Solar Pyrolysis Of Agave And Tomato Pruning Wastes: Insights Of The effect Of Pyrolysis Operation Parameters On The Physicochemical Properties Of Biochar

A. Ayala-Cortés[1], C.A. Arancibia-Bulnes[1], H.I. Villafán-Vidales[1, *], D.R. Lobato-Peralta[1], D. Martinez-Casillas[1], A.K. Cuentas-Gallegos[1],

[1]Author Affiliation: *Instituto de Energías Renovables, Universidad Nacional Autónoma de México, Privada Xochicalco S/N, col. Centro. 62588, Temixco, Morelos, México.*

[*] Corresponding author: hivv@ier.unam.mx

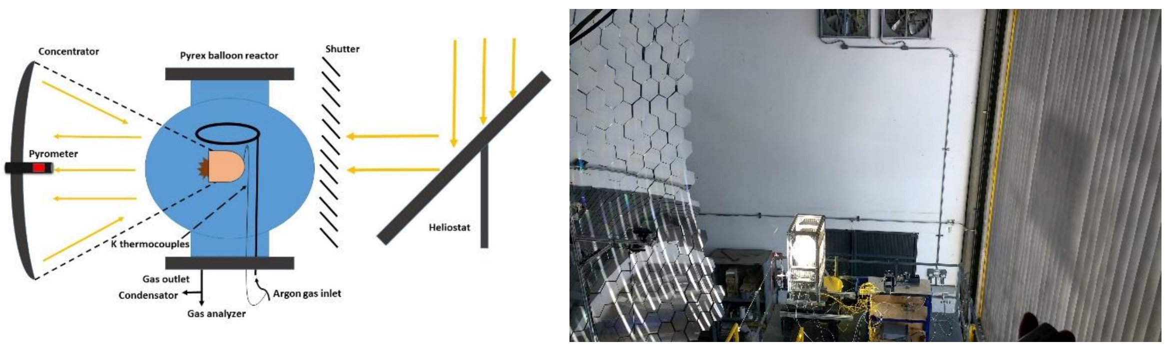
Abstract. Agave *angustifolia* leaves and tomato pruning biomass were processed into char by solar pyrolysis. Then, it was studied the influence of temperature and heating rate (up to 1550°C for agave and up to 900°C to tomato) in the physicochemical properties of different produced chars. The characterization techniques include: elemental (CHONS), surface area by BET and DFT model and capacitance by cyclic voltammetry. It was found that, for both biomass, temperatures below (up to 900°C) are beneficial because a porous char is obtained. the highest values of capacitance and surface area, in a porous char, especially at 600 and 400°C. In addition, it was observed that at higher temperatures (>900°C) the capacitance and surface area tend to decrease.

INTRODUCTION

The Mexican mezcal production industry annually generates several tons of waste. In 2016, 1 875 932.73 tons of this plant were produced [1,2]. The leaves are obtained after the cutting process and are not used for the production of beverages. Mexico has also an important market oriented to the agriculture sector; one of them is the tomato production market, which for the year 2017/2018 is estimated at 3.4 million metric tons [3]. During 2016, 51 861.1 hectares of this plant were harvested, obtaining 3 349 154.20 tons of its fruit, once the fruit is harvested, the plant tends to be discarded, so it becomes an agricultural waste. These two wastes can be used as raw materials to produce value-added materials, such as biochar. Nowadays there are various methods for the transformation of biomass, one of them is the pyrolysis, which interest has grown in the last years due to simplicity of the process [3]. Nevertheless, this process uses high temperatures that are obtained by the combustion of a portion of biomass (between 30-35%), which decreases the energy conversion of the process, and reduces the product output per unit of feedstock [4,5]. These disadvantages can be avoided by using concentrated solar energy as heat source of the processes, obtaining several environmental and efficiency-related benefits. Much of solar pyrolysis research efforts have been devoted to bio-oil and syngas production using various biomass feedstocks, and analyzing several experimental conditions with different reactor prototypes [3, 5-8]. However, only a few works had been studied the influence of solar operation parameters in the distribution of main products and its principal characteristics [5-7], although their importance in the future applications of the products. For example, biochar, which is a carbon rich product, can be used in a wide range of applications, such as water and air decontamination adsorbent, to form electrodes, to produce pills, among others [8], however its final use mainly depends on the following parameters: final composition, surface area, pore structure, reactivity [6]. These properties are highly affected by type of biomass feedstock and pyrolysis operation parameters, i.e. temperature, heating rate, residence time; therefore the physicochemical properties of the solar obtained biochar should be analyzed in detail and its effectivity in the desired application. This work aim to analyze the impact of solar pyrolysis operation parameters on the physicochemical properties of the obtained biochar by using two different types of waste biomasses. The main objective is to find optimal conditions that produce biochar with adequate physicochemical properties to be used in a specific application, for example supercapacitors or lithium batteries.

METHODOLOGY

Pyrolysis experiments were carry out in a spherical-shape borosilicate prototype of 25L, which is set at the focal zone of the IER-UNAM horizontal solar furnace (Power of 25 kW, peak concentrations of 18,000 kW/m^2 and focal zone of 8 cm-diameter placed at 3.68m). The biomass feedstock used to perform solar pyrolysis was *Agave angustifolia* leave fibers, which are a waste of the mezcal production process and tomato pruning. Both biomass were previously dried to remove moisture excess, and then 9-11g of leave fibers or 27-29g of tomato pruning briquette were set in high purity alumina crucible, which is placed inside the solar reactor (Fig. 1). This configuration allow us to directly irradiated the sample with concentrated solar energy, and thus reach reaction temperatures. Experiments were performed under argon flow of 5 NL/min as sweeping gas in order to provide an oxygen-free environment, besides it helps to keep the reactor walls clean. The sample temperature was measured with 5 type-K thermocouples and an optical pyrometer, as showed in the Fig.1.



(a) (b)

FIGURE 1. (a) Sketch of the solar pyrolysis reactor and (b) photo from the experiment.

Experiments of agave were performed for 7 different temperatures (450, 600, 800, 900, 1100, 1400 and 1550°C) and various heating rates with one hour of time residence. Samples of tomato pruning were performed for 450, 600 and 900°C with a heating rate of 30°C/min and 2 hours of time residence, as shown in table 1. After experimentation, biochar was treated to remove the ashes and physicochemically characterized by several techniques. Afterwards, the electrochemical characterization of carbon materials was performed by cyclic voltammetry in acidic (H_2SO_4) electrolyte. The intention of this characterization was to correlate its physicochemical properties with their electrochemical performance, in order to find optimal operational conditions that allow to obtain chars with better capacitance performance.

RESULTS AND DISCUSSION

The elemental analysis of chars produced at different temperatures and heating rates for agave leave fibers and tomato pruning is shown in Table 2. The carbon content increases with temperature due to graphitization of carbon structure [9,10], whereas oxygen and hydrogen content decreases as increasing temperature. This last change could be attributed to the cracking of weaker bonds into the structure of biomass [11]. At temperatures above 1400°C, the elemental composition of char is quite similar, which indicate that at high temperatures, the structural changes predominates over chemical composition conversion. Regarding the heating rate impact on char composition, it is appreciated that a high heating rate increases the content of carbon and hydrogen, while of oxygen decreased. The above mentioned is more evident at low temperatures (450°C) because at this temperature, the cellulose and lignin degradation process is performed, which impacts on char chemical composition.

TABLE 1. Pyrolysis conditions of the leave fibers and tomato pruning char at different temperatures and heating rates.

Biomass	Temperature (°C)	Heating rate (°C/min)	Time residence (min)
Leave fibers	450	30, 8	60
Leave fibers	600	30	60
Leave fibers	800	30, 13	60
Leave fibers	900	30	60
Leave fibers	1100	30	60
Leave fibers	1400	30	60
Leave fibers	1550	30	60
Tomato pruning	450	30	120
Tomato pruning	600	30	120
Tomato pruning	900	30	120

TABLE 2. Elemental analysis of the leave fibers and tomato pruning char at different temperatures and heating rates.

Biomass	Temperature (°C)	Heating rate (°C/min)	C (%)	H (%)	O (%)	N (%)	S (%)
Leave fibers	450	30	71.14	1.90	26.91	0	0.02
Leave fibers	450	8	70.45	1.41	28.13	0	0
Leave fibers	600	30	73.73	1.29	24.93	0	0.02
Leave fibers	800	30	74.98	0.87	24.03	0	0.10
Leave fibers	800	13	74.75	0.94	24.19	0	0.10
Leave fibers	900	30	75.94	0.81	23.11	0	0.12
Leave fibers	1100	30	79.47	0.55	19.84	0	0.12
Leave fibers	1400	30	84.03	0.21	15.65	0	0.09
Leave fibers	1550	30	83.84	0.21	15.84	0	0.09
Tomato pruning	450	30	59.81	2.03	29.31	5.46	3.36
Tomato pruning	600	30	60.39	1.55	29.90	0.09	8.05
Tomato pruning	900	30	67.15	1.21	23.27	0	8.34

Comparing elemental composition of both biomasses, it is observed that tomato pruning chars have a smaller percentage of carbon content, and higher content of hydrogen than leave fiber chars. This could be attributed to the lignin, hemicellulose and cellulose content; According to previous results, tomato pruning biomass has higher amount of hemicellulose than leave fibers biomass. Hemicellulose degradation produces more volatiles, less tars and chars than cellulose \cite{Mohan2006PyrolysisReview}.

The ash content was also analyzed by performing a thermogravimetric study in a TGA Q500 V6.7 Build 203 de TA instruments. This analysis was performed in an oxygen atmosphere at 800°C, after biomass degradation, the chemical composition of ashes were analyzed by XRD. The agave leaves biomass exhibit a 9.31% of ashes, which are mainly composed of $CaCO_3$, $CaSO_4$, K_2SO_4, and $MgSO_4$. On the other hand, tomato pruning biomass show higher content of ashes (36%) consisting of $CaCO_3$, and H_4KNO_4S. This last compound is related with fertilizer used in the tomato production.

The morphology of chars were analyzed by using a high resolution scanning electron microscope (HITACHI, S-550).

Leave fibers biomass is a flat surface with no porosity on its surface (Fig. 2a). The increase of temperature destroy this surface and produces macroporous and fibers on char surface. However, at higher temperatures, the surface changes obtaining bigger particles and more irregular structure (Fig. 2b and 2d). Regarding the heating rate, it is observed that a low heating rate seems to promote the formation of macroporous structure, however a high heating rate the formation of macro and mesoporous is favored.

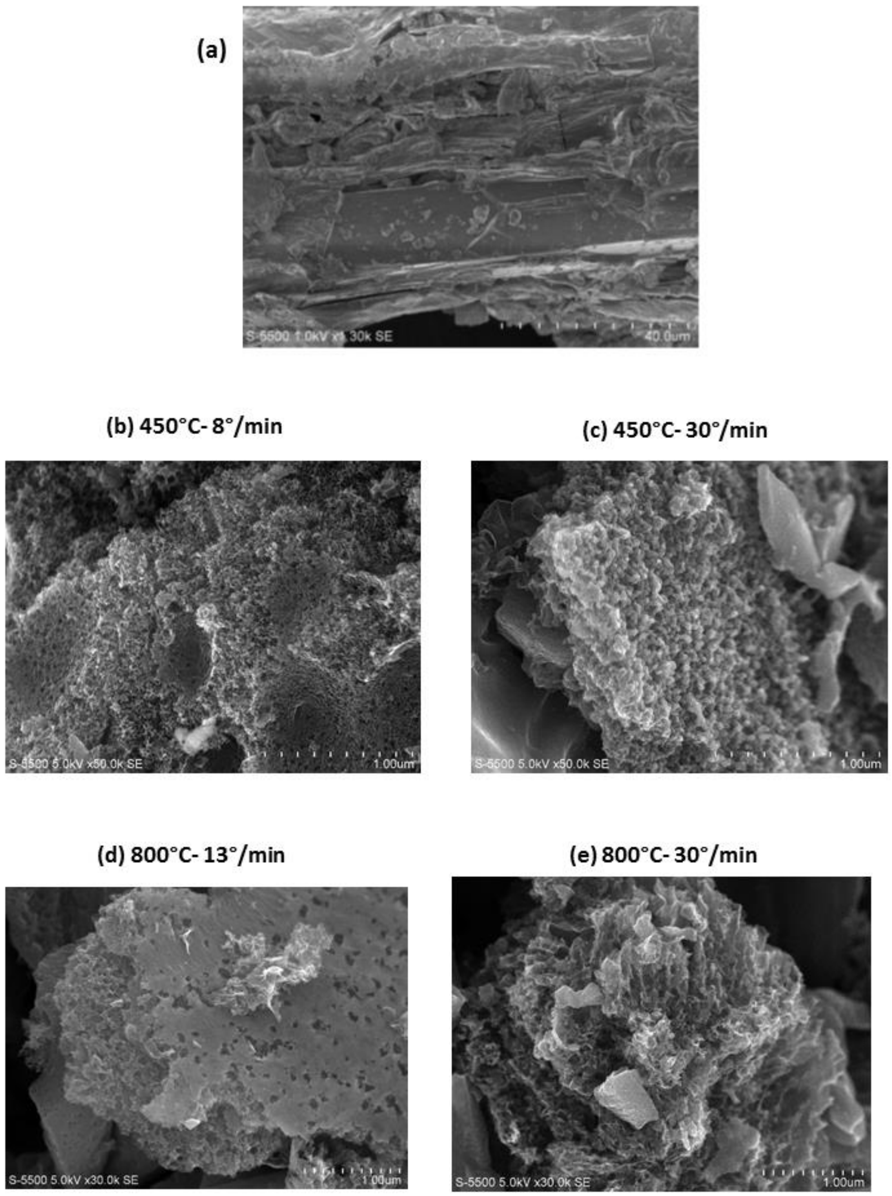


FIGURE 2. Effect of pyrolysis temperature and heating rate on Agave leaves biochar morphology. a) raw biomass, b) 450°C and 8°C/min, c) 450°C and 30°/min, d) 800°C and 13°C/min and e)800°C and 30°C/min.

The effect of temperature in the morphology of char is more evident in Fig. 3. At low temperatures a porous structure similar to a sponge is obtained. This structure has several porous sizes ranging from 1μm to 10μm. When increasing temperatures, the macroporosity seems to disappear, forming micro and mesoporous.
The effect of temperature in capacitance and surface area on chars produced of agave leaves is observed in fig. 4. An increase of temperature augment the capacitance behavior (figs. 4a and 4c) and surface area (figs. 4b and 4d), however at temperatures above 600°C, both (surface and capacitance) decreases. On the contrary, chars produced of tomato

pruning have higher surface area and capacitance at low temperatures (450°C). Comparing both chars produced for different biomasses, it can be appreciated that tomato pruning chars show much higher values than agave leave chars.

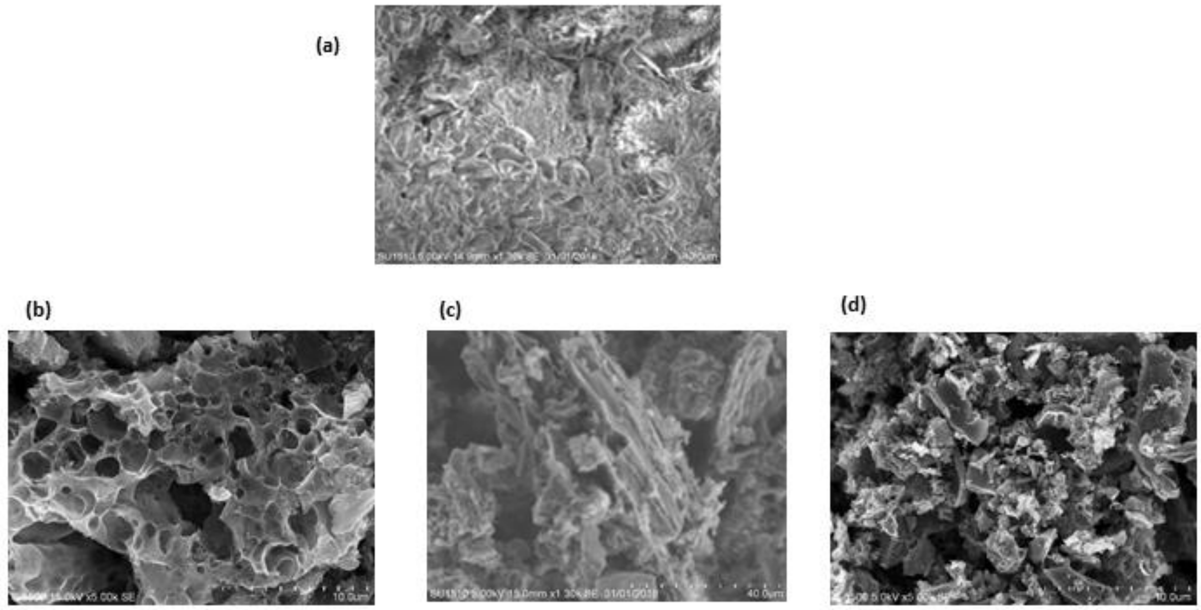
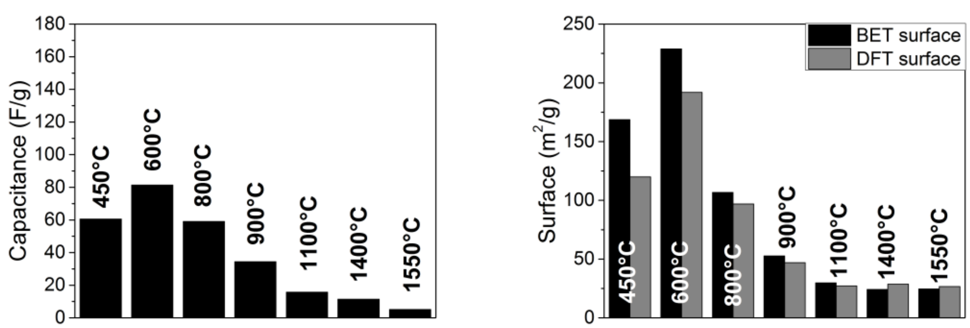
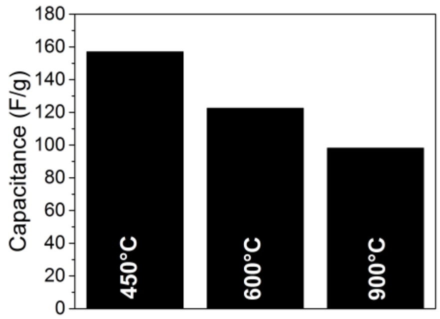


FIGURE 3. Effect of pyrolysis temperature and a constant heating rate of 30°C/min on tomato pruning biochar morphology. a) raw biomass, b) 450°C c) 600°C, and d) 900°C.

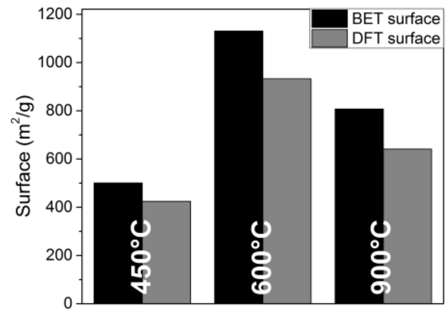
These results show us that the capacitance behavior is not only affected by surface area, but also for other factors. The existence of inorganic compounds in the raw biomass produces an autoactivation process during solar pyrolysis obtaining higher surface surface areas. The tomato pruning biomass showed an important amount of ashes content, therefore it is possible to obtain surface areas above 400 m^2/g. These inorganic compounds also impact on the capacitive behavior, because heteroatoms also participate in the storage process. The nitrogen and sulfur content also promote the energy storage properties because both elements are electrochemically actives contributing to the pseudo-capacitance process. In addition, nitrogen improves the contact between the material and the electrolyte.



(a) (b)



(c)



(d)

FIGURE 3. Effect of pyrolysis temperature on biochar properties. a) agave leaves and b) tomato pruning chars capacitance and c) agave leaves and d) tomato pruning chars surface area.

In figure 4 shows the effect of heating rate on the surface area for agave leaves biochar at temperatures of 450°C and 800°C, and heating rates of 8, 30, 13 and 30°C/min respectively. In this figure, it is observed two tendencies; the specific surface area calculated from the BET model is systematically larger than the one obtained from DFT [13]. The other tendency is that lower heating rates increases the surface area.

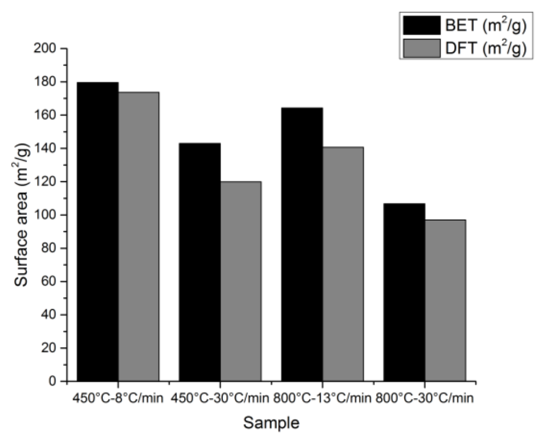
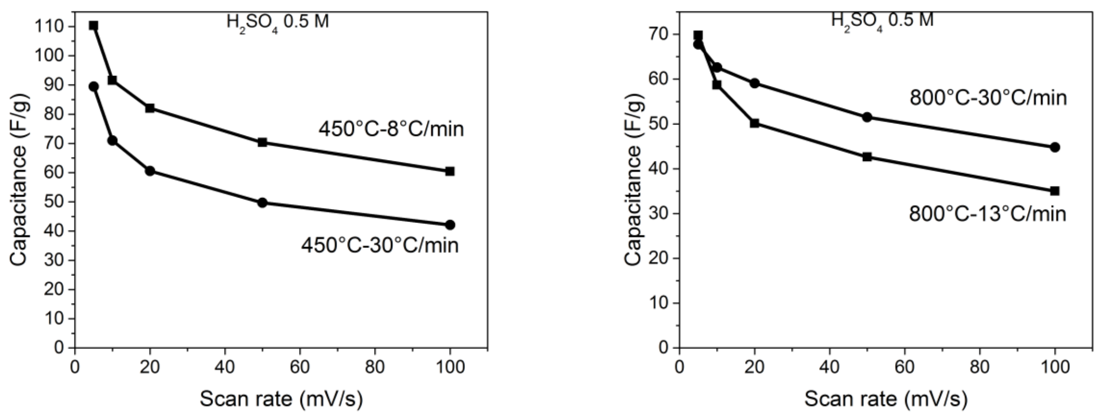


FIGURE 3. Effect of pyrolysis heating rate on the surface area by BET and DFT model, for agave leaves biochar.

In figure 4 capacitances values were calculated from cyclic voltammetry profiles at different scan rates according to the methodology section. It is observed that in carbon materials obtained at 450°C (figure 4a) have a higher capacitance values for any of the five scan rates. However, it is not observed the same tendency at 800°C (figure 4b) where higher heating rates increase the capacitance values, although at 5mV/s there is no big difference between the two heating rates. From figure 3, it could be expected that the lower heating rates would have higher capacitance values, fact that it is showed in figure 4a. Nevertheless, it seems that at 800°C there is no order porous structure.



(a) (b)

FIGURE 4. Effect of pyrolysis heating rate on the capacitance for agave leaves biochar. (a) Capacitance values at 450°C and heating rate of 8 and 30°C/min. (b) Capacitance values at 800°C and 13 and 30°C/min.

CONCLUSION

Agave leaves and tomato pruning biomass were produced by solar pyrolysis in order to analyze the influence of temperature and heating rate of their physicochemical properties. From the characterization of the biochar was found that those biochar produced at low temperature (up to 900°C) have better surface area and capacitance. Which is related to the oxygen content, which decrease with temperature. Besides, it was observed that there is no linear relation between capacitance and surface area. This might be to the need of having an order porous structure, from macro on the surface of the biochar, to meso and finally microporous deep inside. The influence of heating rate was noticed for the agave leaves in the surface area, which showed that at lower heating rates higher surface area values.

ACKNOWLEDGMENTS

The authors acknowledge the financial support from following projects DGAPA-PAPIIT-UNAM IG100217 “Propiedades de Electrodos de Carbón producidos a partir de Biomasa mediante concentración solar” and to the Fondo Sectorial CONACYT-SENER-Sustentabilidad Energética through Grant 207450, within strategic project No. 10, (COSOLPi). The technical support of J.J. Quiñones-Aguilar, in the setup and operation of the experiments in the Solar furnace, Rogelio Morán-Elvira and José Campos-Alvarez with the operation of the SEM, María Luisa Ramón-García for XRD measurements, Patricia Eugenia Altuzar-Coello for the operation of the TGA and Martín Baas López for CHONS analysis.

REFERENCES

1. C. Di Blasi, Combustion and gasification rates of lignocellulosic chars, 2009.
2. V. Dhyani, T. Bhaskar, A comprehensive review on the pyrolysis of lignocellulosic biomass (2017).
3. R. Li, K. Zeng, J. Soria, G. Mazza, D. Gauthier, R. Rodriguez, G. Flamant, Product distribution from solar pyrolysis of agricultural and forestry biomass residues, Renewable Energy (2016).

4. T. Dickerson, J. Soria, Catalytic Fast Pyrolysis: A Review, Energies 6 (2013) 514-538.
5. V. Chintala, Production, upgradation and utilization of solar assisted pyrolysis fuels from biomass. A technical review, 2018.
6. K. Zeng, D. Gauthier, J. Soria, G. Mazza, G. Flamant, Solar pyrolysis of carbonaceous feedstocks: A review, Solar Energy (2017).
7. J. Lédé, Pyrolysis and Gasification of Biomass in Solar and Simulated Solar Environments: The Pioneering Works of Michael J. Antal in the Period of 1976-1989, Energy and Fuels (2016).
8. K. Zeng, D. Gauthier, R. Li, G. Flamant, Combined effects of initial water content and heating parameters on solar pyrolysis of beech wood, Energy (2017).
9. 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, Bioresource Technology (2015)
10. M. Tripathi, J. N. Sahu, P. Ganesan, Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review, 2016.
11. A. Dermibas, Effect of temperature and particle size on bio-char yield from pyrolysis of agricultural residues, Journal of Analytical and Applied Pyrolysis (2004).
12. O. Onay, Influence of pyrolysis temperature and heating rate on the production of bio-oil and char from safflower seed by pyrolysis, using a well-swept fixed-bed reactor, Fuel Processing Technology (2007).
13. Barbieri, O., Hahn, M., Herzog, A., & Kötz, R. (2005). Capacitance limits of high surface area activated carbons for double layer capacitors. *Carbon*, *43*(6), 1303-1310.