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Evaluation and Potential Valorization of Different Wastes from the Honduran Agro-Food Industry

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Abstract: Apart from the usual wastes produced by the agricultural industry, climate change and the extreme meteorological conditions that are taking place in the Caribbean countries result in additional wastes produced by ruined crops which products cannot be sold in the market. However, a valorisation of these wastes can be carried out to improve their integration into the markets as raw materials in other processes, in order to make profit from them. In this way, these raw materials can be employed in the production of biodegradable products more environmentally friendly than conventional plastic, due to their high content in starch and/or proteins. Some authors have studied the production of bioplastics from agro-wastes which are rich in starch and/or proteins by modifying the processing methods used to produce conventional plastic resulting in products whose properties vary depending on the process. This research work addressed the evaluation of four different varieties of agricultural wastes produced in Region 11, Honduras. Their chemical characterization was successfully carried out and one possible valorization route was stablished according to the obtained results. The results have highlighted the possibility of employing the studied agro-wastes as raw materials in other industries improving their profits and decreasing the waste load.

Keywords: agro-wastes; valorization; biodegradable materials, protein; starch.

1. Introduction

Natural resources (energy, water, and raw materials) are limited, and, with a global population estimated to reach 9 billion people in 2050, the linear "use and throw away" system is no longer sustainable [1]. For this reason, the world is turning into a circular economy system which sustains the close loop idea, aiming at enhancing the continuous flow of materials in the value circle while keeping products, components, and materials at the highest utility and value at all times and reducing waste to a minimum [2].

Nevertheless, billions of tons of wastes and by-products from the agro-food industry, usually called agro-wastes, are actually produced and disposed

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around the world each year with no proper valorization, resulting in significant financial loss. This problem is aggravated in areas that especially suffer the consequences of global warming (i.e., Caribbean countries) [3]. Climate change has increased incidents of extreme weather events, affecting especially in the agri-food industry where crops, formerly of great economic value, cannot be used for human consumption, losing their high value. All this, having consequences in the economic activities of these countries due to the great importance of the agri-food industry in them [4-5]. Furthermore, in this region, most economic sectors which are virtually nature-based are affected in multiple ways. For instance, high numbers of job losses occur due to natural disasters linked to climate change, reduction of productivity, decrease in tourist demand due to the increment of the number of violent hurricanes, and other climate-change-related storms [6].

Among these countries, Honduras is especially affected by climate change due to the delicate conditions that its ecosystems exhibit. In between 2016 and 2018, not only variable rain starts but also high-temperature droughts were recorded. The consequences of these climate change were: crop losses, flow reduction, water shortage, and new and more resistant plagues emergence, among others [7]. This situation increases the number of crops that cannot be consumed like food products, becoming agro-waste. Therefore, it is necessary to find alternative uses for these crops in order to obtain an economic benefit and not just losses. In this context, several studies have tried to value this agro-waste as inexpensive and renewable sources for other industrial sectors [8]. However, it is necessary a large amount of research before a potential benefit from these wastes can be achieved.

Among all the possibilities for their valorization, biodegradable materials from renewable agricultural resources such as carbohydrates, starches, and proteins have attracted much attention as possible replacements for plastic [9]. Plastic accumulation is one of the main worldwide environmental problems. If no action is taken to mitigate this problem, there is a high risk of damaging ecosystems and, consequently, biodiversity [10]. Plastic wastes not only affect flora and fauna, but they also put at human risk health, threatening food security [11]. For this reason, interest in agro-wastes is mainly because of their sustainable supply and biodegradability, and it is becoming more and more popular among the population since the public concern regarding the environmental problems mentioned before is increasing [12]. Agro-wastes are a non-expensive, available, and abundant source of resources that can be employed as raw materials in the fabrication of biodegradable value-added products that could be competitive in the global market and even replace traditional plastics. In addition, the well-established techniques and processes employed in the fabrication of conventional plastics could be adapted to process these new materials since they share, in many cases, some of their processability parameters. Although the production of value-added products from agro-waste and by-products may not yet be economically feasible in many cases, mainly because of the low market prices of products, low quantities and seasonality, high transportation costs and water content [13]. For this reason, further research is needed in order to have the proper valorization of agro-wastes, improving their economic and environmental benefit.

In this context, the main objective of this study was to evaluate different agro-wastes produced in Región 11 (Honduras) in order to establish some feasible routes for their valorization. For this, a physicochemical characterization regarding their chemical composition (protein, carbohydrate, ash, water, and lipid) was carried out with the standard methods. In addition, two possible valorizations of these wastes as raw materials have been evaluated.

2. Materials and Methods

2.1. Materials.

The differently evaluated agro-wastes are samples from ruined crops, affected by climate change, which do not meet the food sanitation requirements to be sold in the market. All of them were provided by a different producer who is members of the SAN R11 Bureau (El Paraíso, Honduras). The selected native varieties were: taro, a root vegetable produced by the tropical *Colocasia esculenta* plant, cassava, a tuber of the *Manihot esculenta* plant, green plantain from *Musa paradisiaca* and corn, a cereal grain produced by the variety *Zea mays*.

2.2. Sample preparation.

After the reception of the raw material, the samples were processed in order to obtain a fine powdered flour that could be evaluated. The two different processes employed can be followed by the scheme shown in Figure 1.

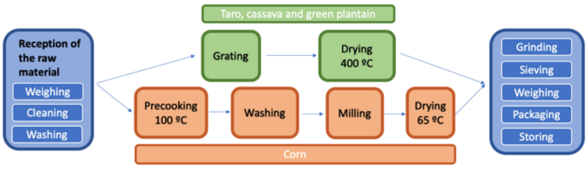

Figure 1. Scheme of the sample preparation.

2.2.1. Taro.

Firstly, taro was cleaned, and its shells removed. Then, the sample was grated into slices with an approximate thickness of 0.5 cm in order to reduce its size. Once grated, it was poured into stainless steel trays, spreading it out, leaving a thin homogeneous layer. Subsequently, the sample was introduced in a conventional oven (Mabe EME7630BEB0, Mexico) at 400 °C for 1-1.5 h in order to dry it. Then, the dried sample was taken out of the oven and let cool for 40 min at room temperature (26 ± 2 °C).

Finally, a hand hammer mill (Corona 8541954764, Colombia) was used to grind the sample for approximately 1 hour until fibrous microparticles were obtained. The obtained product was then sieved to obtain the final powdered flour, which was then packaged and stored.

2.2.2. Cassava and green plantain.

The protocol employed to obtain cassava and green plantain flour was the same used for taro. However, their size was reduced to 1 cm thickness for the cassava and green plantain samples (instead of 0.5 cm).

2.2.3. Corn.

Firstly, corn was washed in order to remove impurities of greater and smaller size than the grain. Once washed, lime was added to the corn (0.04 kg of lime for each 1 kg of corn), and it was precooked inside a casserole at 100 °C for 15 min approximately in order to obtain a product between raw and cooked. The corn was then washed with water to remove all excess lime, loosen the pericarp, and the eye of the grain. Later, the precooked corn passed through a larger opening width mill, to obtain flakes or large granules in order to facilitate its drying. The drying was carried out in a conventional oven (Mabe EME7630BEB0, Mexico), where the material was placed in trays and subjected at a temperature of 65 °C for 3 h.

Finally, as with the other samples, corn fibrous microparticles were obtained by grinding the sample with the hand hammer mill. Then, the product (flour) was sieved, packaged, and stored.

In all cases, the samples were weighed at the beginning and at the end of the preparation process to obtain the relation between the amount of raw material processed and the powdered sample obtained (percentage). This percentage is the yield of the process and was calculated using Equation 1:

$$Yield\ (\%) = \frac{Amount\ of\ powdered\ obtained\ (kg)}{Amount\ of\ raw\ material\ processed\ (kg)} \quad (1)$$

2.3. Chemical composition.

2.3.1. Protein quantification.

Firstly, the samples were evaluated using a LECO TRUSPEC CHNS microanalyzer (Leco Corporation, USA) to measure the nitrogen content of the sample. The used microanalyzer conditions were a temperature of 950-1100 °C and a pure oxygen atmosphere.

Later, this content was multiplied by the factor 6.25 in order to obtain the protein content (wt. % P), as it is expressed in Equation 2 [14].

$$wt.\%\ P = wt.\%\ Nitrogen \cdot 6.25 \quad (2)$$

2.3.2. Lipid quantification.

The Soxhlet extraction method [15] was used to quantify the lipid content. In this method, hexane was used as a solvent due to its affinity with the lipids. Thus, the solvent was heated until its vaporization at 80 °C and, subsequently, cooled until its condensation in a Soxhlet mechanism. In this way, the solvent came into contact with the samples dragging the lipids present in them. This procedure was carried out until a transparent siphoned solvent was obtained (approximately 4 h). Lipid content (wt. % L) was calculated indirectly using Equation 3.

$$wt.\%\ L = \frac{Initial\ weight\ (g) - Final\ weight\ (g)}{Initial\ weight\ (g)} \cdot 100 \quad (3)$$

2.3.3. Ash quantification.

The ash content (wt. % A) was obtained, followed A.O.A.C. method [16]. For this, firstly, 3 g of sample was calcined at 550 °C in a muffle furnace (Hobersal HD-230, Spain) for 5 h in air atmosphere. Then, it was kept in a desiccator, cooling at room temperature (26 ± 2 °C) and weighted again. Ash content was calculated using Equation 4.

$$wt.\%\ A = \frac{Ash\ weight\ (g)}{Initial\ weight\ (g)} \cdot 100 \quad (4)$$

2.3.4. Moisture quantification.

The moisture content (wt. % M) was also determined by A.O.A.C. methods [16]. For this, 3 g of each sample was introduced in a conventional oven (Memmert B216.1126, Germany) at 105 ºC for 24 h. Subsequently, the samples were cooled in a desiccator at room temperature (26 ± 2 ºC). Later, the moisture percentage was obtained using Equation 5.

$$wt.\%\,M = \frac{Initial\ weight\ (g) - Final\ weight\ (g)}{Initial\ weight\ (g)} \cdot 100 \quad (5)$$

2.3.5. Non-quantified sample (NQS).

The non-quantified part of the sample was calculated by percentage difference once the aforementioned tests were performed, that is:

$$wt.\%\,NQS = 100\% - wt.\%\,P - wt.\%\,L - wt.\%\,A - wt.\%\,M \quad (6)$$

2.4. Statistical analysis.

To perform the statistical analysis and calculate the standard deviation, a one-way analysis of variance and an average comparison test (t-test) were applied, using the statistical package SPSS 18. To this end, three replicates (minimum) of each measure were taken to study the result deviations.

3. Results and Discussion

3.1. Yield in sample preparation.

As stated before, part of the raw material received was thrown away during the processing steps carried out in order to prepare the samples to be evaluated. The relation between the amount of raw material processed and the amount of powdered sample obtained (in percentage) was referred to as yield of the process, and it is gathered in Table 1 for all the studied samples.

The process with the highest yield was the one carried out for the obtention of the cornflour with 64%. This yield is significantly high compared to the other samples, which showed yields below 25% in all cases. Although, these differences could be due to the processing method, which differed from the other obtention processes. The second highest yield corresponds to the cassava sample exhibiting a 25% yield, followed by the taro and green plantain samples with 21.16 and 15%, respectively.

Table 1. Yield of the sample preparation process for the different evaluated samples.

Sample	Taro	Cassava	G.plantain	Corn
Yield (%)	21.16	25.00	15.00	64.00

These percentages are too low for the concept of circular economy proposed, having a great loss of raw materials. This loss is possible due to the first discarding of the leaves and shell of the product. However, these wastes have mostly fiber in their composition and can be used as filler in many applications, such as construction. This part of the raw material is not considered in this study because other industrial alternatives with higher economic value are wanted to be evaluated.

3.2. Chemical composition.

3.2.1. Protein quantification.

Table 2 shows the chemical composition of the different samples. Regarding the protein content, the sample which exhibits the highest percentage is the cornflour with 7.35 wt.% protein, a slightly higher but close content to that obtained by Tambo Tene et al. [17] for two varieties of cornflour with 6.43 and 6.82 wt.% protein. These authors also evaluated the protein content of two varieties of cassava flour, obtaining 1.37 and 1.14 wt.% protein, again, slightly lower percentages than that exhibit by the sample studied in this research work with 2.24 wt.% protein content. The second highest protein content is that of the taro flour with 4.16 wt.% protein, about half the percentage obtained by André et al. [18] for the same sample. This difference in the results obtained could be due to the different methods and parameters employed in the processing of the flour. Finally, 2.13 wt.% protein content was obtained for the green plantain flour, a similar percentage, just slightly below, to those obtained by De Souza Viana et al. [19] for the same flour variety (2.66 and 2.85 wt.%).

These percentages cause all the samples to be classified as flours (< 20 wt.% protein content) according to the Pearson classification [20]. This percentage could be increased by lowering the temperature in the method of obtaining the raw materials. Furthermore, these proteins could be isolated by isoelectric precipitation, making it possible to take full advantage of this protein fraction.

3.2.2. Lipid quantification.

Table 2 also shows the results obtained for the lipids quantification. This time, it is also the cornflour that exhibits the highest percentage with 7.44 wt.% lipids, followed by the cassava and the green plantain flours with 2.56 and 2.39 wt.% lipids, respectively. The lowest lipid content corresponds to the taro flour, being 1.35 wt.%. Comparing with the research works mentioned before, Tambo Tene et al. (2019) obtained 7.52 and 4.23 wt.% lipids for their corn samples and 0.63 and 1.72 wt.% lipids for the cassava varieties, respectively [17]. So, the results obtained for the cornflour evaluated in this work is within their range, more similar to the first one, while the cassava flour shows a slightly higher fatty matter content. On the other hand, De Souza Viana et al. (2018) evaluated a green plantain flour sample that accounted for 0.61-0.65 wt.% lipid content, a smaller percentage than that calculated for the present plantain flour [19]. To finish with, the lipid content quantified by André et al. (2009) for a taro flour sample differs more significantly from out result, obtaining just a 0.1 wt.% lipids [18].

3.2.3. Ash quantification.

The results obtained for the ash determination of the different samples differ less from one another than the other quantification results (Table 2). This time, taro and green plantain flours showed the highest percentage, both containing 2.92 wt.% ashes. With 2.62 wt.%, cassava flour followed them, the cornflour being the one showing the lowest result this time. According to André et al. (2009) the number of ashes found in a taro flour sample was higher, exactly a 4 wt.% [18]. On the other hand, De Souza Viana et al. (2018) obtained a more similar ash content for their green plantain sample, 1.60-1.71 wt.% [19]. Continuing with the cassava and corn flour samples, the obtained results are slightly higher than that derived from the research conducted by Tambo Tene et al. (2019) in the case of the cassava samples which accounted for 1.05 and 1.15 wt.% ashes, and slightly lower in the case of the corn samples which ashes content was 2.20 and 4.15 wt.% [17].

This ash content is attributed to possible mineral salts that the residues contain since the used temperature is not high enough for its decomposition. These salts, with little added value, could disturb the obtention of the other components individually. However, if the raw material is used as a global product, it can favor its final properties [21] and processability [22] using them as filler components and providing certain reinforcing links.

3.2.4. Moisture quantification.

The last tests were performed to assess the moisture content of the samples (Table 2). The obtained results for the cassava, corn and taro flour samples decreased in that order being 8.20, 6.08, and 4.72 wt.%, respectively. The results found in the literature are higher in these three cases since Tambo Tene et al. (2019) [17] measured samples with 12.55 and 10.12 wt.% moisture for cassava samples and 13.29 and 12.48 wt.% for corn samples, and André et al. (2009) accounted for 8.5 wt.% for the taro flour sample evaluated, around half our results in the two later cases [18]. Lastly, the green plantain flour sample seems to be the one more similar in terms of moisture content to the sample used to compare with previous studies. De Souza Viana et al. (2018) evaluated samples with 6.69 and 7.16 wt.% moisture, being our sample within that range [19]. The variation found in all these data to the thermal treatment used during the processing of raw materials, since the milder this treatment has been, the greater the amount of water that can adhere to them.

3.2.5. Non-quantified sample.

According to previous studies which addressed the evaluation of similar flours, the samples consisted basically of proteins, lipids, ashes, moisture and carbohydrates, this later group accounting for the highest percentage, always above 80 %. For this reason, it would be a good approximation to attribute to carbohydrates the non-quantified part of the sample, which is gathered in Table 2. Similarly to the bibliography results, three out of four flours account for more than 80 wt.% carbohydrates. The highest percentage is that of the taro sample, which is composed of 86.85 wt.% carbohydrate followed by the green plantain and cassava flours containing 85.51 and 84.38 wt.%, respectively. Finally, the cornflour accounts only for 74.16 wt.% carbohydrates, a lower percentage than the other samples being still composed, basically, by carbs. By comparing these results to the ones gathered in previous research works, it can be observed how carbohydrates are the main components in those samples too, accounting for 82.6 wt.% for the taro flour studied by André et al. (2009) [18], 88.44 and 94.77 wt.% for the green plantain flour evaluated in the research addressed by De Souza Viana et al. (2018) [19], and 96.95 and 95.99 wt.% and 82.83 and 84.80 wt.% for the cassava and cornflour samples studied by Tambo Tene et al. (2019) [17]. These authors also differentiate between proteins, lipids, ashes, moisture, and carbohydrates when evaluating their samples, which validates the established technique of quantifying the carbohydrate content by percentage difference.

3.2.6. Potential valorization route.

As stated before, the proper valorization of agro-wastes is of vital importance, not only for economic reasons but also for environmental purposes. There is no doubt that, by endowing these wastes with a second life, for example, by processing a value-added product like a bioplastic due to its high content in carbohydrates [23], [24]. In this way, the local producers whose crops have been ruined would benefit from their sale as bioplastic raw materials, although the same benefit cannot be obtained as in the food industry. In addition, the biodegradable nature of the materials to be used would provide an environmentally friendly alternative to conventional plastic. These reasons, along with the obtained results regarding the chemical composition of the samples, highlight the bioplastic production as a feasible choice.

To begin with, all samples are basically composed of carbohydrates. In addition, similar samples evaluated in previous works, establish that these carbohydrates consist mainly of starch [17]–[19]. Starch can be found in different plants, and it is in abundance all over the world. It has a granular structure which has to be totally destructured under the action of both temperature and shearing action in order to produce a thermoplastic starch (TPS) [25-27]. TPS exhibits a few attributes, apart from its biodegradability, it is a renewable and flexible material that can be easily shaped by conventional processing methods traditionally employed in the production of synthetic polymers. Plasticizers like glycerol or water have to be used while processing, because of the low decomposition temperature of the granular starch. Processing usually takes place in an extruder, where the starch granules are disintegrated. After that TPS pellets that can be further processed into a biodegradable product by injection molding or compression molding are produced.

There are many studies that address the processing of TPS from agricultural wastes. Tábi & Kovács et al. [28] processed thermoplastic maize starch by injection molding and studied the effect of different injection molding parameters and storing methods on the samples. Glycerol and water were added, and the starch was processed in a twin-screw extruder and then with an injection molding machine. Enríquez et al. [29] characterized and modified native cassava starch for the production of biodegradable packaging. In this research work, the authors studied the physicochemical properties of three cassava starch varieties to address the processing parameters. These two studies are examples of successful attempts to process thermoplastic starch from agricultural wastes into bioplastics, which could be a starting point to the possible valorization route. For that, further characterization to evaluate the thermal properties of the samples should be performed.

On the other hand, the studied samples also exhibit certain protein content. Proteins are good candidates to play a key role in the sustainable production of materials. Proteins are based on several amino acids that differ from each other in the structure of the side chains, which may be polar or non-polar, resulting not only in complex structures but also in high functional diversity that can be used to chemically modify the protein in order to achieve the properties required for specific applications [30]. Some plant proteins, such as wheat protein or soy protein, have already being used for this purpose [31], [32]. Although there seems to be very low protein content in the studied samples, the employed methods to prepare them were not intended to preserve the original protein content. Different techniques, mainly by employing lower processing temperatures (protein have very low decomposition temperatures), can be used to increase the protein content of the samples. In addition, protein extraction processes are well-established techniques that could be applied to work with protein isolates in order to use them for the production of protein-based bioplastics, confirming the chosen valorization route.

Table 2. Chemical composition of the different evaluated flours.

Sample	Wt.% P	Wt.% L	Wt.% A	Wt.% M	Wt.% NQS
Taro	4.16 ± 0.51	1.35 ± 0.28	2.92 ± 1.04	4.72 ± 0.24	86.85 ± 2.93
Cassava	2.24 ± 0.28	2.56 ± 0.47	2.62 ± 0.22	8.20 ± 0.02	84.38 ± 1.40
Green plantain	2.13 ± 0.03	2.39 ± 0.36	2.92 ± 1.06	7.05 ± 0.44	85.66 ± 2.88
Corn	7.35 ± 0.12	7.44 ± 0.70	4.97 ± 0.75	6.08 ± 0.47	74.16 ± 2.88

To sum up, the proposed valorization route involves the employment of the generated agro-wastes as raw materials for the production of biodegradable materials in its as-received state since the chemical evaluation revealed a combined composition of proteins and starches. In addition, different techniques for the isolation of these components for using them on their own could also be of interest.

4. Conclusions

The performed tests allowed the quantification of the protein, lipid, ash, and moisture and the estimation of carbohydrate content (by percentage difference) of the different evaluated samples. The obtained results revealed flours which basically consisted of carbohydrates, and more specifically, by comparing with previous results, on starches.

Based on these results, a potential valorization route consisting of the processing of the agro-wastes in order to obtain biodegradable products was established. For this purpose, further characterization, mainly thermal characterization, should be carried out. The agro-wastes in its as-received state should be employed, and the processing methods should be addressed to the proper utilization of the starch and protein content of the samples. Alternative processing methods directed to obtain starch-based or protein-based products could also be interesting, starting from the isolation of the aforementioned compounds. For the production of protein-based biodegradable products, some modifications in the flour preparation process should be introduced to increase the protein content of the samples.

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Conflicts of Interest

The authors declare no conflict of interest.

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