# Valorization of mexican waste biomasses for bioenergy applications

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## *Introduction*

Mexico is a country that expects to enter the market of bioenergy taking advantage of its climate, orography and variety of exploitable agricultural resources, which are favourable for the production of biofuels as a sustainable alternative to support its economic growth. Particularly, the biomasses are considered a viable option for the energy production in Mexico because a significant amount of agricultural products and agro-industrial wastes is annually generated. The choice of raw materials that could be used in bioenergy processes depends on their physicochemical properties and availability (Parascanu et al., 2017). In this sense, it is necessary to identify biomasses with potential to be used in the bioenergy field. Therefore, the objective of this study was the valorization of several mexican waste biomasses to identify theirs potential uses for obtaining bioenergy. In particular, avocado seed, pepper, corozo palm seed, flamboyant fruit, jatropha seed, coconut shell and nance seed were analyzed and fully characterized. Several properties of these biomasses were determined where the results were valuable to decide their potential bioenergy applications.

## *Materials and methods*

Total solids and ash content were determined by using the methods established by the National Renewable Energy Laboratory (NREL). For the determination of lipid fraction, an extraction process was performed on dried biomass. In a Falcon tube of 50 mL, 5 g of dried biomass were placed with 20 mL of hexane. The system was closed and shaken for 5 min. Then, hexane phase was separated from the residual biomass and evaporated under $N_2$ flow to obtain an oil that was weighed and analyzed. Saponifiable content was determined by direct-esterification with methanol. Specifically, 0.1 g of oil was mixed with 0.1 g of HCl and 4 mL of methanol. The reaction was carried out for 24 h at 100 °C. The non-reacted methanol was evaporated, then the upper phase in the organic mixture was recovered. Methyl esters composition and average molecular weight were determined by gas-chromatography using methyl heptadecanoate as internal standard. FTIR analysis of lipids was carried out to complement the lipids characterization. The acid value of the extracted oils was also determined by titration using NaOH and phenolphthalein solutions as reagents. NREL method for the determination of structural carbohydrates and lignin in biomass was adapted and applied for the residual dried biomass samples in order to evaluate the content and the composition of simple and structural complex sugars. The identification and quantification of simple sugars, from hemicellulose, starch and pectinic sugars, from cellulosic component, were performed using hydrolytic solutions with increasing acidic strength. Sugar quantification was performed using a colorimetric method following the procedure established by Dubois et al. (1956).

## *Results and discussion*

For illustration, the results of chemical characterization of selected mexican biomasses are reported in Tables 1 and 2. Overall, the oil content in these biomasses followed the next trend: corozo palm seed > pepper > jatropha seed > nance seed > avocado seed. Note that the flamboyant fruit and coconut shell biomasses do not contain lipids, while corozo palm seed contained up to 49.8% of lipids. Gas-chromatography analysis showed that the main methyl esters contained in the extracted oils were myristic, palmitoleic, palmitic, oleic, linoleic and stearic acids. FTIR analysis confirmed the characteristic absorption bands of methyl esters around 1740 and 1700-1650 $cm^{-1}$. The determination of acid value of the oils extracted from the biomasses was an indicative of the esterification/transesterification route to follow in order to produce biodiesel.

On the other hand, the coconut shell, nance seed and flamboyant fruit contained 74.1, 49.5 and 48.5 %wt of lignin besides a low water content. These characteristics are desirable in materials that are expected to be used as carbon-based supports for the heterogeneous catalysts synthesis or precursors for the preparation of adsorbents that can be used in biofuels recovery such as bioalcohols. These analyses confirmed the importance of characterizing residual biomasses in order to identify their possible applications. Based on these results, different strategies can be established in order to valorize these mexican biomasses as energy sources under different process configurations like pyrolysis, biochemical conversion, biodiesel production, heterogeneous catalysts, adsorbents for recuperation of biofuels, among others (Parascanu et al., 2017).

Table 1. Chemical composition of several mexican biomasses

| ***Chemical composition (%wt)*** | ***Biomasses*** | | | | | | |
|---|---|---|---|---|---|---|---|
| | ***Avocado seed*** | ***Flamboyant fruit*** | ***Corozo palm seed*** | ***Pepper*** | ***Jatropha seed*** | ***Nance seed*** | ***Coconut shell*** |
| ***Water content*** | 44.4 ± 1.9 | 7.7 ± 0.1 | 6.5 ± 0.1 | 93.2 ± 0.1 | 3.7 ± 0.5 | 4.2 ± 0.5 | 6.08 ± 0.1 |
| ***Total solids composition*** | | | | | | | |
| ***Lipids*** | *4.7 ± 0.3* | - | *49.8 ± 0.5* | *2.3 ± 0.2* | *25.5 ± 0.1* | *6.3 ± 0.1* | - |
| Acid value (mg$_{KOH}$/g) | 13.1 ± 0.9 | - | 1.29 ± 0.4 | 10.9 ± 0.6 | 8.7 ± 0.1 | 14.2 ± 0.6 | - |
| Saponifiable content | 0.76 ± 0.1 | - | 45.0 ± 1.3 | 1.7 ± 0.3 | 15.9 ± 0.9 | 3.6 ± 0.3 | - |
| ***Glucose, fructose and saccarose*** | *5.8 ± 0.1* | *1.2 ± 0.1* | *6.5 ± 0.1* | *7.4 ± 0.1* | *4.7 ± 0.2* | *2.1 ± 0.2* | *1.24 ± 0.1* |
| ***Hemicellulose, starch, pectinic sugars*** | *47.7 ± 0.9* | *32.9 ± 1.5* | *15.8 ± 0.4* | *45.7 ± 0.9* | *12.5 ± 0.1* | *21.8 ± 0.4* | *20.3 ± 0.3* |
| ***Unknown species*** | *34.1 ± 0.9* | *0.4 ± 0.1* | *10.8 ± 0.2* | *20.7 ± 0.5* | *13.7 ± 0.1* | *1.0 ± 0.1* | *3.4 ± 0.1* |
| ***Cellulose*** | *1.3 ± 0.2* | *14.7 ± 0.5* | *6.4 ± 0.3* | *3.5 ± 0.1* | *1.6 ± 0.1* | *17.5 ± 0.1* | *0.5 ± 0.1* |
| ***Lignin*** | *4.7 ± 0.2* | *48.5 ± 0.3* | *7.5 ± 0.2* | *12.1 ± 0.1* | *37.8 ± 0.4* | *49.5 ± 1.9* | *74.1 ± 1.3* |
| ***Ash*** | *1.7 ± 0.2* | *2.3 ± 0.2* | *3.2 ± 0.3* | *8.3 ± 0.2* | *4.2 ± 0.3* | *1.8 ± 0.3* | *0.4 ± 0.1* |

Table 2. Comparison of chemical characteristics of oils extracted from several mexican biomasses

| ***Fatty acids composition (%wt)*** | ***Avocado seed*** | ***Corozo palm seed*** | ***Pepper*** | ***Jatropha seed*** | ***Nance seed*** |
|---|---|---|---|---|---|
| Caprylic acid (C8:0) | - | 6.32 ± 0.4 | - | - | - |
| Capric acid (C10:0) | - | 5.84 ± 0.2 | - | - | - |
| Lauric acid (C12:0) | - | 49.7 ± 0.8 | - | 0.73 ± 0.1 | 0.23 ± 0.1 |
| Myristic acid (C14:0) | 1.09 ± 0.3 | 14.4 ± 0.2 | 0.55 ± 0.1 | 0.39 ± 0.1 | 0.07 ± 0.1 |
| Palmitoleic acid (C16:1) | 2.11 ± 0.1 | 0.05 ± 0.01 | 0.98 ± 0.1 | 0.74 ± 0.1 | 0.22 ± 0.1 |
| Palmitic acid (C16:0) | 17.1 ± 0.6 | 7.57 ± 0.2 | 13.4 ± 0.1 | 15.8 ± 0.2 | 11.2 ± 0.8 |
| Oleic acid (C18:1) and linoleic acid (C18:2) | 69.4 ± 1.3 | 13.5 ± 1.0 | 80.4 ± 0.2 | 74.2 ± 0.1 | 83.2 ± 1.1 |
| Stearic acid (C18:0) | 10.3 ± 1.2 | 2.62 ± 0.1 | 3.16 ± 0.1 | 8.14 ± 0.2 | 5.08 ± 0.2 |
| Other acids | - | - | 1.51 ± 0.4 | - | - |
| ***Average molecular weight (g/mol)*** | ***276.4 ± 0.3*** | ***216.7 ± 1.3*** | ***280.8 ± 0.1*** | ***276.8 ± 0.1*** | ***278.6 ± 0.2*** |

## *Conclusions*

Seven abundant mexican residual biomasses were characterized in order to determine their potential to be valorized as renewable energy sources. A detailed physicochemical characterization of these biomasses has been the first step in order to determine the most appropriate application for these wastes. Our analysis indicated that flamboyant fruit, avocado seeds, coconut shell and nance seeds can be used as carbon-based supports for the preparation of heterogeneous catalysts for biodiesel production or adsorbents for biofuels recovery. On the other hand, the biomasses from pepper, avocado seed, nance seed, corozo palm seed and jatropha can be utilized for biodiesel production due to their fatty acid methyl esters content.

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