

Introduction

The generation of new materials from agroforestry and agricultural residues allows for alternatives to revalue them. Through thermal processes with the obtaining of activated carbons (AC's) we can add value to these residues. Within energy storage, this study allows the assessment as an electrode for capacitors, other alternatives found but not as an object of this study is the use of activated carbons biomass as an adsorbent for colored industrial waters.

Ecuador is among the main cocoa producers' countries; it ranks third with 7% of cocoa's total world production. The African continent leads cocoa's world production with 73.3%, followed by the American continent with 16.7% and Asia with Oceania 10%. The large crop areas of plant species meant for both export and domestic consumption in Ecuador generate large volumes of organic waste (biomass). From these crops, it is possible to highlight; the cocoa plantings (*Theobroma Cacao*) corresponding to two varieties: Fino de Aroma (Criollo or National) and CCN-51 (current). According to the Ministry of Agriculture and Livestock in 2015, the area planted with Cocoa was 537 410 hectares with a production of 297,837 tons, the main producing provinces being Guayas (28%), Los Ríos (23%), and Manabí (13%). Cocoa's wastes include between 60% and 75% of the cocoa pod (wet base) and have no economic value routed to the Ecuadorian market. Moreover, it accounts for an environmental issue due to the large volume the cocoa crops occupy.



Figure.1 Cocoa's fine particles from its residues, Mocache - Ecuador

Methodology

For the implementation of the process, the raw material was characterized by percentage humidity (9%), particle size (0,5 mm), elemental analysis, and TGA/DTG, and the coals were prepared by pyrolysis under a nitrogen atmosphere for four hours in an experimental reactor capable of withstanding high pressures. Its activation was carried out at 850 degrees Celsius with chemical activator K(OH) for three hours.

The electrodes were prepared homogeneously by mixing 90% by weight CA's, acetylene black, and polytetrafluoroethylene (PTFE), forming a thin sheet, which is allowed to dry at 110 °C, after this time; circular sheets of 5 mm are obtained and proceeded to arm the positive and negative electrode with a separation membrane with electrolyte (H₂SO₄).

Reactor



Figure.2. Picture of the 316 stainless steel carbonization reactor.

A 316 stainless steel carbonization reactor was designed and built, with PID temperature control and N₂ inert gas inlet lines, and condensable and non-condensable gas outlet lines. The reactor has heat exchangers for conditioning the exhaust gases.

Results

Elemental Analysis

Cocoa dry residue was characterized by proximal analysis with the Elementar equipment, Vario MACRO Cube.

Elemental Characterization of Cocoa pod husk	
%N	1.69
%C	41.45
%H	6.15
%S	0.25
%O	45.4

Table.1. Cocoa's pod husk Elemental Characterization percentages.

TGA – DTG Analysis

The residual biomass was characterized by means of a thermobalance, Mettler Toledo (TGA), appreciation +/- 1°C.

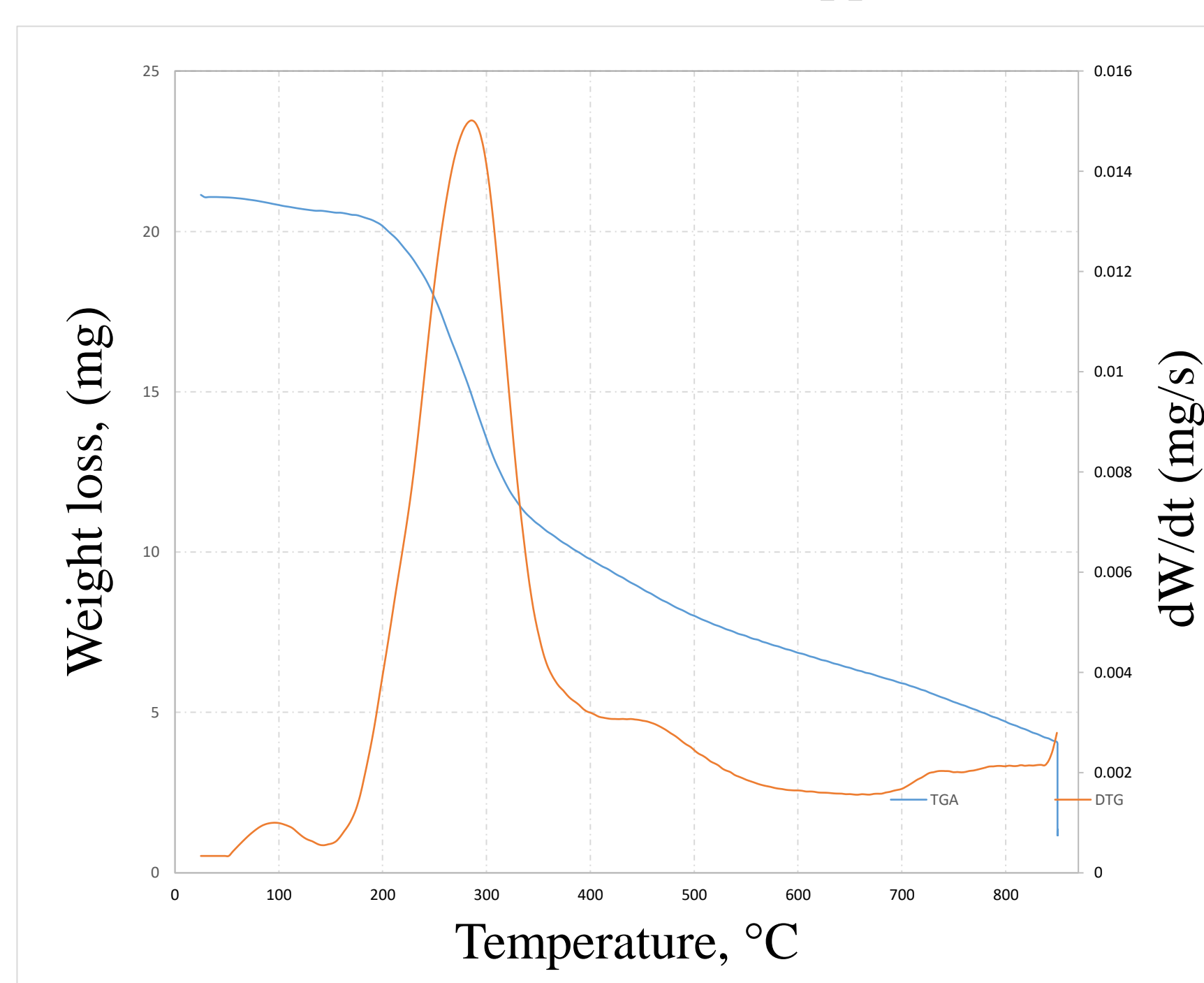


Figure 3. Weight loss versus Temperature, TGA- DTG Biomass Analysis

Characterization wasted Cocoa	
Humidity, (%)	2.04
Volatile compounds, (%)	69.75
Fixed coal, (%)	22.76
Ashes, (%)	5.51

Table 2. Cocoa's pod husk Weight loss Characterization percentages.

Performance

The yield was measured by weight difference analysis, using a Boeco BAS 31 plus scale.

Biomass	Mass, g	Average of carbonization yield, %	Ratio activation K(OH):C	Time (h)	Yield % (Test 1)	Yield % (Test 2)	Average yield %
Theobroma cacao	100	32.87	3:1	1	37.61	36.39	37.00
				2	25.56	29.78	27.67
				3	34.54	32.95	33.75
				4	30.97	31.90	31.43

Table 3 . Activation process average yield percentages.

Surface Area Development

The development of the surface area was measured, obtaining areas between 1800 m²/g up to 3100 m²/g, with a high mesoporous incidence.

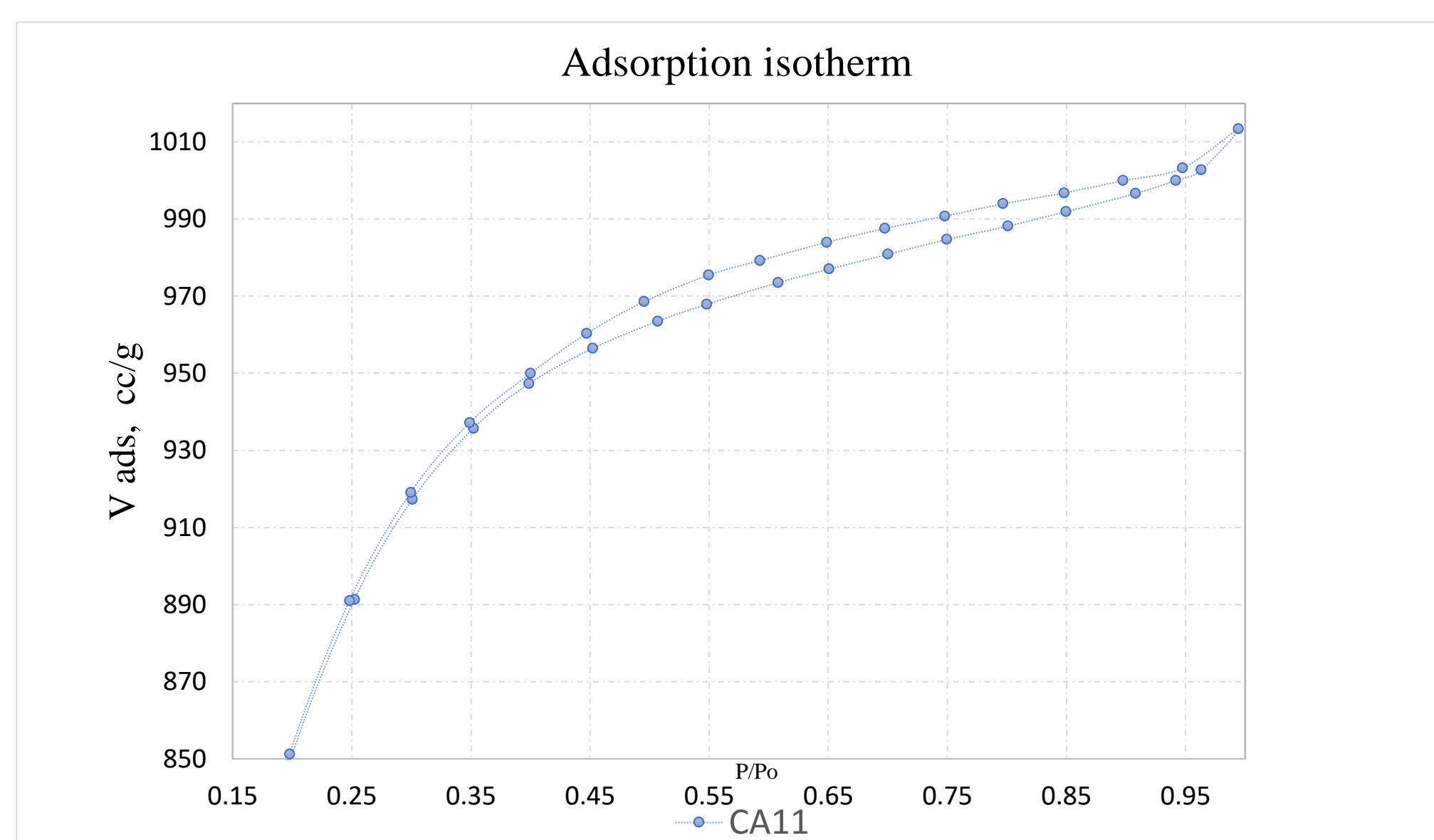


Figure.4 Cocoa's pod husk mesoporous performance.

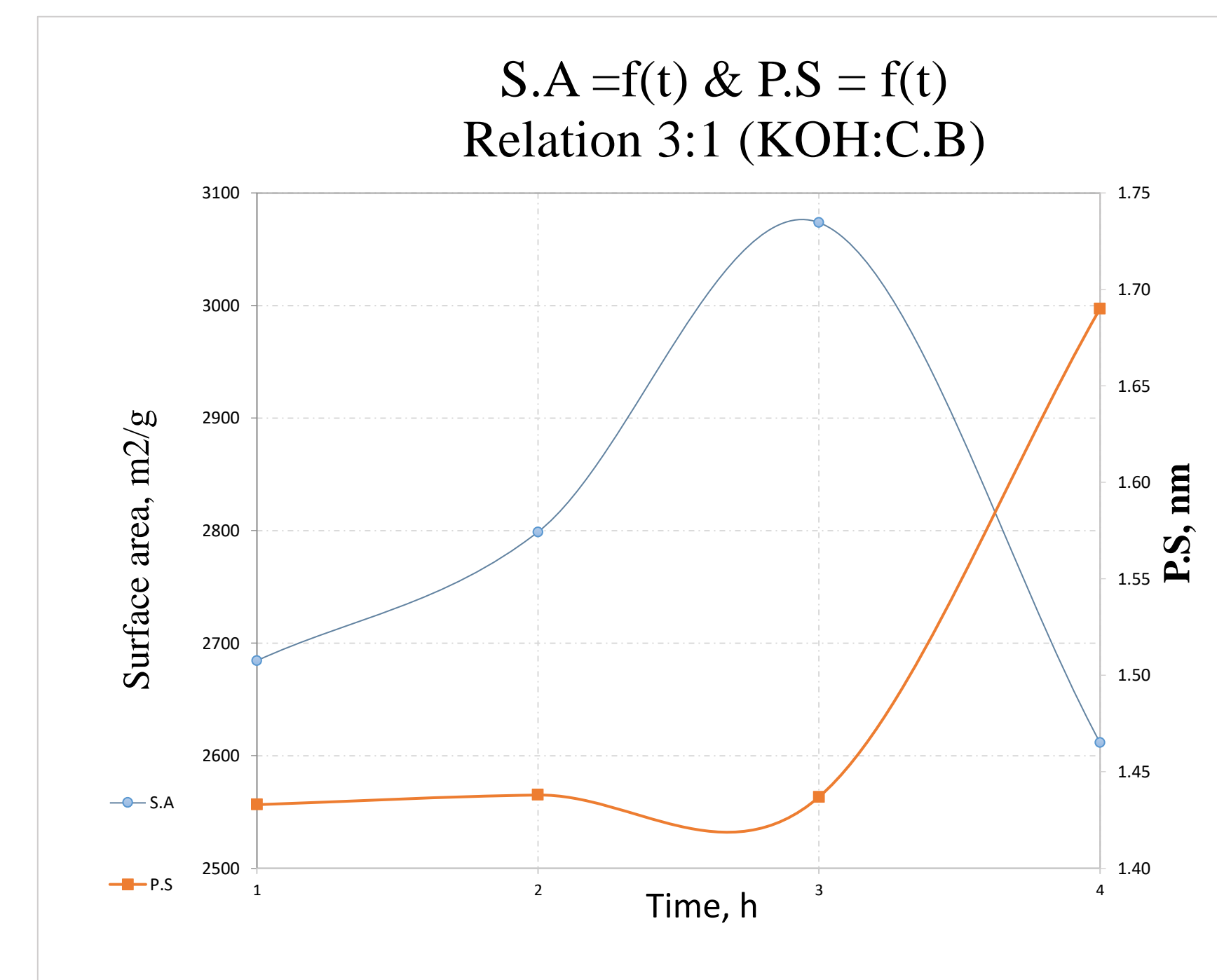
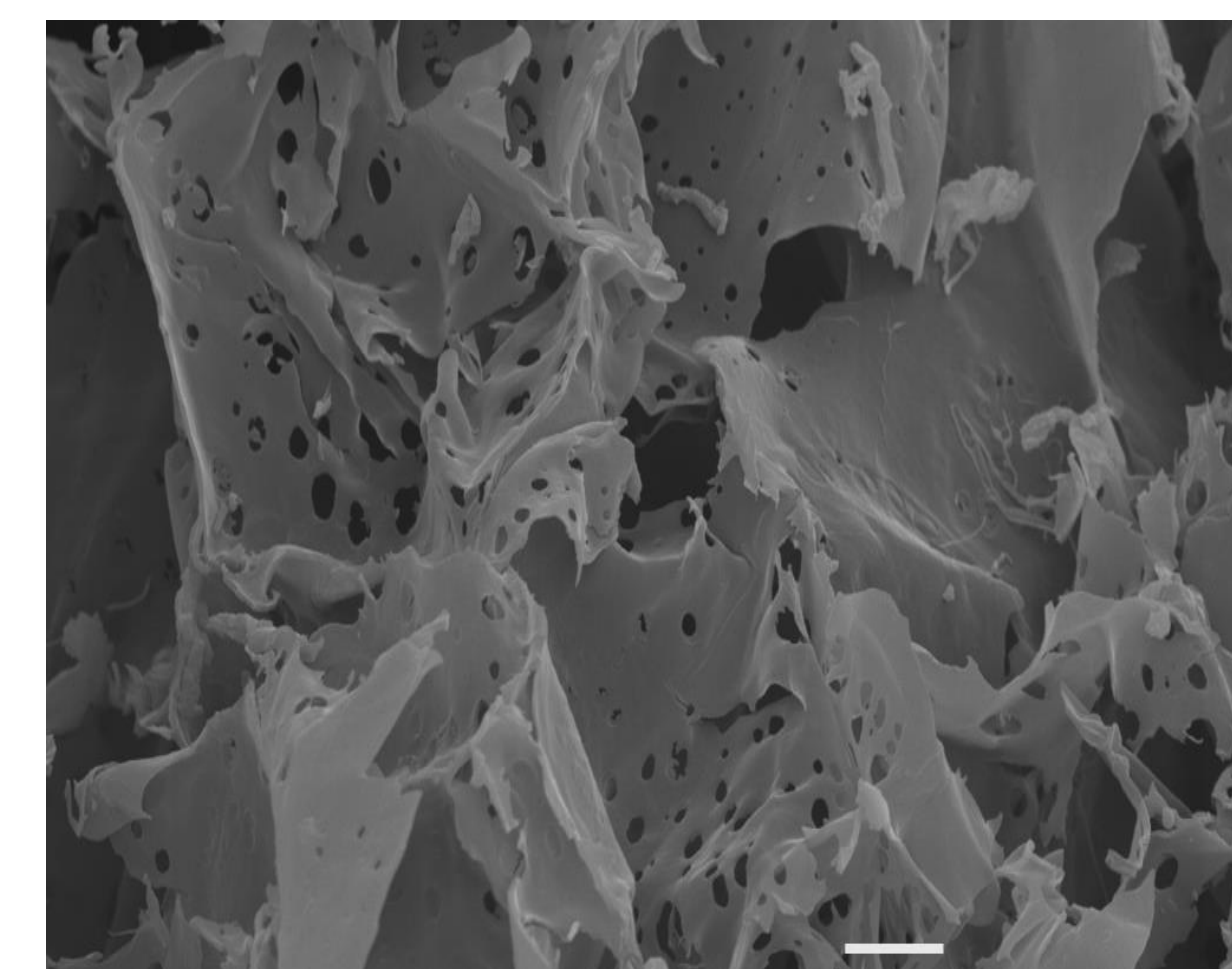


Figure.5 Cocoa's Pod Husk Surface Area Development.

SEM

Figure. 4 SEM of the Activated Carbon Sample.



The characterization of the reminder biomass allows having a starting point quite like the literature's, in the pyrolysis stage a homogeneous and good-looking char was obtained,

which through chemical activation allowed reaching surface areas of more than 3000 g/m². The preparation of the electrode with CA's presented a fine conductivity and homogeneity in the films for carrying out the tests without difficulties.

Cyclic Voltammetric Test

The implementation as a carbon electrode was carried out in a Biologic VMP multichannel potentiostat electroplating potentiostat, testing the electrode up to 0.8 V with the scanning speed of 10 to 500 mV/s with five tests of 0,1 to 50 mA/mg.

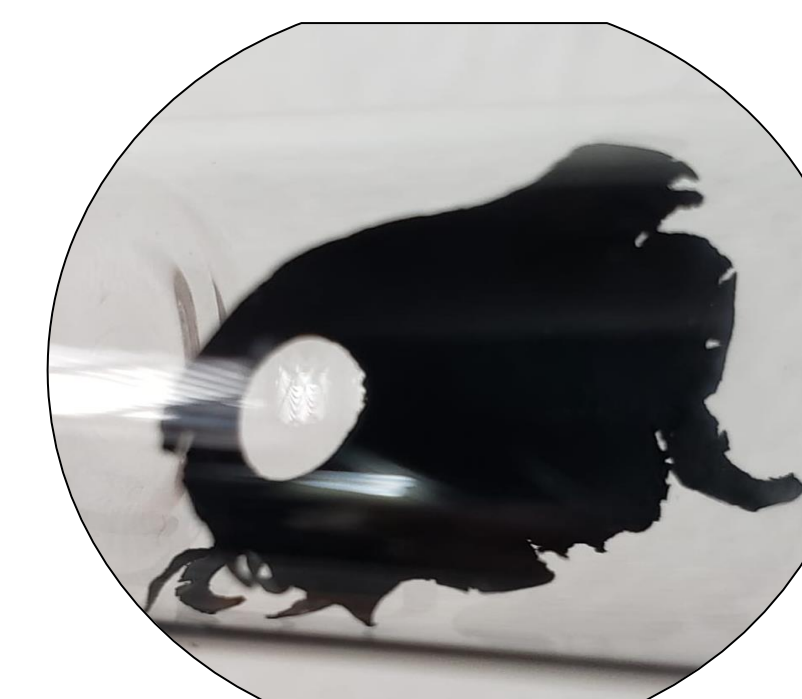


Figure. 6 Electrode Liner Picture

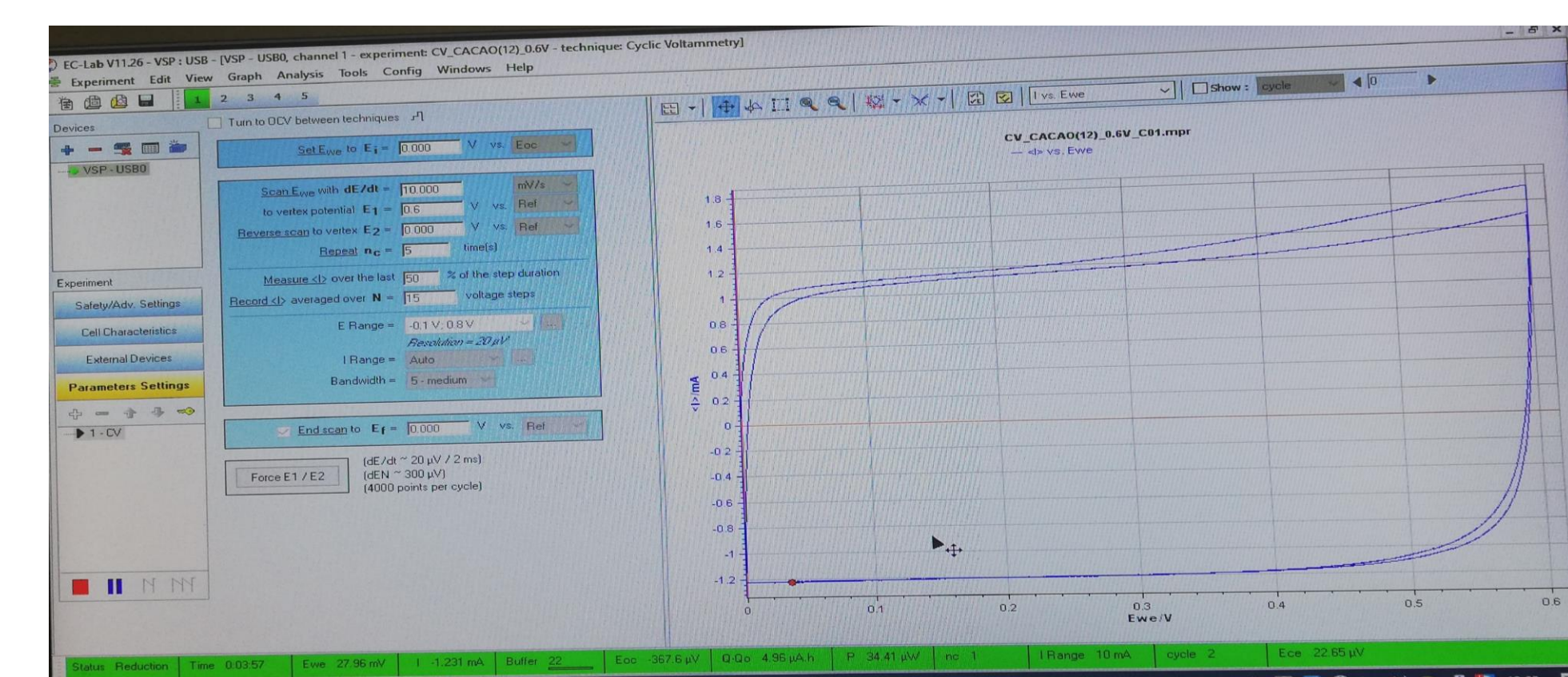


Figure. 7 Showing the Cyclic Voltammetric Performance of the Capacitor.

Conclusion

It is feasible to produce electrodes for capacitors from the reminder cocoa biomass between surface areas of 1800 m²/g to 3100 m²/g, reaching a maximum energy storage capacity of 42 A/g. Moreover, it is determined that cocoa residues can be used as a good color retainer as well as a precursor for the development of electrodes for capacitors.

Acknowledgments

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