Revista Internacional de Investigación e Innovación Tecnológica

Página principal: www.riiit.com.mx

# Physical-chemical characterization of pineapple stubble as possible raw material for bioenergetics

# Caracterización fisicoquímica del rastrojo de piña como posible materia prima para bioenergéticos

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**Technological innovation:** Valorization of agroindustrial waste.

**Industrial application area:** Biorefinery.

Received: december 14th, 2020
Accepted: november 23th, 2021

## Resumen

La presente investigación se centra en la caracterización fisicoquímica del rastrojo de piña, para utilizarlo como sustrato para posteriores procesos de biorrefinería. Costa Rica es líder en la exportación de piña fresca (*Ananas Comosus*) a nivel mundial y se encuentra entre los 10 países con mayor superficie cultivada. Esta alta producción, a su vez, genera anualmente 4,6 x $10^6$ toneladas métricas de rastrojo (raíces, tallos, hojas y brotes laterales). Este material causa un gran impacto ambiental ya que químicos altamente contaminantes (como el 1,1'-dimetil-4,4'-bipiridilo) se utilizan con frecuencia para deshidratar el material y obtener un volumen de fácil manejo de los subproductos de la industria de la piña. Para ello se monitorearon los cantones (San Carlos y Los Chiles) ubicados en la Provincia de Alajuela (Región Norte de Costa Rica). Se muestrearon compuestos de 15 a 20 plantas por lote siguiendo un método de muestreo de cuadrante aleatorio simple de siete fincas de piña ubicadas en la zona en estudio. Todos los datos se expresaron como g / 100 g de materia seca: Contenido de humedad a 60°C (85.58 ± 1.68), cenizas (12.28 ± 3.66);

hemicelulosa (20.30 ± 2.39), celulosa (34.57 ± 2.82) y lignina detergente ácida (4.04 ± 1.58). Para las muestras que contienen de 11% a 15% de humedad, el calor de combustión fue de 15.1 ± 0.8 MJ / kg (como *Tectona grandis* 15.26 MJ / kg, *Elaeis guineesis* 15.83 MJ / kg), y el consumo de energía para eliminar la humedad restante por debajo del 5% es cerca del 10-15% de la energía producida. Los resultados obtenidos muestran que el Rastrojo de Piña tiene potencial para ser utilizado como materia prima para la producción de energía.

**Palabras clave:** Bioenergía, biorrefinería, materia prima, rastrojo de piña.

## Abstract

The present research focuses on the physicochemical characterization of pineapple stubble, to use as a substrate for further biorefinery processes. Costa Rica is a leader in the export of fresh pineapple (*Ananas Comosus*) worldwide and is among the 10 countries with the largest cultivated area. This high production, in turn, generates annually 4.6 x $10^6$ metric tons of stubble (roots, stems, leaves, and side shoots). This material causes great environmental impact since highly polluting chemicals (such as 1,1'-dimethyl-4,4'-bipyridyl) are frequently used to dehydrate the material and to obtain an easy handling volume of by-products from the pineapple industry. To do this, cantons (San Carlos and Los Chiles) located in the Province of Alajuela (at the Northern Region of Costa Rica) were monitored. Composite of 15 to 20 plants per lot were analyzed following a simple random quadrant sampling method from seven pineapple farms located in the zone under study. All data were reported as g/100 g of dry matter: Moisture content at 60°C (85.58 ± 1.68), ash (12.28 ± 3.66); hemicellulose (20.30 ± 2.39), cellulose (34.57 ± 2.82), and acid detergent lignin (4.04±1.58). For samples containing 11% to 15% moisture, the heat of combustion was 15.1 ± 0.8 MJ/kg (like *Tectona grandis* 15.26 MJ/kg, *Elaeis guineesis* 15.83 MJ/kg), and the energy consumption to eliminate the remaining moisture below 5% is close to 10-15% of the energy produced. The results obtained show that pineapple stubble has the potential to be used as a raw material for energy production.

**Keywords:** Bioenergy, Biorefinery, pineapple stubble, raw materials.

## Introduction

Lignocellulosic biomass is the most important raw material in biorefinery processes, especially in the generation of primary energy and in the production of fermentable sugars to convert them into biofuels and biomaterials (Cai et al., 2017; Hasan Ba Hamid & Ku Ismail, 2020). Lignocellulosic biomass comes from agricultural, agro-industrial, or timber activities, making it a renewable raw material (Dimian, 2015; Tursi, 2019). Thus, biorefinery processes are a promising production model to reduce agricultural waste and promote the reduction of air emissions (Hasan Ba Hamid & Ku Ismail, 2020).

The conversion of biomass into energy or value-added products can be carried out in two ways, one thermochemical and one biochemical (Gollakota et al., 2018; Nanda et al., 2014). The thermochemical conversion uses heat and chemical processes such as combustion, pyrolysis, liquefaction, and gasification to produce energy and biomass products (Dimian, 2015; Nanda et al., 2014; Tursi, 2019). Biochemical conversion of biomass uses bacteria, microorganisms, or enzymes to break down biomass into gaseous

or liquid fuels, or intermediate products for further synthesis (Cai et al., 2017).

It should be noted that biomass is a sustainable fuel that offers a significant reduction in net carbon emissions compared to fossil fuels (Saxena & Jotshi, 1994). However, high volatile content and low energy densities should be significantly different from those of mineral or plant coal, limiting substitution ratios in boilers using biomass as fuel (Li et al., 2015; Tian et al., 2016). The choice of biomass and its derivatives generates high expectations to produce fuels, raw materials for synthesis in the petrochemical industry, and fine chemicals (Dimian, 2015; Tursi, 2019). Biomass, in addition to the production of second-generation biofuels (bioethanol and biodiesel), is also of interest to bio-oil production due to its prospects for pyrolysis production (Basu, 2010; Dias et al., 2018; Elkhalifa et al., 2019; Li et al., 2015; Yin & Li, 2017).

Before using lignocellulosic biomass as raw material, it is important to know its chemical composition (cellulose, hemicellulose, lignin, ash) and physical elements such as moisture, combustion heat, density, drying rate or moisture saturation and its availability (Cai et al., 2017; Gollakota et al., 2018; Nanda et al., 2013, 2014). These properties vary depending on the geography, type of crop, or industry that generates it. That is why the types of biomasses in the intertropical zone such as Costa Rica differ greatly from those found at latitudes further north or south. In Costa Rica, you can find a wide variety of lignocellulosic biomass from crops such as sugar cane, coffee, pineapple, banana, oil palm, among others.

The cultivation of pineapple (*Ananas comosus*) reaches approximately 65 671 ha of coverage as reported by the Program of Monitoring Changes of Land Use in Productive Landscapes (MOCUPP) (Vargas et al., 2020). The National Chamber of Pineapple Producers and Exporters (CANAPEP) reports an area of cultivation of approximately 44 500 ha, with annual exports of $930.5 million in 2019 (CANAPEP, 2020). The difference between crop area reports is associated with the non-binding of producers to be registered with CANAPEP.

Concerning the generation of residues in the field (pineapple stubble), once the fruit is harvested, about 250±70 ton $ha^{-1}$, with the moisture of more than 80% are reported (Hernández-Chaverri & Prado-Barragán, 2018). The management of pineapple stubble is done in two ways: (i) in green, which involves processing with mechanical equipment directly in the field for immediate incorporation into the soil, and (ii) dry, where a herbicide is first applied (1,1'-dimethyl-4,4'-bipyridyl) to "dry" the plant, then the waste is burned and then incorporated into the soil, handling involving a high cost to producers and the environment (Hernández-Chaverri & Prado-Barragán, 2018).

Waste burning should be avoided because it carries serious health and environmental risks, as it is associated with air pollution, accelerated soil organic losses, and reduces soil fertility by eliminating microbial soil activity (Naresh Kumar et al., 2019). Burning the residual biomass of crops in the field leads to an increase in breathing problems and irritation in the eyes due to smoke (Lee et al., 2020).

All plants have different chemical compositions, and pineapple stubble is no exception; therefore, it is necessary to carry out fundamental studies on these characteristics in energy processes. Despite a large amount of published information on the use of biomass, studies with detailed characterizations are scarce and limited to the available databases of organizations such as

the National Renewable Energy Laboratory (NREL) and Deutsches Biomasse Forschungszentrum (DBFZ) (Marrugo et al., 2016).

Pineapple as perennial cultivation of bromeliads has the advantage of having an availability of waste throughout the year (Garita-Coto, 2014), and the annual replacement rate between new and old plantations is approximately 40% (Hernández-Chaverri & Prado-Barragán, 2018) in the case of Costa Rica. From the point of view of the use of agro-industrial waste as a raw material in energy production, it makes the stubble of pineapple biomass with high potential due to its availability and concentration in planting areas. In addition, the type of process currently used in the disposal of its agricultural residues, which includes the application of herbicides and the burning of residues (Hernández-Chaverri & Prado-Barragán, 2018), is a potential source of contamination to soil and groundwater (Maglianesi Sandoz, 2013).

For the use of agro-industrial waste directly to produce energy, the study of the drying process is essential. In drying processing, it is important to consider that the diffusivity value of the water is in the matrix of the study sample, and this will depend on the area, porosity, and drying speed, among other factors. Therefore, differential drying curves at constant temperature provide a means to evaluate water diffusivity in porous solids such as mineral solids or lignocellulosic biomass materials. The diffusivity of liquid through porous materials is defined by three properties: a) porosity (void fraction), b) constriction (ratio between the average diameter of the moving liquid molecules and the diameter of the pores) and c) pore tortuosity (Ulate-Segura & Mata-Segreda, 2014). In porous materials with high xc values, it is reasonable to state that fluids diffuse faster (Ulate-Segura & Mata-Segreda, 2014). xc is an indirect measure of the diffusivity of fluids in porous materials, so it can be used to evaluate their relative mobility in groups of porous materials; thus, it is understood that fluids diffuse more easily in solids with high xc values, and tc is the critical drying time, where the linearity inflection occurs. (Conejo-Barboza & Mata-Segreda, 2018). This explains the weak binding of water to the material; therefore, the determination of the critical drying point (xc), where a kinetic transition of the constant drying rate occurs as the drying rate decreases, allows the comparison of water diffusivity between materials (Puente-Urbina et al., 2016). In this case, the obtained results were expressed as drying rates, dx/dt, where x is the extent of the process that occurred at the time t ($x = [m(0) - m(t)] / [m(0) - m(\infty)]$, a simple mass balance), plotted as a function of the residual moisture fraction (1-x) associated with the solid material (Ulate-Segura & Mata-Segreda, 2014). Drying curves given as mass (or x) vs time show an initial linear relationship, implying that -dm/dt (or dx/dt) is constant in that section. Once the value (-dm/dt or dx/dt) is reached ($t_c$, $x_c$), the drying rate decreases as the process takes place (Conejo-Barboza & Mata-Segreda, 2018; Puente-Urbina et al., 2016; Ulate-Segura & Mata-Segreda, 2014).

This research focused on the study of the drying process of fresh pineapple stubble biomass to be used as a raw material in bioenergy or biorefinery processes.

## Materials and methods

### *Materials and equipment*

***Materials.*** The samples were collected on seven farms in the northern region of Costa Rica (10-49'52.7"N 84-42'33.1"W; 10-35'36.0"N 84-29'07.8"W; 10-28'24.0"N 84-37'35.7"W; 10-26'50.3"N 84-17'13.9"W; 10-23'35.8"N 84-10'18.1"W; 10-28'55.1"N 84-

05' 24.6"W; 10-31'06.0"N 84-11'54.0"W), between March 2018 and September 2019.

***Equipment.*** Echo Bear-Cat Sc 3306 chipping machine; Parr Calorimeter; moisture balance Ohaus MB35; autoclave Advantec SV-302; oven SANYO MOV-112; stove Thermo Scientific EM-1240 Thermolyne; ultracentrifugal mill ZM 1-RETSCH with 1 mm ring; and infrared spectrophotometer with transformed Fourier FT-IR Nicolet iS50 Thermo Scientific; SEM Jeol JSM-5900 LV; TGA Q500 (TA Instruments, USA).

***Experimental methods***

***Sampling and treatment of the sample*.** Simple random, with quadrant technique on each farm according to the growing lot, the stubble sample corresponds to discard plants with one harvest (approximately 18 months) or two harvests (approximately 28 months). Each sample was composed of 15 to 20 plants. The plants were washed with plenty of water to remove residues from the soil. Subsequently, the plants were cut into 5 cm pieces in a cutting machine, then crushed into a chipping machine twice. The average particle size distribution was 61% < 2 mm, 9% was between ≥ 2 mm ≤ 4 mm and 30% > 4 mm.

***Characterization of pineapple stubble.*** The samples were taken to the Animal Nutrition Research Center (CINA) of the University of Costa Rica for characterization. The parameters that were determined were dry matter (DM), ash (ASH), moisture (MOI) according to the official methods of AOAC (2001); in the case of acid lignin (LIG), cellulose (CEL), and hemicellulose (HEM), the methodology described by Van Soest and Robertson (2001) was followed.

***Heat of combustion***. Was determined following ASTM D-5865-04 procedure and the moisture content was determined with a moisture balance at 105°C.

***Physicochemical treatment.*** A physicochemical treatment was performed on 20 samples of 10 g pineapple stubble, with moisture less than 10%. They were divided into two groups of 10 samples, group 1 (TA0.1M) and group 2 (TA1M), 15 ml of $H_2OS_4$ with a concentration of 0.1M and 1.0M, respectively, were added to each sample. Subsequently, they were subjected to autoclaving at 121 ± 1°C for 30 min. The samples were then washed and filtered with a vacuum pump to remove traces of acid and soluble solids (1.0 liters of distilled water). The TA0.1M and TA1M groups were in turn divided into two new groups, and the drying process was applied.

***Drying process.*** Drying was carried out under laboratory conditions of 55±5% relative humidity, 87 kPa barometric pressure for the area where the laboratory is located. A moisture balance was used. The samples used were fresh (freshly processed from the farm) or dry (those that were rehydrated for 12 hours, when the sample was previously dried for preservation), in both cases the excess water was removed with paper towels, applying slight manual pressure until moisture was not perceived in the towel. Approximately 10 g was placed on a 92 mm diameter aluminum disc, suitable for the balance. The drying temperature was set at 50ºC, the data collection was done manually. Raw mass-time data is recalculated as the drying extension x - time, obtained from the single mass balance x = [m (0) - m (t)] / [m (0) - m (∞)]. The extent of the initial zero-order kinetic phase was obtained by determining the slope of the x–time data pair group (linear adjustment of least squares), for which a linear correlation is valid with a Pearson correlation coefficient rp = 0.9990 (Ulate-Segura & Mata-Segreda, 2014). The value -dm/dt corresponds to the initial rate of

surface evaporation and the validity range allows the calculation of $x_c$. The effective surface flow area of the samples was calculated from the initial constant rate and evaporation rate of the previously determined water at 50ºC and 87 kPa (11.37 mmol $s^{-1}m^{-2}$) (Puente-Urbina et al., 2016).

***Energy cost of drying.*** From the drying kinetics and the operating conditions of the moisture balance (110 V and consumption of 4 A), the energy cost of drying could be estimated. Therefore, for a given experiment, the total electrical energy used is equal to the amount of 110 V × 4 A × time. The fraction of electrical energy used for the evaporation of water is obtained as the ratio between the thermal energy of evaporation of M grams of water (M × 2259 J $g^{-1}$) to the total electrical input. M is the difference between the initial mass of the sample and the final mass of the dry sample. An empirical regression equation was used as a function of M, where the fraction of energy = $1.091 \times 10^{-3} + 3.520 \times 10^{-4}$ M – $1.466 \times 10^{-5}$ $M^2$, with $R^2$ equal to 0.998 (Puente-Urbina et al., 2016).

***Fourier-Transform infrared spectroscopy (FTIR).*** A sample of approximately 0.1 g of material with particle size less than 63 µm (Mesh 230) was taken. The samples were analyzed in an infrared spectrophotometer, where sampling is performed with ATR accessory (total attenuated reflectance) with diamond cell. All data were obtained under laboratory conditions, in a spectrum range of 4000 to 400 $cm^{-1}$, with an accumulation of 32 sweeps per sample and a resolution of 4 $cm^{-1}$ to 100% transmittance. The obtained IR spectra were processed with OMNICTM Series 9 v9.8 software.

***Morphological analysis by scanning electron microscopy (SEM)***. An electron microscope with an acceleration voltage of 5 kV was used. The samples were mounted on 51 mm diameter aluminum bases with double-sided tape and coated with a gold layer.

***Thermogravimetric analysis (TGA).*** Small subsamples of 8-9 mg from the films were analyzed in the TGA under nitrogen atmosphere (60 ml $min^{-1}$ flow rate and 10°C $min^{-1}$ heating rate). The experiments ran from ambient temperature up to 1000°C. The analysis of data, which includes determination of initial degradation temperature (Ti), maximum degradation temperature (Tmax), final degradation temperature (Tf), percentage of remaining mass at initial temperature (MRi), remaining mass at maximum temperature (MRmax), and remaining mass at final temperature (MRf), was performed using the TA Instruments Universal Analysis Q500 (Rigg-Aguilar et al., 2020).

***Statistical analysis***. Unless otherwise noted, all analytical measurements were performed in triplicate. The results were expressed as averages ± standard error. The data for each evaluation were statistically analyzed using a one-way ANOVA with a significance level of $p \leq 0.05$, using MINITAB 19 software. To find differences between the stockings, the Tukey-Kramer test was performed.

## Results and discussion

***Characterization of pineapple stubble***. Characterization of pineapple stubble with one harvest (18 months) or two harvests (28 months) showed no significant differences ($p>0.05$) in parameters such as moisture, hemicellulose, cellulose, lignin, ash (Table 1). There was a significant difference between individual samples in parameters such as ash, lignin, cellulose, hemicellulose ($p\leq0.05$), this is associated with the physiological age of the plant, geolocation (soil type), season of the year of sample collection, and the stimulation process for its

growth according to the application of fertilization "packages" (Garita-Coto, 2014).

**Table 1.** Characterization of pineapple stubble as raw material for harvest age of 18 and 28 months of the plant between 2018 and 2019.

| Geolocation | MOI (%) | ASH (g/100g) | MD 60 °C (g/100g) | LIG (g/100g) | CEL (g/100g) | HEM (g/100g) |
|---|---|---|---|---|---|---|
| **Harvest Age (18 months)** | | | | | | |
| 10-23'35.8"N 84-10'18.1"W | 80.9±0.6 [b] | 19.06±0.67[b] | 19.1±0.6 [b] | 2.1±0.2 [b] | 28.9±1.2 [b] | 18.6±1.2 [a] |
| 10-26'50.3"N 84-17'13.9"W | 85.2±0.6 [a] | 16.55±0.58[c] | 14.8±0.6 [a] | 1.6±0.2 [c] | 32.7±1.2 [a] | 20.6±1.2 [a] |
| 10-26'50.3"N 84-17'13.9"W | 85.6±0.6 [a] | 17.23±0.60[c] | 14.4±0.6 [a] | 3.8±0.2 [a] | 38.4±1.2 [c] | 24.7±1.2 [b] |
| 10-35'36.0"N 84-29'07.8"W | 84.5±0.6 [a] | 11.74±0.41[a] | 15.5±0.6 [a] | 3.2±0.2 [d] | 35.4±1.2 [a] | 20.3±1.2 [a] |
| 10-49'52.7"N 84-42'33.1"W | 86.6±0.6 [a] | 11.47±0.57[a] | 13.4±0.6 [a] | 5.0±0.2 [e] | 35.9±1.2 [a] | 19.5±1.2 [a] |
| 10-35'36.0"N 84-29'07.8"W | 86.5±0.6 [a] | 12.15± 0.43[a] | 13.50±0.6 [a] | 4.2±0.2 [a] | 35.6±1.2 [a] | 22.7±1.2 [b] |
| **Average ±STD** | **84.9±2.1** [a] | **14.70±3.30** [a] | **15.1±2.1** [a] | **3.3±1.3** [a] | **34.5±3.3** [a] | **21.1±2.2** [a] |
| **Harvest Age (28 months)** | | | | | | |
| 10-28'55.1"N 84-05'24.6"W | 87.2±0.6 [a] | 12.10±0.43[a] | 12.8±0.6 [a] | 3.2±0.2 [d] | 35.4±1.2 [a] | 20.2±1.2 [a] |
| 10-31'06.0"N 84-11'54.0"W | 84.5±0.6 [a] | 8.81±0.31[f] | 15.5±0.6 [a] | 3.7±0.2 [a] | 31.7±1.2 [a] | 18.7±1.2 [a] |
| 10-26'50.3"N 84-17'13.9"W | 86.0±0.6 [a] | 12.43±0.44[a] | 14.0±0.6 [a] | 4.2±0.2 [a] | 35.8±1.2 [a] | 21.0±1.2 [a] |
| 10-28'24.0"N 84-37'35.7"W | 85.6±0.6 [a] | 6.69±0.23[e] | 14.4±0.6 [a] | 7.2±0.2 [f] | 32.5±1.2 [a] | 17.3±1.2 [c] |
| 10-49'52.7"N 84-42'33.1"W | 85.9±0.6 [a] | 9.56±0.48[d] | 14.1±0.6 [a] | 6.3±0.2 [g] | 33.7±1.2 [a] | 22.7±1.2 [b] |
| 10-49'52.7"N 84-42'33.1"W | 85.8±0.6 [a] | 9.58±0.34[d] | 14.2±0.6 [a] | 4.0±0.2 [a] | 38.8±1.2 [c] | 23.3±1.2 [b] |
| **Average ±STD** | **85.8±0.9** [a] | **9.86±2.1** [a] | **14.2±0.9** [a] | **4.8±1.6** [a] | **34.7±2.6** [a] | **20.5±2.3** [a] |

*Results expressed as average. Values represented with different letters are statistically different with p≤ 0.05.
In Table 2, the results of this research are compared with previous characterization studies of pineapple stubble carried out at the CINA-UCR, (the authors do not report standard deviations). Here, it is important to note that there is no significant difference (p≤ 0.05), whether the stubble comes from a plant with one or two harvests. From these comparisons it is possible to **establish preliminary scopes** of the composition of pineapple stubble: ash [(7.3-15.9) g/100g], lignin [(1.8-6.6) g/100g], hemicellulose [(18.6-29.9) g/100g], cellulose [(31.8-37.7) g/100g], dry matter [(7.8-16.3) g/100g].

**Table 2.** Parameters of characterization of pineapple stubble such as ash, cellulose, hemicellulose, lignin, dry matter.

| Constituents | References | | | This investigation |
|---|---|---|---|---|
| | (López-Herrera et al., 2009) | (López-Herrera et al., 2014) | (López-Herrera et al., 2016)* | |
| Cellulose (g/100g) | 32.2 | 37.7 | 35.9 | **34.6±2.8** |
| Hemicellulose (g/100g) | 21.0 | 29.9 | 24.8 | **20.8±2.2** |
| Lignin (g/100g) | 2.8 | 6.6 | 1.8 | **4.0±1.6** |
| Ashes (g/100g) | 10.8 | 7.3 | 7.6 | **12.7±3.7** |
| Dry matter (g/100g) | 12.3 | 9.4 | 7.8 | **14.6±1.6** |

*Corresponds to fruit crowns.

***Heat of Combustion***. Pineapple stubble has an average heat of combustion of 15.1 ± 0.8 MJ/kg, in a moisture range of 12.9 ± 1.5%. The energy benefit of pineapple stubble is like other biomass sources, such as *Tectona grandis* 15.26 MJ/kg, *Elaeis guineesis* 15.83 MJ/kg (Moya-Roque et al., 2015). For the TA0.1M treatment, the heat of combustion was 18.3 ± 0.4 MJ/kg, and for the TA1M treatment it was 18.9 ± 0.3 MJ/kg with a humidity between 8-12%, which are higher values than the heat of combustion of pineapple stubble, which shows that when treating the stubble by chemical hydrolysis the residual solid material increases its caloric power. To bring stubble to the moisture of between 10 - 20% or lower, there is an intrinsic energy cost since stubble has natural moisture of about 85%. This leads to the need to establish the drying conditions and properties of pineapple stubble for direct energy use.

***Drying curves.*** Typical drying curves were obtained for pineapple stubble with harvest ages of 18 and 28 months (Figure 1). In general, two periods are observed during which moisture loss occurred. One is fast and of constant speed during the first 30 min, followed by another of decreasing speed, which lasted until mass stability was reached at 210 min. Determining the fraction of moisture that can completely cover the surface of particles is useful data for scaling drying processes and obtaining operational energy efficiency parameters.

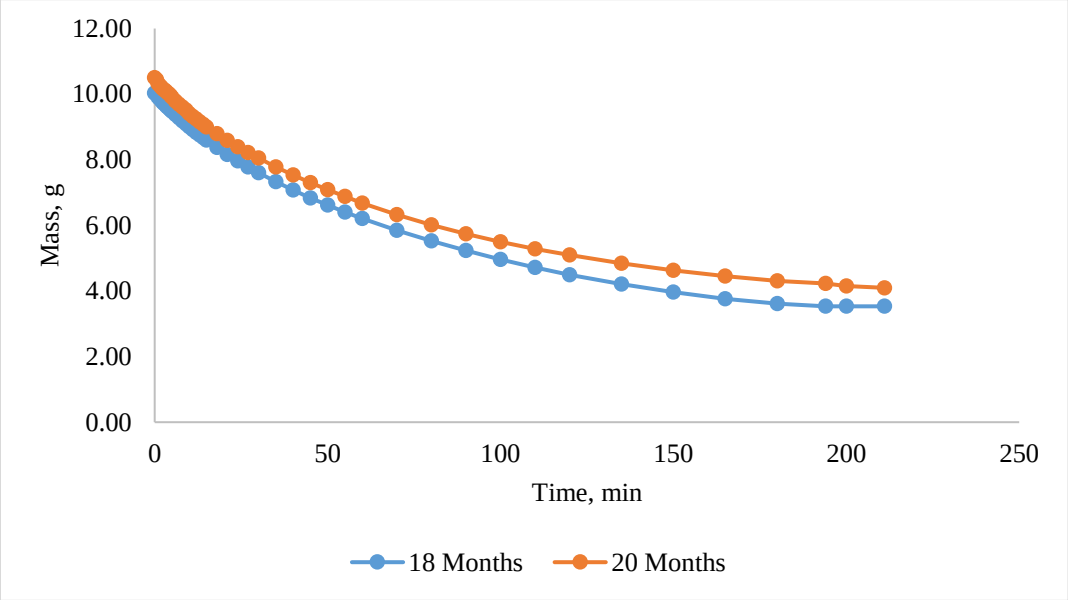



**Figure 1.** Drying curve of pineapple stubble with mean particle size distribution 61% <2 mm, 9% is between ≥ 2 mm ≤ 4 mm and 30%> 4 mm at 50°C, 60 % relative humidity, and 87 kPa.

Figure 2 shows the constant drying section and the decreasing section, which allows determining the fraction of loss of critical moisture $x_c$, for the stubble of pineapple at 50ºC in differential form (60% RH and 87 kPa). Linear segments in all cases were taken as those in which mass-time data pairs correlate with a Pearson rp equal to 0.999.

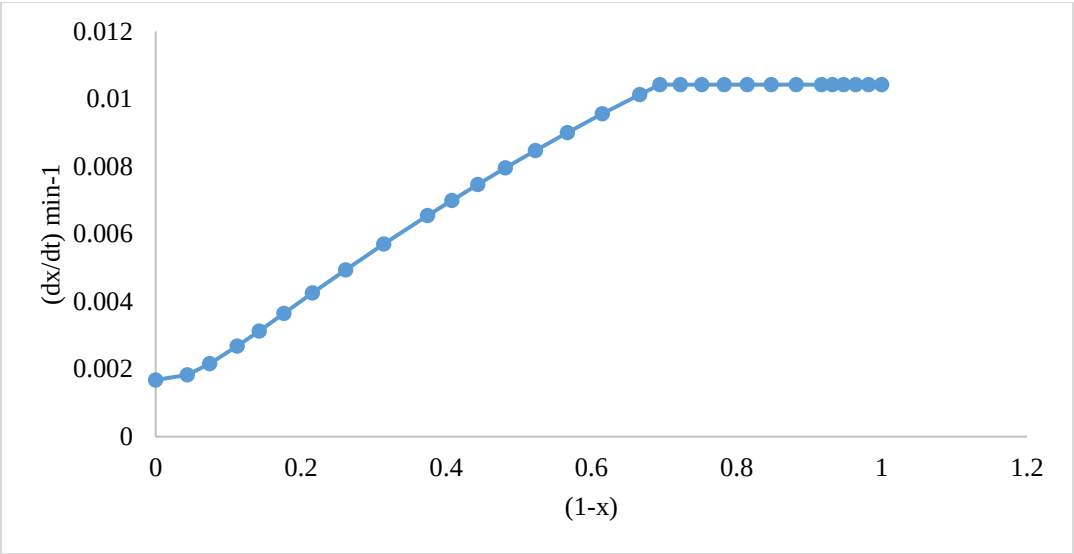



**Figure 2.** Krischer curve for pineapple stubble with mean particle size distribution 61% <2 mm, 9% is between ≥ 2 mm ≤ 4 mm and 30%> 4 mm at 50 °C, 60 % relative humidity, and 87 kPa.

Table 3 shows the drying parameters associated with ($x_c$), specific fluxional area, and specific k (associated with the transfer area), depending on the area of the drying curve (Figure 2). The $x_c$ can be used as a relative measure of water diffusivity between a group of porous materials, in addition to a macroscopic indication of the weakly bonded moisture fraction in the drying material. Diffusivity is an important factor in heterogeneously catalyzed processes, in which catalyst molecules must move and act through networks of pores, such as the manufacture of wood pulp or the saccharification of lignocellulosic materials (Conejo-Barboza & Mata-Segreda, 2018).

**Table 3.** Drying parameters according to the area of the drying curve and the energy conditions required for drying.

| | | Harvest Age | | Treatment | |
|---|---|---|---|---|---|
| | **Parameter** | **18 months** | **28 months** | **TA0.1M** | **TA1M** |
| | % Moisture Removed | 62.80±3.99 | 64.84±4.02 | 62.15±2.51 | 74.78±1.22 |
| ZONE 1 | Critical moisture content, $x_c$ | 0.27±0.06 | 0.27±0.09 | 0.25±0.04 | 0.30±0.03 |
| | Specific fluxional area, $m^2 kg^{-1}$ | 1.968±0.342 | 1.974±0.925 | 2.186±0.109 | 2.331±0.281 |
| ZONE 2 | k specific, $s^{-1} m^{-2}$ | 0.034±0.008 | 0.027±0.009 | 0.040±0.004 | 0.024±0.005 |
| | Drying Energy for $x_c$, Ec, (MJ $kg^{-1}$) | 0.135±0.040 | 0.176±0.148 | 0.116±0.032 | 0.225±0.024 |
| ENERGY | Total Drying Energy, Et, (MJ $kg^{-1}$) | 1.285±0.144 | 1.597±0.281 | 1.361±0.272 | 2.004±0.431 |
| | Energy to dry up to 15-20 % Moisture, (MJ $kg^{-1}$) | 0.575±0.093 | 0.693±0.172 | 0.642±0.069 | 1.024±0.202 |
| | Energy fraction for drying, (1-(Ec/Et) | 0.89±0.04 | 0.90±0.07 | 0.92±0.01 | 0.89±0.01 |

For the parameters of $x_c$, specific fluxional area, and specific k, there are no significant differences ($p < 0.05$) for stubble with 18 and 28 months of age. Indicating that the fraction of surface water in the pineapple stubble follows a similar model of diffusivity regardless of harvest age, which at the industrial processing level allows the mixing of material according to its annual availability. An average value of $x_c$ was obtained for pineapple stubble of 0.27 ± 0.07;

like the value reported by Ulate-Segura and Mata-Segreda (2014) of 0.30 ± 0.01.

***Energy cost of drying***. The cost of drying energy is obtained by associating the thermal energy necessary for the removal of the remaining moisture as a function of the residual moisture in the sample, as observed in Figure 3. Information related to energy needs can be obtained from this graph to bring an initial residual moisture sample to residual moisture between 15-20%. From that value, it can be established that in the case of the pineapple stubble studied, the energy required to dry it to a residual moisture value between 15-20%, it is necessary to use about 5% energy (0.734 MJ/kg) of the total that the stubble can provide (15.1 MJ/kg).

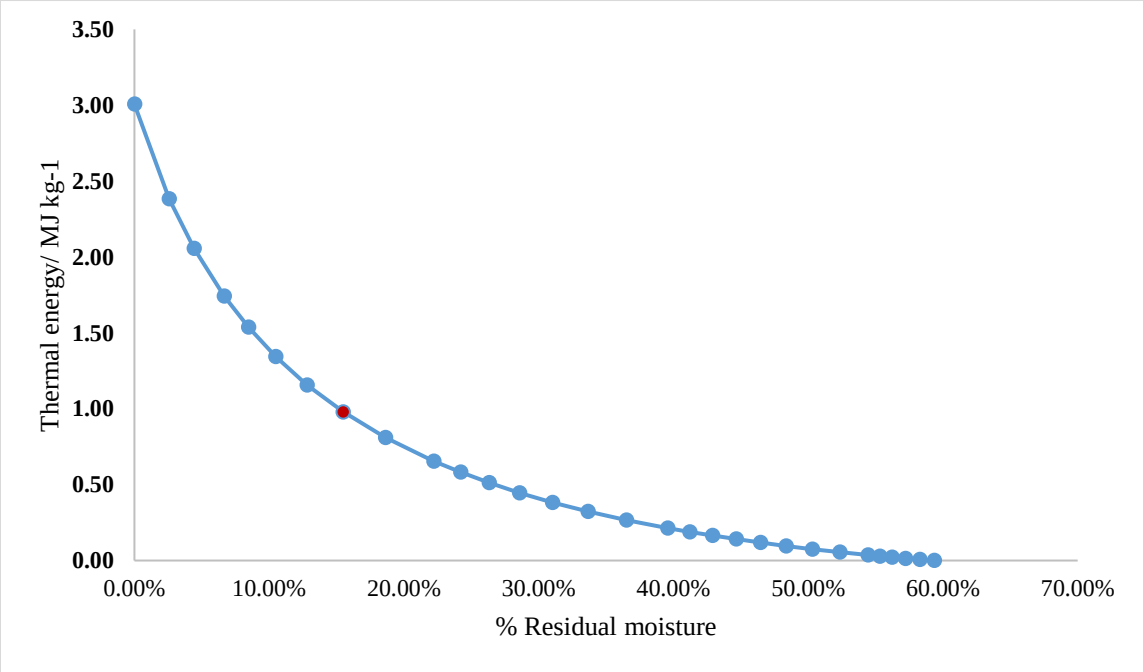



**Figure 3**. The typical curve for the energy cost for drying Pineapple stubble at 50°C, 60% relative humidity, and 87 kPa.

***FTIR analysis***. In Figure 4, the blue color represents the spectrum of the pineapple stubble (R.P.S), in green the TA0.1M treatment, and black the TA1M treatment. It can be observed that there is a notorious peak at 3344 $cm^{-1}$ for treated and untreated samples, this is characteristic of the O-H hydroxyl group, there is another peak at 2917 $cm^{-1}$, which corresponds to a vibration of the C-H link (Sena Neto et al., 2013).

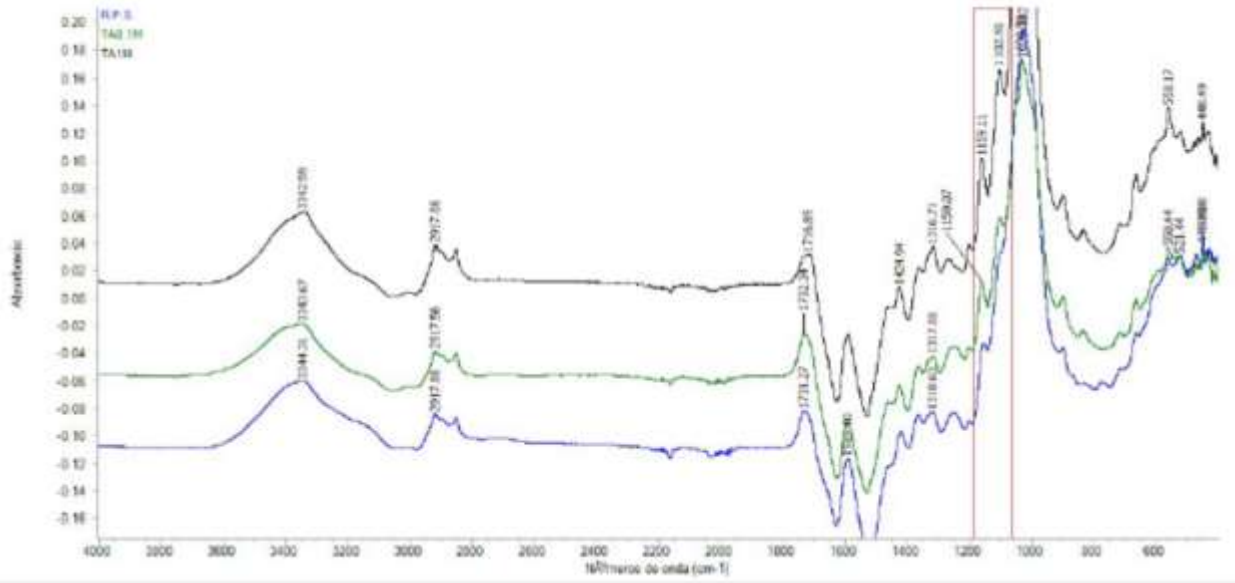
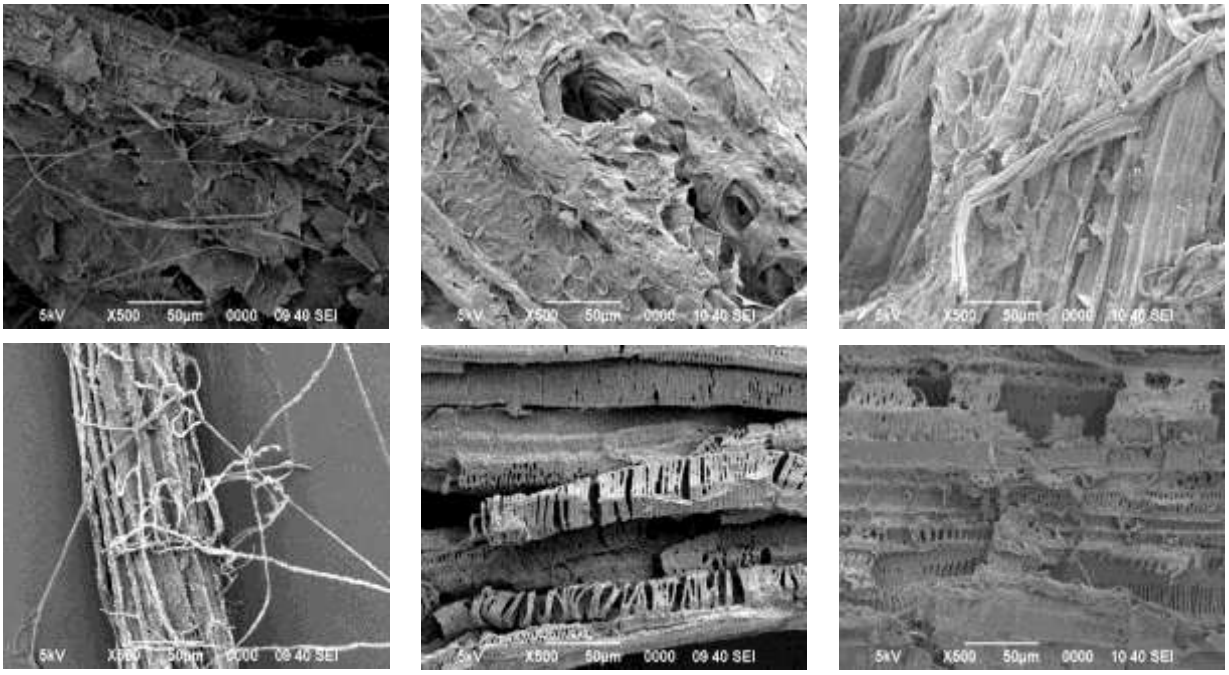


**Figure 4**. FTIR analysis for untreated and treated pineapple stubble.

Characteristic peaks of lignocellulosic materials were observed at 1716 $cm^{-1}$ and 1318 $cm^{-1}$, corresponding to acetyl groups and C-O bonds, characteristic of hemicellulose (Sena Neto et al., 2013; Toribio-Cuaya et al., 2014). These bands are affected by the presence of pectin, whose peaks are at 1680-1600 $cm^{-1}$ and the value of 1260 $cm^{-1}$. A lignin peak is found in the band of 1589 $cm^{-1}$ due to the aromatic vibrations in the C-C plane (Sena Neto et al., 2013; Solís Nicolas et al., 2019; Toribio-Cuaya et al., 2014). Cellulose is characterized by the 1170-1150 $cm^{-1}$, 1050, and 1030 $cm^{-1}$ bands, which are associated with aromatic skeletal vibrations attributed to lignin (Solís Nicolas et al., 2019) and are especially exposed with TA0.1M and TA1M treatments. The peaks at 1424 $cm^{-1}$ and the others around it are associated with the torsional vibrations of the groups -$CH_2$ and C-O of the aromatic rings (Solís Nicolas et al., 2019). The peak at 1244 $cm^{-1}$ belongs to the stretch link C–O of the lignin, while between 1030 $cm^{-1}$ and 1160 $cm^{-1}$ peaks corresponding to absorptions attributed to the deformation of the oscillating vibration C–H and the stretch of the skeleton of the pyranose ring C –O – C are observed (Xu et al., 2013). This intense peak at 1030 $cm^{-1}$ can also be attributed to the C–O bonds, the double C-C and C–C–O stretching bonds present in lignin, cellulose, and hemicellulose (Rigg-Aguilar et al., 2020; Sena Neto et al., 2013).

***SEM Analysis***. The fiber sections shown with the SEM technique (Figure 5) were chosen randomly; for pineapple stubble as for treatments TA0.1M and TA1M. In Figure 5A the fibers show a coating that is associated with the cell wall of the material, while in Figure 5B and 5C there is a degradation of the cell wall and greater damage associated with the increase in the concentration of $H_2SO_4$ 0.1 M to 1 M.



**(A) Pineapple stubble** **(B) TA0.1M** **(C) TA1M**

**Figure 5.** SEM analysis for untreated and treated pineapple stubble.

The effects (treatments) work on the cell wall and fibers, which indicates that the remaining cellular matrix (cellulase, hemicellulose) has been degraded, and promotes its decomposition into smaller C5 and C6 molecules; this establishes the potential of pineapple stubble to be integrated into a biorefinery process for obtaining primary energy and other compounds for industrial use.

***TGA analysis.*** Table 4 shows the results for the analysis of each degradation stage for pineapple stubble, TA0.1M, and TA1M. In stage 1 it is observed that the loss of water and volatiles occurs below 128$^{o}$C, the mass loss ranges from 7.0% for pineapple stubble to 3.8% for TA1M treatment.

**Table 4.** TGA analysis for untreated and treated pineapple stubble associated with the stage of the curve.

| Analysis stage | Pineapple Stubble | TA0.1M | TA1M |
|---|---|---|---|
| Stage 1 | 128.40°C, 7.04% (0.587 mg) | 128.40°C, 4.26% (0.345 mg) | 128.40°C, 3.80% (0.309 mg) |
| Stage 2 | 394.31°C, 55.19% (4.604 mg) | 459.35°C, 73.18% (5.927 mg) | 487.09°C, 75.29% (6.114 mg) |
| Stage 3 | 994.99°C, 24.29% (2.027 mg) | 994.99 °C, 16.19% (1.311 mg) | 994.99°C, 8.91% (0.724 mg) |

In the second stage of degradation that starts at 128.4$^{o}$C, for each of the samples, the final temperature increases according to the type of sample [(394.31$^{o}$C, pineapple stubble); (459.35$^{o}$C, TA0.1M); (487.09$^{o}$C, TA1M], indicating that treatment has been effective in the degradation of the lignocellulosic matrix, degrading cellulose and hemicellulose, which implies that the amount of residual lignin is higher in the sample with the TA1M

treatment. For the next stage of degradation, the traces of lignin are consumed, and the residues are the inorganic materials present. Figure 6 shows the differences in the TGA in each sample. This can be related to the increase in the heat of combustion between the pineapple stubble and each of the treatments applied. In addition, water loss and structural changes between the pineapple stubble and the treatments are evident in the TGA and IR (Figures 4 and 6); Figure 5 shows the structural damage to the stubble fibers.

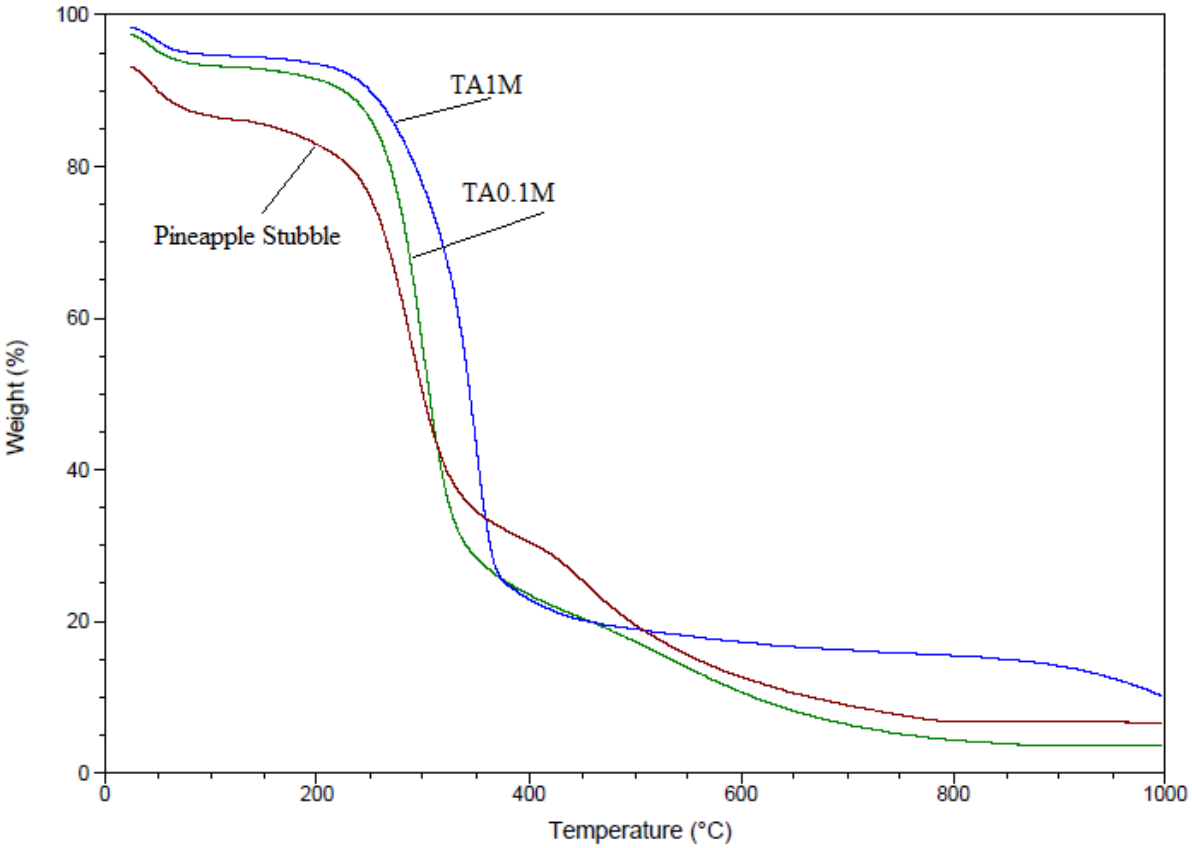



**Figure 6.** Multiple TGA analysis of pineapple stubble, TA0.1m, and TA1M.

## Conclusions

Pineapple stubble can be considered a potential raw material for bioenergy and biorefinery processes, given its caloric power and low theoretical energy consumption for a drying process. The application of a physical, thermal, and chemical treatment structurally affects the pineapple stubble, so it is important to continue analyzing this process for the identification of added value substances and the final residues that could be used to obtain primary energy.

## Acknowledgment

Institutional Improvement Program AMI-UNED and to the Institutional Scholarship Council for the allocation of scholarships for doctoral studies, to the Vice-rector for Research of the UNED for continuous support.

## References

Basu, P. (2010). Biomass gasification and pyrolysis: practical design and theory. Academic Press.

Cai, J., He, Y., Yu, X., Banks, S. W., Yang, Y., Zhang, X., Yu, Y., Liu, R., & Bridgwater, A. v. (2017). Review of physicochemical properties and analytical characterization of lignocellulosic biomass. In Renewable and Sustainable Energy Reviews (Vol. 76). https://doi.org/10.1016/j.rser.2017.03.072

CANAPEP. (2020). Estadísticas | CANAPEP. https://canapep.com/estadisticas/

Conejo-Barboza, G., & Mata-Segreda, J. F. (2018). Drying kinetics as Tool for the Assessment of Dynamic Porosity of Catalyst-Support Materials. International Journal of Renewable Energy & Biofuels, 1–10. https://doi.org/10.5171/2018.901967

Dias, A. F., Andrade, C. R., de Paula Protásio, T., de Melo, I. C. N. A., Brito, J. O., & Trugilho, P. F. (2018). Pyrolysis and wood by-products of species from the Brazilian semi-arid region. Scientia Forestalis/Forest Sciences, 46(117). https://doi.org/10.18671/scifor.v46n117.06

Dimian, A. C. (2015). Biorefinery, the future of chemical process industries. Bulletin of the Romanian Chemical Society, 22(1), 15–44. https://www.researchgate.net/publication/283721472

Elkhalifa, S., Al-Ansari, T., Mackey, H. R., & McKay, G. (2019). Food waste to biochars through pyrolysis: A review. In Resources, Conservation and Recycling (Vol. 144, pp. 310–320). Elsevier B.V. https://doi.org/10.1016/j.resconrec.2019.01.024

Garita-Coto, R. A. (2014). La Piña (Primera). Editorial Tecnológica de Costa Rica.

Gollakota, A. R. K., Kishore, N., & Gu, S. (2018). A review on hydrothermal liquefaction of biomass. Renewable and Sustainable Energy Reviews, 81(March), 1378–1392. https://doi.org/10.1016/j.rser.2017.05.178

Hasan Ba Hamid, H. S., & Ku Ismail, K. S. (2020). Optimization of enzymatic hydrolysis for acid pretreated date seeds into fermentable sugars. Biocatalysis and Agricultural Biotechnology, 24. https://doi.org/10.1016/j.bcab.2020.101530

Hernández-Chaverri, R. A., & Prado-Barragán, L. A. (2018). Impacto y oportunidades de biorrefinería de los desechos agrícolas del cultivo de piña (*Ananas comosus*) en Costa Rica. UNED Research Journal, 10(2), 455–468. https://doi.org/10.22458/urj.v10i2.2059

Lee, M., Lin, Y.-L., Chiueh, P.-T., & Den, W. (2020). Environmental and energy assessment of biomass residues to biochar as fuel: A brief review with recommendations for future bioenergy systems. Journal of Cleaner Production, 251. https://doi.org/10.1016/j.jclepro.2019.119714

Li, J., Paul, M. C., Younger, P. L., Watson, I., Hossain, M., & Welch, S. (2015). Characterization of biomass combustion at high temperatures based on an upgraded single particle model. Applied Energy, 156, 749–755. https://doi.org/10.1016/j.apenergy.2015.04.027

López-Herrera, M., Wing, R., Jones, C., Rojas-Bourrillon, A., & Rodríguez-Chacón, S. (2014). Valor Nutricional del ensilaje de rastrojo de piña con niveles crecientes de urea. Nutrición Animal Tropical, 8(1), 1–20.

López-Herrera, M., Wing Ching-Jones, R., & Rojas-Bourillon, A. (2016). Bromatología de ensilados de corona de piña con pulpa de cítricos, heno y urea. Agronomía Mesoamericana, 27(1), 37–47. https://doi.org/doi.org/10.15517/am.v27i1.21876

López-Herrera, M., Wing Ching-Jones, R., & Rojas-Bourrillón, A. (2009). Características fermentativas y nutricionales del ensilaje de rastrojo de piña (*Ananas Comosus*). Agronomía Costarricense, 33(1), 1–15. https://revistas.ucr.ac.cr/index.php/agrocost/article/view/6731

Maglianesi Sandoz, M. A. (2013). Desarrollo de las piñeras en Costa Rica y sus impactos sobre ecosistemas naturales y agro-urbanos. Biocenosis, Vol. 27 (1-2), 62–70.

Marrugo, G., Valdés, C. F., & Chejne, F. (2016). Characterization of Colombian Agroindustrial Biomass Residues as Energy Resources. Energy & Fuels, 30(10), 8386–8398. https://doi.org/10.1021/acs.energyfuels.6b01596

Moya-Roque, R., Rodríguez-Zúñiga, A., Tenorio, C., Valdez, J., & Valaert, J. (2015). Evaluación de la combustión de comprimidos cilíndricos fabricados con cultivos forestales y agrícolas en Costa Rica utilizando un quemador doméstico. Revista Forestal Mesoamericana Kurú, 13(30), 33. https://doi.org/10.18845/rfmk.v13i30.2458

Nanda, S., Mohammad, J., Reddy, S. N., Kozinski, J. A., & Dalai, A. K. (2014). Pathways of lignocellulosic biomass conversion to renewable fuels. Biomass Conversion and Biorefinery, 4(2), 157–191. https://doi.org/10.1007/s13399-013-0097-z

Nanda, S., Mohanty, P., Pant, K. K., Naik, S., Kozinski, J. A., & Dalai, A. K. (2013). Characterization of North American Lignocellulosic Biomass and Biochars in Terms of their Candidacy for Alternate Renewable Fuels. Bioenergy Research, 6(2), 663–677. https://doi.org/10.1007/s12155-012-9281-4

Naresh Kumar, M., Ravikumar, R., Thenmozhi, S., Ranjith Kumar, M., & Kirupa Shankar, M. (2019). Waste and biomass valorization. https://pubag.nal.usda.gov/catalog/6437660

Puente-Urbina, A., Morales-Aymerich, jean P., Kim, Y. S., & Mata-Segreda, J. F. (2016). Drying Kinetics and Assessment of Relative Energy Cost for Drying of Woody Biomasses. International Journal of Renewable Energy & Biofuels, March, 1–7. https://doi.org/10.5171/2016.701233

Rigg-Aguilar, P., Moya, R., Oporto-Velasquez, G. S., Vega-Baudrit, J., Starbird, R., Puente-Urbina, A., Mendez, D., Potosme, L. D., & Esquivel, M. (2020). Micro- And Nanofibrillated Cellulose (MNFC) from Pineapple (Ananas comosus) Stems and Their Application on Polyvinyl Acetate (PVAc) and Urea-Formaldehyde (UF) Wood Adhesives. Journal of Nanomaterials, 2020. https://doi.org/10.1155/2020/1393160

Saxena, S. C., & Jotshi, C. K. (1994). Fluidized-bed incineration of waste materials. Progress in Energy and Combustion Science, 20(4), 281–324. https://doi.org/10.1016/0360-1285(94)90012-4

Sena Neto, A. R., Araujo, M. A. M., Souza, F. v.d., Mattoso, L. H. C., & Marconcini, J. M. (2013). Characterization and comparative evaluation of thermal, structural,

chemical, mechanical and morphological properties of six pineapple leaf fiber varieties for use in composites. Industrial Crops and Products, 43(1), 529–537. https://doi.org/10.1016/j.indcrop.2012.08.001

Solís Nicolaas, E., Vega-Baudrit, J.-R., Rodríguez, E., & Meseguer Quesada, L. C. (2019). Estudio del efecto de la adición de nanocelulosa obtenida del desecho del rastrojo de piña en mezclas para materiales de construcción. Revista Iberoamericana de Polímeros, ISSN-e 0121-6651, Vol. 20, No. 1, 2019, Págs. 21-43, 20(1), 21–43. https://dialnet.unirioja.es/servlet/articulo?codigo=6839948&info=resumen&idioma=ENG

Tian, L., Shen, B., Xu, H., Li, F., Wang, Y., & Singh, S. (2016). Thermal behavior of waste tea pyrolysis by TG-FTIR analysis. Energy, 103, 533–542. https://doi.org/10.1016/j.energy.2016.03.022

Toribio-Cuaya, H., Pedraza-Segura, L., Macías-Bravo, S., González-García, I., Vásquez-Medrano, R., & Favela-Torres, E. (2014). Characterization of lignocellulosic biomass using five simple steps. In JCBPS (Vol. 4, Issue 5). www.jcbsc.org

Tursi, A. (2019). A review on biomass: Importance, chemistry, classification, and conversion. Biofuel Research Journal, 6(2), 962–979. https://doi.org/10.18331/BRJ2019.6.2.3

Ulate-Segura, D., & Mata-Segreda, J. (2014). Drying Kinetics as a Method for the Evaluation of Relative Diffusivity of Water in Porous Biomass Materials. International Journal of Renewable Energy & Biofuels, 2014, 1–7. https://doi.org/10.5171/2014.970016

Vargas, C., Miller, C., & Arguedas, C. (2020). Informe: Monitoreo del estado de la piña en Costa Rica para año 2018. MOCUPP.

Xu, F., Yu, J., Tesso, T., Dowell, F., & Wang, D. (2013). Qualitative and quantitative analysis of lignocellulosic biomass using infrared techniques: A minireview. In Applied Energy (Vol. 104, pp. 801–809). Elsevier Ltd. https://doi.org/10.1016/j.apenergy.2012.12.019

Yin, C., & Li, S. (2017). Advancing grate-firing for greater environmental impacts and efficiency for decentralized biomass/wastes combustion. Energy Procedia, 120, 373–379. https://doi.org/10.1016/j.egypro.2017.07.220