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Mexican biomass wastes: valorization for potential application in bioenergy

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The conversion of biomass into biofuels and biochemicals, represent a useful way to reduce the use of fossil fuels and maintain a sustainable energy production. In this context, Mexico is a country with a wide variety of exploitable agricultural resources that can be used to support its economic growth. In this study, several Mexican biomass wastes (avocado seeds, palm seeds, peppers, flamboyant fruit, jatropha seeds, coconut shells and nance seeds) were analyzed and fully characterized, in order to obtain a complete exploitation of their energy potential.

Key words: Bioenergy, valorization, waste biomass, biodiesel, renewable energy, biorefinery

INTRODUCTION

As a result of population growth combined with the gradual depletion of fossil fuels and the environmental problems associated with their use, an increase of energy demand worldwide will be expected [1,2].

For this reason, the use of alternative renewable energy is necessary in order to maintain a sustainable energy production. The conversion of biomass into of biofuels and biobased chemicals represent a useful way to mitigate the global warming and diversify the energy sources [3-5]. Biomass is a renewable resource that can be obtained from agricultural residues [6], industrial and animal wastes [7] and sludge from water treatment plants [8,9]. It is more evenly distributed over the Earth's surface respect to fossil fuels such as oil, coal and natural gas and it can be developed by using environmentally friendly technologies. Fuels derived from biomass are biodegradable, renewable, oxygenated with higher combustion efficiency and lower sulphur and aromatics content [10]. In addition, biomass is a valuable source of chemicals, pharmaceuticals and food additives [11]. Energy from biomass, also known as bioenergy, it was identified as the highest potential renewable energy in Mexico (from 2635 to 3771 PJ/year), with this research topic that was increasingly explored by Mexican academia. Furthermore, the Mexican General Law for Climate Change aims to generate 35% of its energy needs from renewable energy by 2024 [12]. The choice of raw materials that can be used in bioenergy processes depends on their physico-chemical properties and availability. In this sense, it is necessary to identify biomasses with potential to be used for the production of bioenergy. In this work, a study of the valorization of the principal Mexican biomass wastes was performed, in order to identify their potential applications for the production of fuels and value-added chemicals. In detail, avocado seeds, palm seeds, peppers, flamboyant fruit, jatropha seeds, coconut shells and nance seeds were analyzed and fully characterized, by evaluating the possible industrial applications.

MATERIALS AND METHODS

Reagents and Instruments

All chemical reagents used in this work were of analytical grade and were used directly without further purification or treatment. Avocado seeds (Persea Americana), peppers (Hungarian yellow and red variety) and seeds of palm (Palma de Coroco), jatropha (Jatropha Curcas), nance (Byrsonima crassifolia) were purchased from a local market of Aguascalientes (Mexico).

Fatty Acid Methyl Esters were identified by gas chromatography-mass spectroscopy (GC-MS) by using a Perking Elmer Clarus 500 equipped with a Clarus spectrometer. Quantitative determinations were carried out with a Varian 3800 GC-FID. Both instruments were configured for cold on-column injections with a HP-5MS capillary column (30 m; Ø 0.32 mm; 0.25 μm film).

Determination of Total Solids and Ashes

Total solids (TS) were determined according to the ISO 11465 method [13]. 10 g of biomass were placed in an oven at 105 °C for 24 h, until a constant weight was obtained. Then, the dried samples were heated in a muffle furnace at 550 °C for 3 h and ashes content was also determined. The results were expressed as weight percentage (%wt) of residual

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solids obtained after each thermal treatment, respect to the starting material.

Extraction of raw oils

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 10 min. At the end of process, a biphasic system was obtained: i) an organic phase in which raw oil was dissolved and ii) a lower phase of wet solid. Then, the organic phase was then separated from the residual biomass and recovered. The extraction procedure was repeated other three times with all organic fractions that were collected together. Finally, the solvent was evaporated under nitrogen flow and raw oil was weighed and analyzed in terms of Acid Value, Fatty Acid profile and Average Molecular Weight.

Determination of Acid Value

In a flask of 250 mL, 1 g of raw oil was placed with 100 mL of diethyl-ether:ethanol solution (1:1 v/v) in presence of phenolphthalein as indicator. Then, the organic mixture was titrated with 0.1 N KOH solution to the phenolphthalein endpoint. The results were expressed as milligrams of KOH required to neutralize 1 g of the raw grease (mg KOH/g).

Fatty Acid profile and determination of Average Molecular Weight (AMW)

20 mg of raw oil and 2 mL of toluene, methanol and concentrated H_2SO_4 (2:2:0.01 v/v/v) were placed in a glass tube of 10 mL. The system was closed and heated at 70 °C for 5 h. Then, 1 mL of 1000 ppm methyl heptadecanoate toluene solution was added as internal standard and the resultant solution was analyzed. Average Molecular Weight (*AMW*) was determined according to the following equation:

$$AMW = \frac{\Sigma A_i \, MW_i}{\Sigma A_i} \qquad (1)$$

where *Ai* and *MWi* are the area and molecular weight of FFAs, respectively.

Determination of Structural Carbohydrates and Lignin

NREL method for “Determination of Structural Carbohydrates and Lignin in Biomass” was partially adapted and applied on residual dried samples in order to evaluate the content and the composition of simple and structural complex sugars [14]. In detail, by using different hydrolytic solutions, with increasing acidic strength, it was possible to identify and quantify separately simple sugars, from hemicelluloses, starches and pectinic sugars, from cellulosic component. 2 g of residual dried solids (after extraction procedure with hexane) were suspended into 100 mL of 4%wt H_2SO_4 and stirred at room temperature for 1 h. 2 mL of this suspension was filtered, opportunely diluted if necessary and analyzed for determination of free sugars (glucose, fructose and saccarose were complexively found). Then, the suspension was refluxed for 4 h. The resultant cooled suspension was filtered: limpid solution was brought again to 100 mL of mQ (milli-Q) water, diluted if necessary and analyzed, by allowing hemicelluloses, starches and pectinic sugars to be determined. On the other side, the solid filtered from the suspension was washed with over 100 mL of mQ water, dried at 105 °C for 24 h and weighted. 200 mg of this residue was suspended and kept under agitation at 4 °C for 24 h in 3 mL of 72% H_2SO_4. Then, it was brought to 100 mL with mQ water, the resulting solution was transferred into a 250 mL glass balloon and kept under reflux for 4 h. The suspension was cooled and filtered on a filter previously prepared and weighted. The clear solution was diluted if necessary and analyzed for sugars determinations. Finally, filtered solids were abundantly washed with mQ water and dried at 105 °C for 24 h and weighted. Insoluble lignin was calculated by the difference between this weight and the respective ashes obtained after putting the same filtering crucible into an oven at 550 °C for 3 h.

ANALYSIS OF RESULTS

Analysis of the chemical composition of Mexican biomass wastes

In Figure 1 were reported the results obtained from the chemical characterization of Mexican biomass wastes. Considering the different water content and consequently the respective TS values, an oily component was observed in most of the samples analyzed. In particular, seeds of palm and jatropha present the highest oil content range between 48-50% and 25-27%, respectively. On the other hand, structural carbohydrates such as hemicellulose, starch, pectin sugars cellulose are present in high amounts in biomass like avocado seeds and peppers, until to reach 44-50% of the overall biomass. Finally, in the case of flamboyant fruit, nance seeds and coconut shells, lignin turns out to be the main component (50-75%wt). Based on these data, different strategies can be adopted, in order to obtain a complete exploitation of their energy potential.

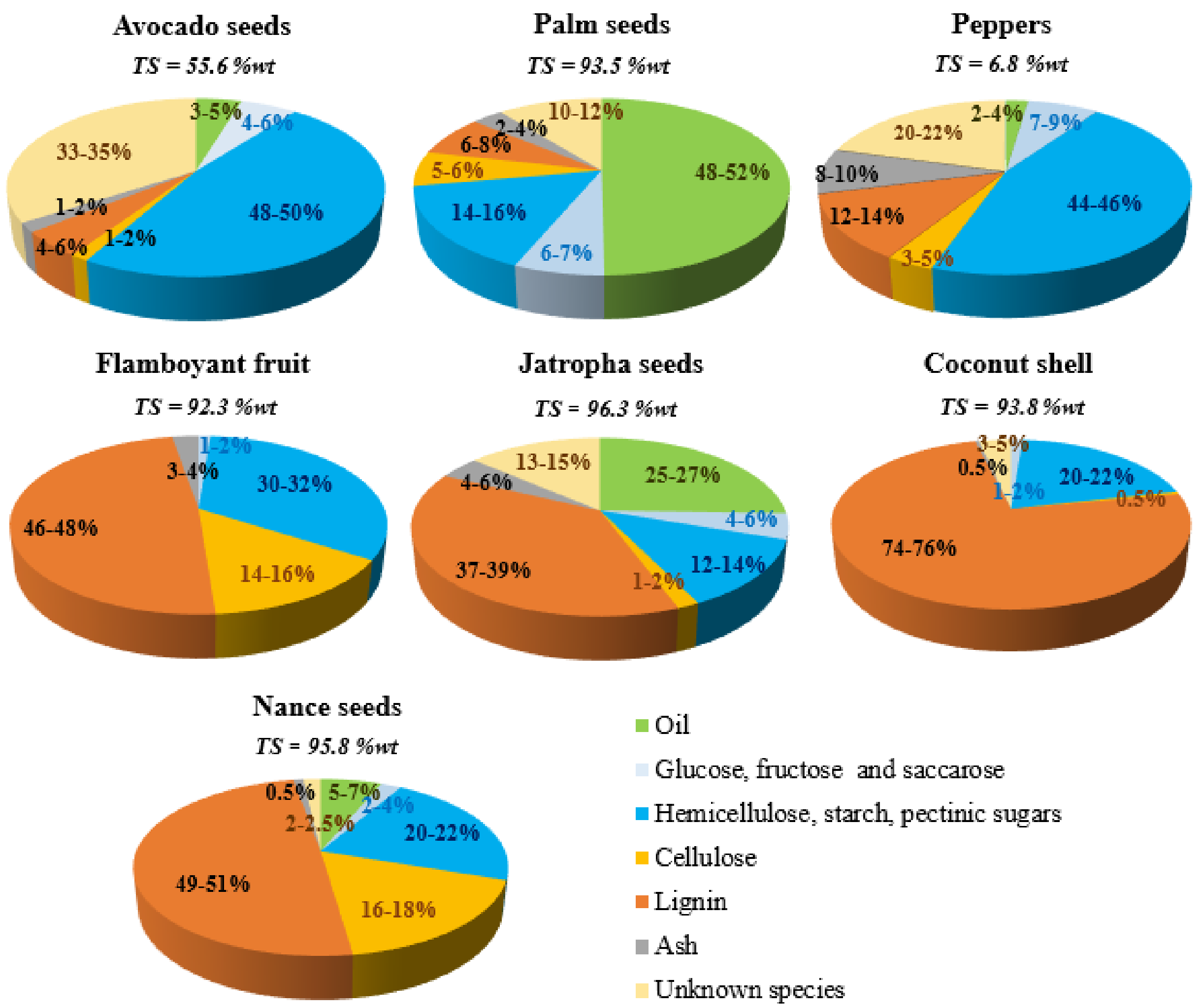

Fig. 1. Chemical composition of several Mexican biomass wastes.

Biodiesel production from non-edible oils

The use of non-edible oils as feedstock for biodiesel production represent a useful way to reduce the manufacturing costs and does not compete with food production. Biodiesel or Fatty Acid Methyl Esters (FAMEs) is typically produced by trans-esterification of vegetable oils and animal fats with methanol in presence of homogeneous basic catalysts [15]. The presence of a large amount of Free Fatty Acids (FFAs) leads to the formation of soaps with the consequent deactivation of the catalyst and difficulty in the product separation [16]. For this reason, a preliminary study of the chemical composition of the oils extracted was carried out in terms of Acidity, Fatty Acids profile and AMW. The results are reported in Figure 2.

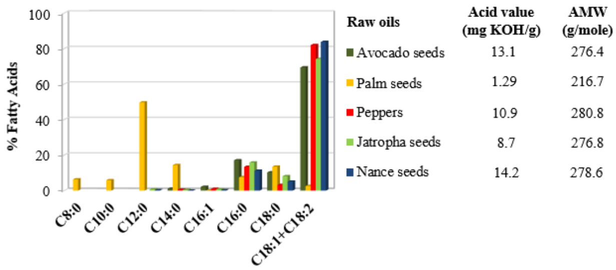

Fig. 2. Comparison of chemical characteristics of raw oils extracted from Mexican biomass wastes.

Raw oils contain high amounts of FFAs between 1 and 15 mg KOH/g with oleic and linoleic acids which represent the main component (>70%). In this case, a two-step approach can be efficiently adopted for the biodiesel production, in which metal hydrated salts are firstly used for the esterification of FFAs, followed by trans-esterification of lipids with sodium or potassium hydroxide [7]. Biodiesel obtained was found to EN 14214 specifications.

Direct conversion of structural carbohydrates into biofuels and chemicals

The conversion of structural carbohydrates (simple sugars as glucose and fructose, hemicellulose, cellulose and starch) into chemicals represents an alternative method for the synthesis of new molecules with added value and biofuels [17,18]. Ethyl levulinate is a promising platform molecule obtainable from simple and complex carbohydrates, which can be used for the production of biochemicals such as herbicides, plasticizers, resins, solvents, as well as biofuels [19]. A combined Lewis-Brønsted acid ethanolysis by using sulphuric acid and aluminum chloride hexahydrate as catalysts (Figure 3), allows the synthesis of Ethyl Levulinate in a single step from several kind of biomass in high yields with a low environmental impact [20].

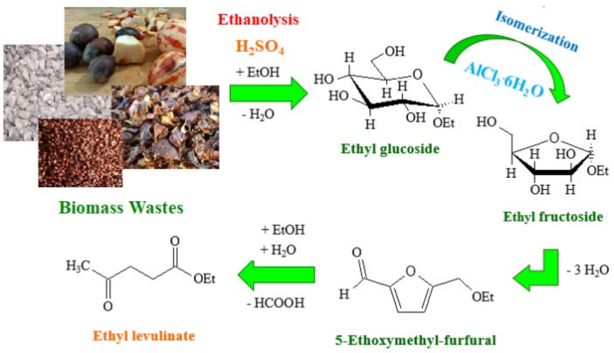

Fig. 3. Biodiesel production from non-edible oils by using supported catalyst with 20%wt of Ca loaded.

Synthesis of bioadsorbents for the removal of heavy metals from wastewater

Activated carbon has been widely used as adsorbent for the removal of heavy metals from wastewater [21]. In recent years, the necessity of safe and economical methods for the treatment of contaminated waters led to the production of low-cost alternatives respect to the commercial product. Biomass wastes can be efficiently used as precursors for the preparation of bioadsorbents and employed to the removal of heavy metals like lead, chromium, mercury, cadmium and arsenic [22, 23].

CONCLUSION

In this work, a detailed physico-chemical characterization of several Mexican biomass wastes biomass was carried out, in order to determine their potential applications as renewable energy sources. Different technologies can be adopted for a complete valorization of these resources, according to the principles of the green economy.

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