chemosphere.2021.131961*.