Revista Industrial Data 26(2): 7-23 (2023)
DOI: https://doi.org/10.15381/idata.v26i2.25392.g20348
ISSN: 1560-9146 (Impreso) / ISSN: 1810-9993 (Electrónico)
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Utilization of Hass Avocado Seed (*Persea Americana*) Via Fast Pyrolysis and Its Evaluation in the Production of Bio-Oil and Biochar

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Submitted: 24/05/2023 Accepted: 19/07/2023 Published: 15/12/2023

ABSTRACT

The study aims to explore the potential use of waste from the Peruvian export agro-industry, particularly the seed of the Hass avocado, to produce bio-oil and biochar by pyrolysis. The process takes place in an empty vacuum tubular reactor with a heating rate of 8.4°C/min, a particle size of < 2 mm, and at temperatures of 300°C, 400°C, and 500°C for a period of three hours and three replicates. The results indicate that temperature has a significant impact on the yield of bio-oil and biochar. The highest bio-oil yield (46.47%) was obtained at 500°C, while the highest biochar yield (45.33) was obtained at 300°C. Additionally, it has been statistically proven ($p > 0.05$) that there is a significant difference in yield between bio-oil and biochar, as well as between yields at different temperatures.

Keywords: avocado seed; agro-industrial waste; industrialization; thermochemistry; biomass pyrolysis.

INTRODUCTION

As Peruvian exports increase, more and more by-products and waste from field and plant processes are being generated, and thousands of tons are discarded each year, resulting in an economic loss for the companies while at the same time polluting the environment.

The avocado agro-industry produces a large amount of waste, such as skin and seeds, that can be transformed into high-value-added products for the industry. This can be achieved via biorefining, which combines biomass transformation processes to produce a variety of products, including biomolecules, biomaterials, bioenergy, and biofuels (Dávila et al., 2017). The enormous quantities of by-products generated by the avocado industry represent an important source of raw material for energy applications and the production of carbonaceous materials, which are of great importance for reducing environmental water pollution (Colombo & Papetti, 2019).

Martinez et al.(2021) state that agro-industrial residues can be transformed into new products via thermochemical and biological processes; pyrolysis and gasification are thermochemical processes. Agro-industrial avocado biomass has a significant potential for commercial biochar and liquid fuel production via torrefaction and pyrolysis (Lara et al., 2018). Residual biomass produced in the avocado sector results from the large number of avocado producers that generate byproducts with a high energy content, suitable for thermal energy production (Perea et al., 2016).

This study is relevant because it provides an alternative for industrializing the thousands of tons of avocado seeds that are discarded every year as part of the avocado freezing process in Peru to obtain biofuels, such as bio-oil and biochar, which can

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be used as energy sources and can contribute to the sustainability of the agro-industry over time.

The topic discussed in this paper is the starting point to provide an industrial alternative to use residual biomass from the avocado agro-industry to produce bioenergy. Further research is necessary on the chemical analysis of the products obtained by pyrolysis, as well as on industrial scaling up to evaluate the technical and economic feasibility of its implementation in the country.

Therefore, this study aims to analyze how the temperature used during the pyrolysis of Hass avocado seed affects the yield of bio-oil and biochar, thus maximizing the use of avocado freezing process by-products from the Peruvian agro-industry. The use of these residues would contribute towards the reduction of environmental pollution.

The general hypothesis is that the yield of bio-oil and biochar from avocado seed is equal. The specific hypothesis is that the yield is the same at temperatures of 300°C, 400°C and 500°C.

Theoretical Framework

Food agro-industrial by-products mainly include peels, seeds, stems, bagasse, kernels, and husks. Due to their overproduction and the lack of sustainable management, such by-products are rejected and disposed of in landfills, which leads to environmental, social, and economic issues (Gómez et al., 2021). However, using crop residues for energy generation has partially contributed to resolving inappropriate handling practices, thus reducing their environmental impact. Crop residues are rich in fixed carbon and could be used as a source of feedstock for energy generation and significantly contribute to soil sequestration, maintenance of soil quality, and ecosystem functions; therefore, it is essential to assess them critically and objectively to realize their full potential. (Prasad et al., 2020).

Biomass energy has become the fourth largest energy source, following coal, oil, and natural gas, due to its abundantly available sources. Currently, the primary products obtained through biomass pyrolysis are oil and biochar. However, there is still untapped potential in biomass products that deserves further exploration (Zhang et al., 2023). In turn, Garcia et al. (2023) state that avocado seeds and peels have no specific industrial use, so it is necessary to establish valorization pathways to obtain high-value-added products to close the loop and make the avocado value chain more sustainable and efficient. Dyjakon et al. (2022) argue that exotic fruit seeds, such as from the avocado and mango, can be used to produce energy through the valorization method of torrefaction at temperatures ranging from 200°C to 300°C.

From the processing of the avocado, seeds and peels are obtained. On average, avocado seeds account for 15%-16% of the fruit's weight; they are an excellent source of fiber and contain high-value compounds, such as polyphenols and antioxidants (Barbosa et al., 2016).

According to Domínguez et al. (2014), avocado pulp is the only part of the fruit that is commercially utilized, while the rest is discarded in landfills. The production of avocado involves centralized processing plants; the seeds can account for up to 26 wt% of the fruit's weight. Although the seeds have high starch content, they cannot be used as livestock feed due to the high concentration of polyphenols that give them a bitter taste and can be toxic in large quantities.

Martín and Calero (2020) define pyrolysis as a thermochemical process that involves the thermal decomposition of organic matter, such as that found in biomass, by releasing energy in the form of heat into an inert atmosphere or vacuum. They also define torrefaction as a thermochemical process performed at temperatures ranging from 200°C to 300°C to convert biomass into a higher-quality solid fuel. According to Fabbri et al. (2021), pyrolysis is regarded as a promising "green" technology due to its inherent simplicity and the lack of chemical reagents involved.

Biochar is a valuable product that is obtained using thermochemical energy conversion technologies. Its yield and properties vary greatly depending on the type of feedstock, technology, and operating parameters used during production. Slow pyrolysis is the most successful technology for producing biochar, which can yield biochar in the range of 25-50 wt%. However, the yield can exceed 70% depending on the type of feedstock used. In contrast, fast pyrolysis yields higher bio-oil yields in the range of 50-75 wt%, but the biochar yield is generally lower at around 12% of the total feedstock (Safarin, 2023).

The heating value is the amount of heat released by a material per unit mass when burned under specific conditions. In turn, the higher heating value (HHV) is the heat released when a material is burned in a closed vessel, plus the heat generated by the vaporization of water. The pressure varies depending on the amount of gases produced by combustion, including CO_2, N_2, SO_2, and water vapor (Velásquez, 2018).

Yarbay et al. (2020) conducted research on the pyrolysis process of avocado seeds using a Heinze reactor at 500°C with a heating rate of 10°C/min and a retention time of 20 min. The pyrolysis experiment yielded liquid product (32%), solid product "char" (34%), and non-condensable gas (34%) with a biomass conversion of 67%. The study confirms that avocado seeds have potential as bio-waste, as demonstrated by the pyrolysis results. However, further evaluation is necessary to determine the liquid properties of the liquid product as a bio-fuel oil and the solid product "char" as an activated carbon.

As part of their research, Durak and Aysu (2014) conducted a study on the slow pyrolysis of avocado sees in a fixed-bed tubular reactor. The experiment was conducted with and without a catalyst (KOH, Al_2O_3) at temperatures ranging from 400°C to 600°C, with heating rates of 50°C/min. The results showed that the main pyrolysis parameters influencing yield were temperature and catalysts. The highest liquid yield (37.5%) was obtained using a 10% KOH catalyst at 600°C at a heating rate of 50°C/min, employing 0.150 mm particle size raw material and a 100 cm^3/min sweeping gas flow rate.

Based on the research by Nizami et al. (2017), the composition of liquid oils produced by bio-refinery processes varies with feedstock. For instance, woody biomass contains water (30%), phenolics (30%), aldehydes (30%), ketones (20%), alcohols (15%), etc. Moreover, bio-oils can be converted into a liquid hydrocarbon with similar characteristics to crude oil through a hydrodeoxygenation (HDO) process.

The solid product of fast pyrolysis, known as biochar, consists mainly of biocarbon but also contains ash. Biochar represents 12-15 wt% of the products of fast pyrolysis (Brown & Wang, 2017). The elemental composition of biomass bio-oil contains 35-45 wt% oxygen. Chemically, bio-oils comprise quite a lot of water, solid particles, and hundreds of organic compounds, including acids, alcohols, ketones, aldehydes, phenols, ethers, esters, sugars, and furans (Boateng, 2020). Furthermore, as stated by Mantilla et al. (2015), bio-oil is a mixture of nearly 300 types of organic compounds, including phenols which are produced during oil refining. Phenols are commonly used as fuel additives, food antioxidants, and in the synthesis of various other chemicals.

Sánchez et al. (2016) suggest that most of the bio-oil obtained through low-temperature pyrolysis (300°C) contains 80.2% water, while the remaining 19.8% is composed of organic products that contribute to the energy value of the condensable fraction. As part of their research, Aysu and Durak (2015) liquified avocado seeds in a reactor at various temperatures, and the resulting bio-oils obtained at 270°C and 290°C were analyzed using spectroscopy and chromatography techniques. These compounds were found to contain various molecular structures such as monoaromatic, aliphatic, oxygenated, nitrogenous, and polyaromatic compounds and derivatives. Among the monoaromatic compounds found were benzene, furans, and phenols; among the aliphatic compounds were alkanes and alkenes; and among the oxygenated compounds were aldehydes, ketones, esters, and carboxylic acids. The Fourier-transform infrared spectroscopy (FT-RI) analysis conducted on the bio-oil obtained revealed the presence of phenols, alcohols, alkanes, alkenes, aldehydes, and ketones, among others.

In their study, Caldeira et al. (2020) pointed out that several aspects must be taken into account for the development of sustainable industrial processes based on the valorization of food waste. These include the technical feasibility of the processes at an industrial scale, an analysis of their techno-economic potential, and an environmental assessment of the benefits.

METHODOLOGY

Research Type and Design

This research study follows a quantitative approach and a 2×3×3 factorial experimental design. The first factor is the product, which has two levels (bio-oil and biochar); the second factor is temperature, which has three levels (300°C, 400°C and 500°C). Each will have three replicates.

The research was conducted at the thermochemistry laboratory of the School of Petroleum, Natural Gas and Petrochemical Engineering of Universidad Nacional de Ingeniería (UNI) in Lima, Peru. Physical analyses were also conducted at UNI.

Thermogravimetric (TGA) proximate analysis of Hass avocado seed was carried out at the Renewable Energies laboratory of Universidad Nacional Agraria La Molina (UNALM).

The following process flow (Fig. 1) was used for the fast pyrolysis of Hass avocado seed:

a. Acquisition: Samples of ripe Hass avocado were purchased from supermarkets in Lima.

b. Skinning/cutting: Hass avocado pulp and skin were removed and only the seed was kept.

c. Drying: The seed was dried in an oven to reduce its moisture content to 10%.

d. Milling: The seed was crushed in a mill unit to obtain a particle size of < 2 mm.

e. Sieving: The crushed seed was sieved until only particles smaller than 2 mm remained.

f. Pyrolysis: The dried, crushed seed was put into a vacuum fixed-bed tubular reactor (67.461 kPa abs), at a heating rate of 8.4°C/min at 300°C, 400°C and 500°C during a 3-hour period. A load of 50 g of powder sample (< 2 mm) with a moisture content of less than 10% was used. Three replicates were run for each set temperature condition.

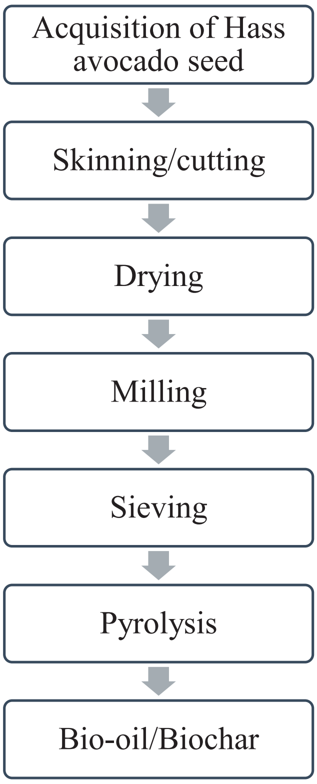

Figure 1. Process Flow Diagram of Fast Pyrolysis.

Source: Prepared by the author.

Finished Product Characterization

Upon completion of the fast pyrolysis process of the Hass avocado seed, the solid and liquid products obtained under the most favorable temperature were characterized.

RESULTS

Avocado Seed Analysis

Hass avocado seeds were analyzed at the UNALM Renewable Energy laboratory complying with the ASTM D7582 standard. The results obtained are shown in Tables 1 and 2.

Table 1 shows that the Hass avocado sample has a large amount of water with a mean moisture content of 46.36%, a large amount of volatile matter with a mean of 45.29%, a mean of 1.7% ash, and a mean of 6.65% fixed carbon.

Table 2 displays the experimental pyrolysis yields obtained in the thermochemistry laboratory. Note that the highest bio-oil average yield (46.47%) was obtained at 500°C, and the highest biochar average yield (45.33%) was obtained at 300°C.

Characterization of the Products Obtained

Table 3 shows the characterization of the products obtained from the fast pyrolysis at 500°C.

The higher heating value of bio-oil could not be determined due to its high percentage of water content. In contrast, the heating value of biochar was determined at 28,282 kJ/kg.

Figure 2 shows the inverse correlation between bio-oil and biochar yields. The higher the temperature, the higher the bio-oil yield; the lower the temperature, the higher the biochar yield.

Hypothesis Testing

A 2×3×3 factorial design was used for hypothesis testing.

General Hypothesis Testing

H_g: Bio-oil and biochar yields are equal.

H_0: Bio-oil and biochar yields are not equal.

An analysis of variance was performed as shown in Table 4. If the *p*-value > 0.05, the null hypothesis is accepted. If the *p*-value < 0.05, the null hypothesis (H_g) is rejected and the alternative hypothesis (H_0) is accepted as true.

From the results, H_g is rejected with a *p*-value of 0.0000007 and H_0 is accepted, evidencing a significant difference in bio-oil and biochar yields. Therefore, the type of product used has a significant effect on yield.

The model summary is presented in Table 5.

Table 1. *Proximate Analysis of Avocado Seed on Wet Basis.*

Run	Moisture %	Volatile Matter %	Ash %	Fixed Carbon %
1	34.27	55.38	2.29	8.06
2	46.36	45.09	1.41	7.14
3	58.44	35.4	1.4	4.76
Standard Deviation	12.085	9.992	0.511	1.703
Mean (%)	46.36	45.29	1.7	6.65

Source: Prepared by the author.

Table 2. *Experimental Pyrolysis Results.*

Treatment	Factor 1 (Product)	Factor 2 (Temperature)	Yield 1 %	Yield 2 %	Yield 3 %	Average Yield
1	Bio-oil	300°C	35	35	37.2	35.73
2	Bio-oil	400°C	40.8	44.4	44	43.07
3	Bio-oil	**500°C**	43.4	47.8	48.2	**46.47**
4	Biochar	**300°C**	44	46.2	45.8	**45.33**
5	Biochar	400°C	34	33.6	33.6	33.73
6	Biochar	500°C	30	30.2	28.8	29.67

Source: Prepared by the author.

Table 3. *Characterization of (Liquid and Solid) Products Obtained at 500°C, at which Maximum Yield of Liquid Product is Attained.*

Parameter	Method	Value
	Liquid Product	
Density (g/m^3)	ASTM D5002	1.0622
Higher Heating Value	ASTM D240	ND
	Solid Product	
Higher Heating Value (kJ/kg)	ASTM D240	28,282

ND: The product has a high water content and does not burn in the bomb calorimeter.
Source: Prepared by the author.

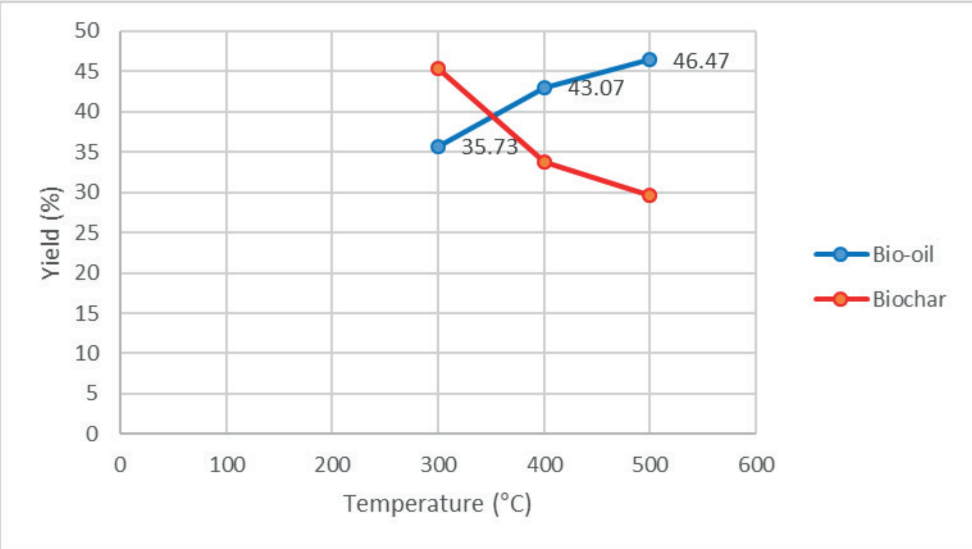

Figure 2. Inverse Correlation Between Bio-oil and Biochar Yields.
Source: Prepared by the author.

Table 4. *Analysis of Variance.*

Source	df	Adj. SS	Adj. MS	F	P
Model	5	713.76	142.752	58.67	0.000
Linear	3	158.17	52.723	21.67	0.000
Product	1	136.68	136.68	56.17	0.000
Temperature	2	21.49	10.747	4.42	0.037
Interaction of 2 Factors	2	555.59	277.796	114.16	0.000
Product*Temperature	2	555.59	277.796	114.16	0.000
Error	12	29.20	2.433		
Total	17	742.96			

Source: Prepared by the author.

Table 5. *Model Summary.*

S	R-Squared	Adj. R-Squared	Pred. R-Squared
1.55991	96.07%	94.43%	91.16%

Source: Prepared by the author.

Specific Hypothesis Testing 1

H_g: Yield is equal at 300°C, 400°C and 500°C.

$H_{0:}$ Yield is not equal at 300°C, 400°C and 500°C.

Table 4 displays the analysis of variance conducted. If $p > 0.05$, H_g is accepted; if $p < 0.05$, H_g is rejected and it is assumed that H_0 is correct.

From the results, H_g is rejected with a p-value of 0.036525 and H_0 is accepted, thus showing that there is a significant difference in yield at different temperatures. It is therefore reasonable to state that temperature significantly impacts yield.

DISCUSSION

This is a quantitative, experimental research study. Based on the results, the alternative hypothesis stating that there is a significant difference between bio-oil and biochar yields was accepted.

It is apparent from the results in Table 2 that the highest bio-oil yield (46.47%) was obtained at 500°C, and the highest biochar yield (45.33%) was obtained at 300°C. They were treated at a vacuum pressure of 67.461 kPa (abs) at a heating rate of 8.4°C/min during a 3-hour period. Results show that both yields have an inverse correlation, i.e., the lower the temperature, the higher the biochar yield. In a study by Yarbay et al. (2020), pyrolysis was carried out in a Heinze reactor at 500°C at a heating rate of 10°C/min and a retention time of 20 min, obtaining a liquid product yield of 32% and a solid product yield of 34%. Similarly, in their study, Sánchez et al. (2016) used a rotary reactor at temperatures ranging between 150°C and 900°C and obtained the optimal biochar yield (36.7%) at 304°C; the liquid fraction represents 53%-56% of the original mass. Char yield varies based on the pyrolysis temperature, as low temperatures yield more char and high temperatures yield less (Basu, 2010).

The characterization of the bio-oil and biochar products obtained at 500°C is presented in Table 3. Bio-oil density was determined at 1.0622 g/cm^3; however, determination of its heating value was not possible due to its high water content that prevented ignition. In contrast, a higher heating value of 28,282 kJ/kg was determined for biochar. Sánchez et al. (2016) obtained a higher heating value of 30.2 MJ/kg for biochar and a higher heating value of 3 MJ/kg for bio-oil by torrefaction of avocado seed at 500°C.

Figure 1 shows the inverse relationship between temperature and bio-oil and biochar yields. An increasing trend of bio-oil is observed, while biochar yield decreases as temperature increases, from 45.33% at 300°C to 29.67% at 500°C. According to Sánchez et al. (2016), the core of the avocado pyrolysis process takes place at temperatures between 300°C and 500°C, resulting in the formation of a liquid fraction. Thus, bio-oil yield increases progressively at 500°C.

CONCLUSIONS

The pyrolysis process made it possible to use avocado seeds for industrial applications, resulting in bio-oil, biochar, and non-condensable gases, although the latter have not been studied in this particular research.

The highest average yield of bio-oil obtained was 46.47% pyrolyzed at 500°C, while the highest average yield of biochar obtained was 45.33% pyrolyzed at 300°C. A technical-economic study is recommended for the industrial scaling up of bio-oil and biochar, due to their industrial applications as fuel, soil improver, and filtering material, among others.

Biochar was obtained as a by-product with a higher heating value that can be used as fuel. It was not possible to determine the heating value of the bio-oil obtained due to its high water content.

There is also an inverse relationship between bio-oil and biochar yields.

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