




Socioeconomic analysis of bioproducts derived from babassu nut breakers pyrolysis in legal amazonia communities

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Abstract

Lignocellulosic biomass residues can generate interesting materials for the chemical and food industries. Physical activation processes were developed by cold pressing and slow pyrolysis, as well as physical chemical activation with zinc chloride (ZnCl₂), to produce bio-based products, including bio-oil (30%) and biochar (31%), with good yields. Charcoal and biooil provided good results, respectively, with regard to adsorption capacity (357 m² g⁻¹ of surface area BET) and the possibility of extracting chemical compounds (phenols with 45.81% and aldehydes with 32.76%). Moreover, the key economic performance indicators of the process were analyzed, and the results indicate that the proposed process is economically feasible and attractive with \$422,416.10 profits. Finally, after dialoguing with the babassu nut breakers and understanding their needs, the feasibility of economically developing the contacted families through technology transfer for extracting the oil, cake, biochar, and bio-oil from babassu coconuts was studied, demonstrating the possibility of income generation based on the profitability achieved in this study.

Keywords: lignocellulosic biomass; bio-oil; biochar; energy.

Practical Application: Production of sustainable bioproducts from the wastes of Cerrado, Brazil, with technologies to help reduce the need for fossil diesel imports, improving the security of the energy supply. Therefore, socioeconomic analysis of this biomass improves the quality of life of the extractive communities that depend on this raw material.

1 Introduction

The generation of lignocellulosic residues is increasing every year, and due to their advantages, the residues have found many applications with a positive market value (Marasca et al., 2022; Rambo et al., 2017; Santos et al., 2022). In 2018, the electricity production from biomass energy products was 54.4 thousand gigawatt-hours (GWh), representing 9% of all electricity produced in Brazil (Instituto Brasileiro de Geografia e Estatística, 2021).

Using babassu residues for energy generation and value addition by different thermo-chemical processes may replace a significant portion of conventional energy sources (Bauer et al., 2020; Scheufele et al., 2021). Pyrolysis is one of the thermochemical processes carried out in the absence of oxygen. It yields carbon-rich char, condensable vapors, and non-condensable gases. The bio-oil is a dark brown liquid that can be used in boilers and diesel engines for power generation to replace fossil fuels (Rambo et al., 2020). On the other hand, biochar is a stable, porous carbon-rich material formed by the pyrolysis of biomass feedstocks with a slow heating rate and at a relatively low temperature (between 400 and 700 °C) (Tomczyk et al., 2020; Pourhashem et al., 2019).

As a renewable alternative for the country, the babassu fractions (mesocarp and endocarp), which belong to the *Arecaceae* family and contain more than 36 described species, are a good

candidate. *Attalea speciosa* Mart ex. Spreng (babassu) is naturally abundant in Central and Southern America, especially Mexico, Peru, Bolivia, and Brazil (Hiura & Rocha, 2018). In Brazil's northern and northeastern states, especially Maranhão, Piauí, and Tocantins (15 million hectares), forests contain around 25 billion trees (Araruna et al., 2020). It is one of the most important palm species in Brazil and can reach between 10 and 30 m in height. It produces up to five bunches that yield from 250 to 500 fruits (coconuts), each of which has between 3 and 5 kernels (Santos et al., 2017).

Babassu fruit is widely consumed in Brazil's north and northeast regions and is considered an important resource in economic, social, and nutritional terms. This is mainly related to the exploitation of the culture of the "Quebradeiras de Coco" (Bauer et al., 2020). The average percentages of each of its components are 11% fibrous epicarp, 23% mesocarp, 59% endocarp, a hardwood layer, and almond 7% (Santos et al., 2017).

In the current context of growing environmental concerns, the recovery of babassu waste from an economic point of view is of great interest. The struggle of coconut breakers in the semi-arid transition region with the Amazon biome is historic. After decades of oppression and resistance by landowners, the

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Interstate Movement of Babaçu Coconut Breakers (MIQCB) was born in Maranhão, Pará, Piauí, and Tocantins. The MIQCB is one of the fifteen Brazilian ethnic identities recognized as traditional communities and deserves protection as to their way of life by the state. Their conquests were primarily the result of the articulation of the women of the region (Souza et al., 2011).

In this study, babassu residues were evaluated to produce bio-oil and biochar with a higher potential. There is a pressing need for biomass components to have a wide range of applications and fields related to social and economic insights.

2 Experimental

2.1 Physicochemical characterization

Samples

The babassu epicarp was collected at the Grota do Chico site, located in the municipality of Ananás, in the state of Tocantins. It is located at a latitude of 06° 21' 55" south and a longitude of 48° 04' 22" west, at an altitude of 220 meters. The collected material was processed in the Chemistry Laboratory of the Federal University of Tocantins, where the fractions were separated manually. The shells were dried in an oven at 50 °C for 24 hours, ground (to 48 mesh) in a Willye knife mill (model Star FT 50, Fortenox, Piracicaba, Brazil), following standardized procedures (Associação Brasileira de Normas Técnicas, 1983; American Society for Testing and Materials, 1996a), and were then stored in hermetically sealed vials.

Extraction and yield of oil from crude biomass

The oil extractions from the babassu coconut endocarp samples were performed using the Soxhlet system and hexane as an extractant (solvent) at an initial temperature of 60 °C. In our work, we used the solvent hexane because its boiling point is lower than ethanol's. Hexane is the most used solvent in solvent extraction because it is apolar and allows extracting lipids, hydrocarbons, and glycerides at not too high temperatures (Chaudhary et al., 2021). The extractions had ten siphoning, and after extraction, the sample was rotary evaporated to eliminate the solvent, and then anhydrous sodium sulfate was added to remove water particles from the sample. The oil was then filtered and analyzed.

Analysis of oil volatiles from crude biomass by gas chromatography coupled to the gas chromatography-mass spectrometry detector (GC-MS)

The chromatographic analyses were performed using a gas chromatograph, model 7890B, coupled to a mass spectrometer (GC-MS), model 5977B selective mass detector systems (MSD), from Agilent Technologies (Santa Clara, United States). The HP-5MS capillary column, measuring 30 m x 250 µm x 0.25 µm with helium carrier gas, was used as a stationary phase of the mass spectrometer. The sample injection into the equipment occurred directly with the introduction of 1 µL of sample in 1:50 split sample mode with the dissolution of the oil sample in a 1/100 percentage by volume (V/V) ratio in hexane. The system temperatures were as follows: injector, 155 °C; programming of

the oven temperature starting at 45 °C for three minutes with subsequent increase to 150 °C, remaining for five minutes at a rate of 20 °C/min, ending at 250 °C with a run time of 48min; ionization source at 230 °C; and the quadrupole analyzer at 150 °C.

2.2 Pyrolysis process

A fixed-bed quartz tubular reactor (Pyrex, Cotia, Brazil), 10 cm outside diameter and 100 cm long, was used with 30 g of biomass at 500 °C with a heating rate of 20 °C for 30min inserted into the reactor in batch mode. Water vapor was used as the carrier gas. A condensing system consisting of a Friedrich-type condenser, a vacuum flask, two tubes, and a 20 L water tank was attached to the end of the reactor for cooling the condenser. The steam passage allowed the biogas to be separated from the liquid products (bio-oil and acid extract), which are retained in the vacuum bottle. For the separation of the bio-oil and the acid extract, 20 mL of dichloromethane (Merck, Darmstadt, Germany) were used (Pedroxa et al., 2017). The yield of the pyrolyzed products was determined from the mass loss calculated from the initial dry mass of the source biomass, considered to be 100%, and the final mass of the obtained product sample (Bueno, 2017).

2.3 Bio-oil

Hydrogen potential (pH) determination

The biochar samples were mixed with distilled water at a ratio of 1:20 (w/v) to form a homogeneous suspension. After 1.5 h (Bardalai & Mahanta, 2018), pH was established using a QUIMIS® model Q400-AS pH meter (Diadema, Brazil) with a combined active surface electrode (Ag/AgCl) glass electrode model QA338 (Diadema, Brazil) and a combined electrode (ECV) with a readability of 0.01 pH. The pH of the bio-oil was determined by the direct immersion of the digital pH meter in the solution.

Density determination

The actual density of the biomass was established by the 25 mL pycnometer method in a thermostatic bath at 20 °C. For the bio-oil, the density was obtained using a portable digital densimeter, the Direct Mercury Analyzer (DMA) 35 (Anton Paar, São Paulo, Brazil), using 5 mL of sample. American Society for Testing and Materials (1996b) standardizes the procedure.

Analysis by GC-MS

With the aid of GC-MS QP2010 Plus equipment (PerkinElmer do Brazil Ltda, São Paulo, Brazil), equipped with a capillary column Rtx-5MS WCOT (30 m x 0.25 mm x 0.25 µm), the organic and aqueous bio-oil fractions were separated. For the chromatographic separation, the planning for the use of temperatures was followed: for 1 min (isothermal), raised to 7 °C/min at 100 °C and then at 4 °C/min at 320 °C followed by 10 min at 320 °C. The carrier gas used was helium at 1.90 mL/min. The ionization energy (IEI) mode (with an ionization energy of 70 eV) was used to obtain the mass spectra. The peak area carried out the quantification of the components.

2.4 Biochar

Biochar activation

The biochars produced were immersed in a solution of zinc chloride, $ZnCl_2$, from Merck (Darmstadt, Germany), at a concentration of 10% w/v in a proportion of 1:5 (biochar: $ZnCl_2$ solution). The samples were covered with plastic film and left to rest for 24h. After this time, the samples were washed with distilled water and dried in an oven at 110 ± 5 °C. The washed material was pyrolyzed again by thermal treatment in a muffle furnace oven at 600 ± 5 °C for 2h. The activated carbon was washed with hydrochloric acid, HCl (2 M) (Merck, Darmstadt, Germany), to remove and unclog the pores. At the end of the process, the sample was dried in an oven at 110 ± 5 °C for 24h and was named biochar (Costa et al., 2015).

Surface area: Brunauer-Emmett-Teller (BET)

The biochar samples (0.5 g) were taken to the Surface Area System and Porosimetry equipment (ASAP 2010 micro-merit model Norcross, GA 30093 USA) to establish the surface area of N2- BET, the arrangement, and size of the pores. The diameter range used as a standard was 0.35 to 300 nm for the pores and 0.01 to 3,000 m^2/g in the surface area range. The temperature of the treatment ranged from 30 to 350 °C.

2.5 Approximate social and economic feasibility

The study population, estimated at 12,139 inhabitants in 2019, was composed of nut breaker communities in the municipality of São Miguel do Tocantins -TO, located in the central region of Tocantins at a latitude $05^\circ 33' 18''$ S, longitude $47^\circ 34' 40''$ W and altitude of 160 m. This region has an area of 398,820 km^2 (Marques de Oliveira, 2019). A total of 130 nut-breaker women from the village were interviewed. The data were collected systematically in July 2022.

The sociodemographic survey, as well as the investigation of the use of babassu residues, was performed by structured interviews consisting of closed and open questions using a semiquantitative method. Another resource used was the photographic and imagetic register of events and situations, which was a very adequate strategy for the dialog with the social agents.

We analyzed the answers by analyzing the frequencies of the words, using a word cloud created through an online platform called Mentimeter (2004).

The economic analysis of the pyrolysis was performed to evaluate the process's feasibility. The effects of economic parameters (biomass cost, electricity cost, and total product price) were investigated. The total income of this process comes from the sales revenue of the main products, and the prices of these products are summarized in Figure 4 according to the market values obtained by Sigma-Aldrich (Saint Louis, Missouri, USA). The total can be calculated based on the cash flow of inputs and outputs (Detchusananard et al., 2022).

3 Results and discussion

3.1 Characterization of gross biomass

The physicochemical composition of babassu mesocarp has already been presented in other work (Santana et al., 2020). The holocellulose content is satisfactory (67.7%), with low extractive content (2.37%), and intermediate lignin values (30%). The low ash (1.7%) and moisture (7.25%) contents of babassu favor its use in the pyrolytic process. Rambo et al. (2015a) evaluated the physicochemical composition of babassu fractions and reported holocellulose content higher than 60% and the same range of values for extractives and lignin. In the species analyzed only the ash (6.0%) and moisture (8.3%) contents were relatively higher.

The total ion chromatogram (Table 1) shows the signals referring to the volatile compounds detected in the babassu coconut endocarp oil (after extraction) using the GC-MS technique. The compounds belonging to the hydroperoxide and alcohol functions were the most prominent. All samples presented the same chromatographic profiles with an even number of carbon atoms and the presence of three medium-chain saturated atoms (C6:0, C8:0, and C9:0) and one long-chain saturated atom (C16:0). The results obtained for the babassu oils are in accordance with data reported in the literature for ethanol soxhlet extraction (Rambo et al., 2015b; Santos et al., 2022).

3.2 Pyrolysis products

Biochar and bio-oil

The yield of biochar found was 31%, a result similar to that found for other lignocellulosic biomasses submitted to pyrolysis in the temperature range of 400-700 °C, even under different residence times, according to the studies contained in Table 2.

Table 1. Babassu endocarp oil volatile compounds.

	Compounds	Molecular Formula	Trx (min.)	KI	IRL NIST	Area (%)
1	2,4-Dimethyl-3-hexanol	$C_8H_{18}O$	11.101	925.319	-	2.956
2	1-ethylbutyl hydroperoxide	$C_6H_{14}O_2$	12.128	947.505	-	33.374
3	1-methylpentyl hydroperoxide	$C_6H_{14}O_2$	12.586	957.399	-	24.476
4	2,3-Epoxypropylhexyl ether	$C_9H_{18}O_2$	13.062	967.682	-	16.681
5	dibutylphthalate	$C_{16}H_{22}O_4$	47.544	1877.126	1954	10.707

Trx: retention time of the compounded rate of interest in minutes; KI: Kovats index; IRL NIST: NIST library linear retention index; Area (%): The percentage area corresponds to the abundance of the compound.

Table 2. Biochar yield from lignocellulosic biomasses residues from the literature.

Biomass	Temp (°C)	Residence time (min)	Yield (wt. %)	References
Coconut pith	500	60	36.16	Johari et al. (2016)
Coconut shell	500	20	38.30	Siengchum et al. (2013)
Coconut shell	700	5	29.22	Almeida et al. (2013)
Baru	450	30	48.00	Rambo et al. (2020)
Pequi	500	30	34.00	Brito et al. (2020)
Rice husk	450	60	35.00	Biswas et al. (2017)
Cotton by-products	400	240	44.38	Chen et al. (2016)
Pine nut shells	550	20	34.11	Qin et al. (2020)
Sawdust	500	50	38.60	Soni & Karmee (2020)

Mohammad et al. (2013) obtained biochar with 29.79-30.22% by weight using a catalytic process in the pyrolysis. This shows that the biochar obtained in the present work had better yields (31%) and was produced without additional steps.

The pH values found in the biochar and bio-oil were 6.7 and 3.0, respectively, and the densities were 1.43 and 1.49, respectively. Other data obtained from the pyrolysis of babassu coconuts, such as elemental analysis, calorific value, and functional groups of the biochar surface, were studied in other work, indicating good biochar stability with a neutral pH in nature, and therefore, suitability for use in soil (Santana et al., 2020).

The average pore diameter was 0.162 nm, and the total pore volume was 0.1341 cm³/g (Table 3). This was in agreement with the BET surface area (357.2716 m²/g). The pore size distribution confirmed the presence of micropores (0–2 nm). Hence, biochar activation substantially increased the adsorption capacity, and the biochar obtained in this work was found to have a surface area superior to the biochar obtained under N₂ and CO₂ atmosphere from other works (Das & Goud, 2020).

Regarding the bio-oil with a 30% yield, the main compounds identified are water, acids, alcohols, aldehydes, esters, ketones, carbohydrates, hydrocarbons, phenols, and other substances derived from lignin and cellulose (Figure 1). Phenol (45.81%) and aldehyde (32.76) values were found in the bio-oil composition, as were lower ketone (11.7%), alkene (5.24%), alcohol (1.88%), acid (1.7%), and hydrocarbon (0.91%) values. Similar results were found by Almeida et al. (2013) for coconut, with 55.2% phenols, 14.2% aldehydes, 10.2% ketones, and 4.1% alcohols.

3.3 Social and economic analysis

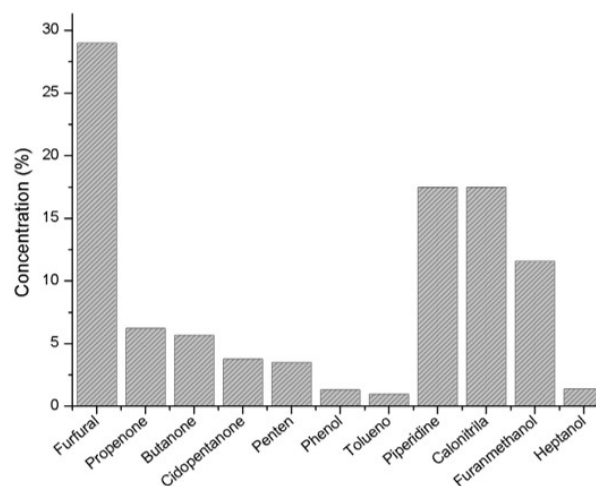
Social analysis

In the conversation circle, they discussed how babassu has become a source of income and how extraction is used as an additional source of income. We also investigated other functions performed by women babassu nut breakers to complement their family income. The most frequent words in the conversations were “source of income,” “partnership,” “struggle,” “incentive,” and “knowledge” as shown in the word cloud (Figure 2). It was found that the breakers do not live off the fruit alone. These are important and emblematic actions of the National Policy for Food and Nutritional Security, in which the state and federal governments provide thousands of farmers, a fair market, and

Table 3. Surface area of the biochar from babassu mesocarp.

Components	Biochar	
	ABB	CAC
Surface Area BET (m ² g ⁻¹)	357.2716 ± 7.1770	597.33
Surface Area Langmuir (m ² g ⁻¹)	475.2720 ± 2.4261	-
Micropores Volume (cm ³ g ⁻¹)	0.134160	0.22
Microporos Area (nm)	0.162	

ABB: Activated Babassu Biochar; CAC: commercial activated carbon.

**Figure 1.** Chemical composition of bio-oil from babassu.**Figure 2.** Cloud of words elaborated from the content of the dialogues carried out with the members of the Interstate Movement of the Quebradeiras of Coco Babaçu (MIQCB).

healthy food to people in food and nutritional vulnerability. The Brazilian Research Network on Food and Nutritional Sovereignty and Security conducted this study in 2020 and revealed that 55.2% of Brazilians have some degree of food insecurity, of which 9% are at a severe level, equivalent to hunger. This picture, aggravated by the COVID-19 pandemic, is associated with the dismantling of public policies to combat hunger and ensure food and nutritional security and is reflected in Brazil's return to a scenario of heightened vulnerability for a large part of its population (Rede Brasileira de Pesquisa em Soberania e Segurança Alimentar e Nutricional, 2021).

When asked about the coconut residues, the mesocarp presented good uses. From its mass comes the input used in the preparation of cakes, puddings, cookies, and others. From the endocarp, they make charcoal for domestic and commercial use.

On the other hand, the negative aspects pointed out by the extractivist women continue to be the lack of incentives coupled with the difficulty of selling the products at low prices since the raw material is difficult to handle. A positive point has been the creation of the Law of Free Babassu, where the collection of coconuts is not hindered by the breakers in the region (Figure 2). According to the Movimento Interstadual das Quebradeiras de Coco Babaçu (2019), the movement's vision for the future is to "[...] be a reference as babassu forest guardians in the valorization

of traditional knowledge in the fight for rights of access to land, territory, free babassu, and the practice of agroecology." Thus, the MIQCB plays an important role in preserving the customs and traditions of babassu nutbreaker women since it functions as the main articulator of these women's collective action and raises issues relevant to the daily lives of these communities, such as sustainability and women's leadership (Souza et al., 2011).

Production estimate

The estimation of production costs of bioproducts from babassu was performed in two processes (Figure 3). Considering that the equipment capacity for breaking the babassu coconut is 500 kg/h, 45 kg/h of almonds and 455 kg/h of residue are obtained with a daily production of approximately 4,000 kg/day, with 360 kg/day of almonds and 3,674 kg/day of residue. In terms of annual production, it is estimated that over 1,000 tons of babassu coconut will be processed.

In the second step, we estimated the cost of babassu oil extraction by cold pressing, considering the equipment capacity of 100 kg/h of the kernel, 66% of which is extractable oil and 34 kg of fiber (cake). From the cake, 55.70% oil (18.938 kg/h) and 15.06 kg/h of cake can be obtained. By converting this process using the oil density, we have a volume of approximately 121,862.40 L/year.

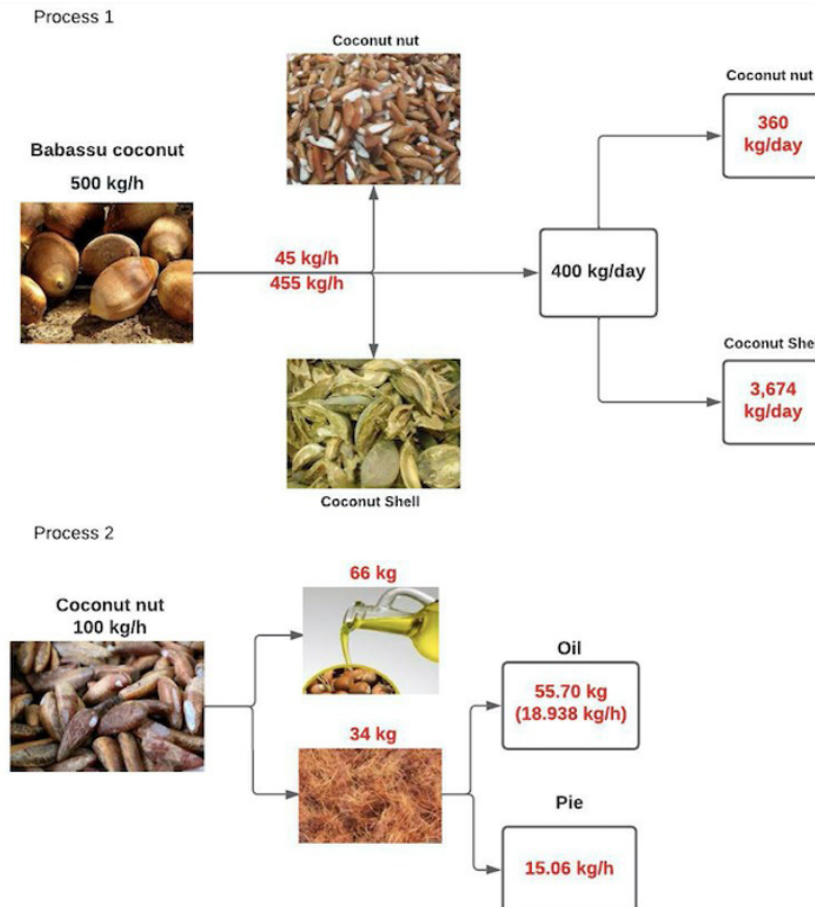


Figure 3. Production estimate.

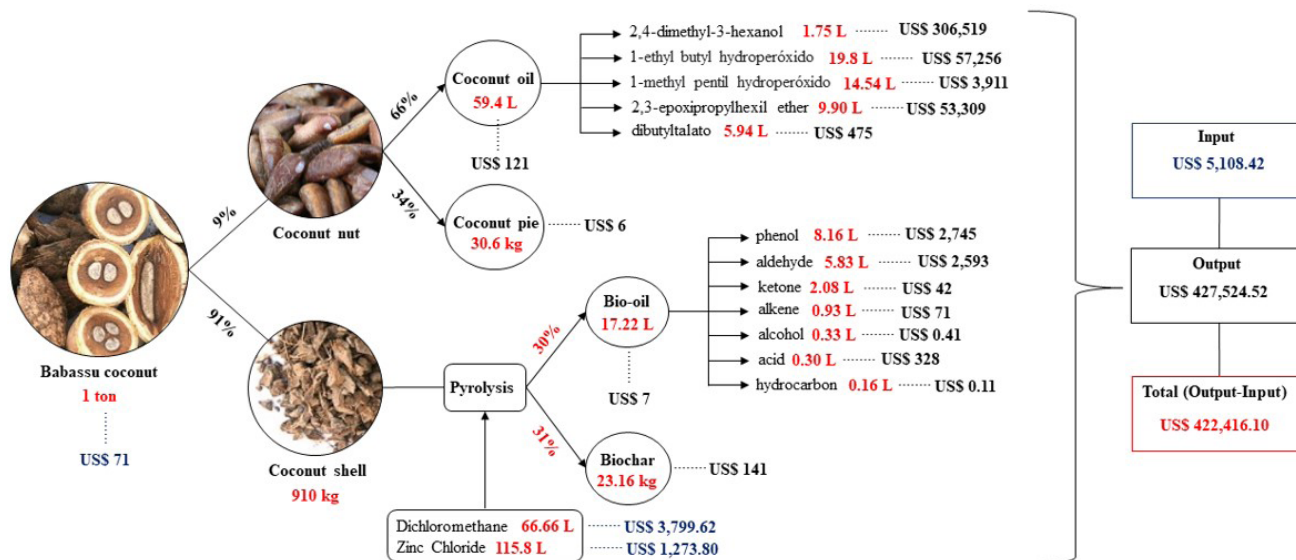


Figure 4. Product yield and theoretical energy potential obtained from babassu coconut processing.

Economic analysis

Babassu coconut processing costs

Four products resulting from babassu coconut processing were considered, including coconut oil, coconut cake, bio-oil, and biochar. Assuming the market values from Sigma Chemical Company (Sigma-Aldrich, 2022) (Figure 4), the costs for obtaining the biomass, and the reagents used (dichloromethane and zinc chloride), it was possible to obtain a total balance of US \$422,416.10 with the processing of one ton of biomass. The chemical compounds found can be separated and purified to be used in different applications in the chemical industry (Soni & Karmee, 2020).

Literature searches pointed out that the main costs arising from this production are, firstly, the value of the equipment and the associated costs of keeping it running, which include fuel and basic services such as electricity, water, rent, and labor. Including installation, repair, and maintenance costs, it is observed that the useful life of a pyrolysis machine is estimated between five and eight years (Cohen & Oliveira, 2022).

Considering the direct costs of transportation and energy needed for processing the babassu coconut, where 55 L will be used per week, multiplied by \$1.33 (the liter) times 4 weeks times 12 months equals \$3,511.2/year. In the processing, two pieces of equipment will be used: a 5 HP shredder and a 10 HP mini press. Calculating the consumption of electrical energy required (1 HP = 0.98 HP = 735 W), the cost is US \$776.16/year for the peeler and US \$1,552.32/year for the mini-press, resulting in a total cost of US \$2,328.48 for electrical energy.

The raw material was calculated considering the annual babassu quantity needed of 1,056 tons per year, i.e., 1,056,000 kg x US \$0.07 (value paid per kilo), totaling US \$73,920.00. According to annual production data (Table 4), the total cost would be US \$79,810.04.

Table 4. Direct Cost of Annual Babassu Coconut Processing.

Direct Production Cost - Annual	Value US\$
Fuel	3,509.20
Electrical energy of peeling machine	793.61
Electrical energy of mini press machine	1,587.23
Raw material (kg/year - babassu coconut)	73,920.00
Total	79,810.04

Reference month: May/2022.

Given the costs described in Figure 4 and Table 4, obtaining bioproducts from babassu shell is considered economically advantageous because a total income of up to US \$344,571.20 can be obtained. In a similar situation, Romão et al. (2022), using green coconut biomass and discarding transportation and energy costs, obtained an income of US \$81,017.48. The feasibility of biochar co-production and Santana et al. (2020) discovered a profit of US \$12,131.73 under similar conditions, ignoring energy and transportation costs. It should be noted that the products obtained are without emulsion and that, to reach these values, they need separation and purification steps, changing the cost of the process. Therefore, the value presented here is only an estimate.

4 Conclusions

The yields of biochar (31%) and bio-oil (30%) obtained via pyrolysis were satisfactory, proving to be a good treatment method for babassu coconut shells. The chemical compounds from coconut oil can be very profitable if isolated and commercialized. The study suggests that the whole babassu coconut processing, from the fruit to the cake and oil by cold pressing, is efficient when combined with the products obtained from the residue via pyrolysis. These activities can positively impact the families involved in coconut agro-extractivism, starting with the valorization

of their work, the insertion of more people from the community with the generation of more jobs, and improving their sources of income according to the profitability reached in this study.

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