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RESEARCH ARTICLE

Highlighting the reuse potential of molasses (Panela Honey), a neglected sugar industry by-product, through its proximate analysis in Côte d'Ivoire

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Abstract

Suitable methodologies and modern research facilities such as gas chromatography (GC) coupled with atomic absorption spectrometry (AAS) were used to characterize sugarcane molasses in order to foresee its reuse potential, as it has long been considered as a neglected by-product of the sugar industry in Côte d'Ivoire. The results showed that molasses dry matters (DM) contain about 75% of simple sugars essentially made up of sucrose (62.50%), glucose (14.38%) and fructose (14.39%). Proteins and nitrogen represent 5.45% and 0.87% of the DM respectively. The ashes representing 16.61% of DM were full of potassium (K^+) with a rate of 45,209 ± 34.94 mg/kg. Lesser contents in magnesium (Mg^{2+}: 2,109 mg/kg), calcium (Ca^{2+}: 2,050 mg/kg), sodium (Na^+: 551 mg/kg), phosphorus (PO_4^{3-}: 260 mg/kg), iron (Fe^{2+}: 166 mg/kg), manganese (Mn^{2+}: 23 mg/kg), zinc (Zn^{2+}: 6 mg/kg) and copper (Cu^{2+}: 4 mg/kg) were also quantified. These interesting contents in crude proteins, nitrogen and various essential minerals make molasses, an important by-product of the sugar industry, as it can be reused as a fertilizer in agriculture and as an ingredient in the preparation of certain foods for new-borns and pregnant women. The high content of simple carbohydrates makes molasses an ideal raw material for the production of bioethanol, a high value added and environmentally friendly product of global relevant interest.

Keywords: *Saccharum officinarum* L.; Adding-value to molasses; Sugarcane by-products; Industrial waste reuse; Côte d'Ivoire

Introduction

According to a report of African Development Bank Group (Woldemichael et al. 2017), manufacturing sector remains one of the weakest in terms of value addition and employment in African agriculture. Also, the services sector is mainly oriented towards domestic consumers. There is therefore no doubt that, to better sustain its development, Africa needs to transform its economic structure, and agribusiness presents a promising prospect (Diao et al. 2010).

Agribusiness has the potential to support a range of ancillary services and support activities in the secondary and tertiary sectors. The perishable nature of agricultural produces paves the way for the establishment of processing industries along with the small-scale processing units. Indeed, their impact on rural non-farm activities, employment, and overall poverty reduction is usually very significant (Woldemichael et al. 2017).

In sub–Saharan Africa, the industrialization and the development of rural areas really took place at the beginning of independence by the establishment of various governmental agro-industrial factories (Austin et al. 2017). As regards Côte d'Ivoire, a West African country, this industrial policy was mainly focused on the implementation of sugarcane plantations and sugar industries. The Ivorian sugar plantations cover a total area of about 30,000 hectares as of now since 1968 and is still not self-sufficient (Roch 1988). In 2020 for example, Côte d'Ivoire imported 81.1 million

USD value of raw sugar, becoming the 70th largest importer in the world. Although the initiative of implementing sugar industries was relevant and laudable, the project did not achieve to date the target. It was aimed for the raw sugar production for local consumption and export, and with the extra income from sugar sector, economic and social development were to be ensured, at the same time, in the northern part of country (Koffi-Bikpo 2016). However, the turnover generated is not sufficient to cover all these investments. Therefore, alternative strategies have to be developed.

Nowadays, the upward trend in world market prices for sugar (Maitah and Smutka 2019), as well as the increase in energy prices (Amigun et al. 2008), are major assets that could contribute to a revitalization of sugar industries and, at the same time, to shift from sugar only production towards coproducing valuable products for more economic profitability (Lin et al., 2020). Indeed, in several industrialised countries, an integrated concept of reusing bagasse and molasses from several plant sources as raw materials for the co-production of value-added products (biohydrogens, bioalcohols and biovinegar) and for fungal enzymes production is gaining momentum as it avails opportunities for local population employment thus creating jobs (Özgür et al. 2010; Veana et al. 2014; Miranda et al. 2020; Sakai et al. 2020). However, in developing countries such as Côte d'Ivoire, where the sugar industry is still operational, its by-products remain under-exploited. Only a small part is used for cattle feed and soil fertilisation, while the main portion is rejected into the environment (Hoste et al. 1982; Makita-Ngadi et al. 1993).

As a result of the above, it seems appropriate to valorise the sugarcane molasses produced in Côte d'Ivoire through its reuse as an industrial raw material. However, to meet the industry-desired standards and be competitive on the market, we need to ensure that the used raw materials have safety aspects of the end products intended to consumers, as well as appropriate laws and legal declaration requirements. Therefore, efficient and reliable techniques for these materials analysis have to be chosen. This study aims to valorise molasses, a neglected and currently discarded by-product of the Ivorian sugar industry (UEMOA 2006), through qualitative and quantitative characterisation in order to foresee, as an industrial raw material, it reuses potential for the production of high-value products of economic and environmental profit.

Materials and Methods

Plant material

The sugarcane molasses samples were obtained from the main sugarcane industry of Côte d'Ivoire, Ferké I. The molasses samples were collected after centrifugation during the process of sugar crystallization under steam heating conditions. It was dark brown in colour and viscous (Chauhan et al. 2011).

Instruments and reagents

The main instruments used in this study were: a GC/MS Agilent apparatus, (Genesis 5) UV-Visible spectrophotometer and HACH-DR3900 Series atomic absorption spectrophotometer (AAS). All the reagents used such as strong acids and bases as well as specific solvents and compounds are of analytic grades.

Moisture

The water content of sugarcane molasses was determined by oven drying using the procedure of Uniform Methods of Sugar Analysis (ICUMSA METHOD GS7-5, 1994). 10 g (W1) of molasses were weighed out in a porcelain dish and were kept for drying at 80°C for 3 to 6 hours. Then, the sample was removed from the oven, cooled in a desiccator for 30 to 45 minutes and weighed again (W2). The moisture content of the samples was obtained from the mass difference (W1 – W2).

Crude proteins

The crude proteins of the cane molasses samples were calculated by Kjeldahl (ISO1871 2009). Nitrogen from nitrates and nitrites is not taken into account by using this dosing principle. 0.5 g of dried sample was first digested by heating in 15 ml of strong sulphuric acid in the presence 1 g catalyst which helps in the conversion of the amine nitrogen to ammonium ions. This digestion step ends in 30 min with the appearance of a green coloration. After digestion, the ammonium ions were dissolved in 250 ml of distilled water containing 5 drops of phenolphthalein and 75 ml of a 1 M sodium hydroxide solution. The contents were heated and distilled. The liberated ammonia gas was led into a trapping solution of 10 ml of boric acid solution (10 g/l) and few drops of a mixed indicator dye (methyl red + bromocresol green) where it dissolved and became an ammonium ion once again. Finally, the amount (150 ml) of the ammonia that has been trapped was determined by titration with a 0.1 N hydrochloric acid solution.

Carbohydrates

The cane molasses carbohydrates were quantified by using the standard method of AOAC 938.02 (1938). To 3 ml of the sample, add 2 ml of acetonitrile and 0.1 g of NaCl and the mixture was vortexed and centrifuged at 5,000 rpm for 10 min. 100 µl was withdrawn from the supernatant layer and evaporated to dryness under vacuum. Add 100 µl of dichloromethane (DCM) to the dried sample and repeat the evaporation process. Again add 100 µl of bis (trimethylsilyl) trifluoroacetamide (BSTFA). Finally, the whole mixture was dried in an oven at 80°C for 30 min and the resulted solution made up to 1.5 ml with acetonitrile then put in a vial for chromatographic analysis.

Sugars (glucose, fructose and sucrose)

Simple sugars were quantified according to the AOAC 938.02 (1938) method.

Free sugars contents: 10 g of molasses sample were dissolved in 100 ml of a distilled water. 10 ml of the dissolved sample was taken in a 250 ml Erlenmeyer flask and 20 ml of a 5 mM iodine solution and 5 ml of 2 M sodium hydroxide (NaOH) were added. After homogenization, the mixture was kept in dark for 20 min and then, 7 ml of hydrochloride acid were added and titrated using 0.1 N of sodium thiosulfate.

Total sugars: 1 g of molasses was dissolved in 50 mL of a 2 M hydrochloric acid solution and boiled for 30 minutes. 10 ml of this solution was boiled again for 30 min with 40 ml of 2 M hydrochloride acid. After cooling, mix 10 ml of the mineralized solution with 20 ml of a 5 mM iodine solution and 10 ml of 1 M NaOH. The mixture was kept in the dark for 20 min and then. 7 ml of hydrochloride acid were added and titrated using 0.1 N of sodium thiosulfate.

Ash and inorganics

The minerals were quantified by following the ICUMSA method GS1-10 (1998). 2 g (W3) of the previously dried sample were incinerated at 600 °C for 3 h in a graphic oven. After cooling in a desiccator for 45 min, the resulted powder was weighed (W4) and the ash content was determined.

For elemental analyses, procedures of ICUMSA were followed: iron (Method GS2/3/7/8-31 1994), phosphorus (Method GS7-15 1994), magnesium (Method GS7-19 1994), copper (Method GS2/3-29 1994), calcium (ICUMSA method GS8/2/3/4-9 2000), potassium and sodium (Method GS6-7 2007) and heavy metals namely cadmium, arsenic, mercury and lead were quantified as described in Segura-Munoz et al. (2005) following the ICUMSA Method GS9-1 (2019). The ashes obtained from 2 g sample of dry molasses were dissolved successively in 2 ml of nitric acid and 98 ml of distilled water. Most of metal ions were quantified by gas chromatography (GC) coupled with an atomic Absorption spectrophotometer (AAS).

Iron: The acidic solution was first neutralised (pH 7.0) using a 2 M NaOH. To 10 ml of the neutralized solution, 100 µl of a FerroVer Iron reagent was added, mixed vigorously and then, kept for a while and spectrophotometrically quantified.

Mercury (Hg): 10 ml of the neutralised sample was taken and 1 ml of 0.5 M sulphuric acid, 2 ml of acetic acid and 5 ml of chloroform were added. Shake for a minute and remove the organic phase. Then, add 5 ml dithizone, shake again for 1 min and the aqueous phase was analysed at 500 nm.

Phosphorus: 1 g of dried molasses sample in 5 mL of a Mg(NO3)2 solution was boiled at 105 °C for 30 min. The homogenised mixture was incinerated at 500 °C for 3 h and the ash obtained was dissolved in 2 ml of a hydrochloric acid solution and made up to 50 ml with distilled water. Then, 20 ml of the resulted solution was withdrawn and the pH was adjusted to the range 3-10 by adding 2 N sodium hydroxide (NaOH). The half of this solution was used for blank while the second part, was mixed with a prepacked packet of PhosVer3 phosphate reagent, homogenized and allow to react for 3 min the absorbance value was measured at 880 nm.

Statistical analysis

Results are the means ± standard deviation (SD) of three replicates.

Results and Discussion

Organic compounds

The main organic compounds of the molasses samples studied are summarized in Table 1. Results obviously show that, carbohydrates are the main constituents in molasses dry matter followed by proteins (5.45 ± 0.21%). They represent more than 75% and are mainly made up of 90% of sucrose (62.5%), Glucose (14.38%) and fructose (14.39%). The average moisture content is of value of about 5.60 ± 0.64% (Table 1). As opposed to moisture content, the DM reached an average value of 96.0 ± 1.73%. This mean of DM was about twenty units greater than the overall mean of those (76.8 ± 1.02%) reported for sixteen other worldwide molasses's samples recently characterized (Palmonari et al. 2020). The relatively higher concentration of DM obviously reflects an important amount of organic matter or the presence of new chemicals in Ivorian molasses as asserted by Zhang et al. (2021).

Table 1. Descriptive statistics of moisture and main organic compounds content of a tropical sugarcane molasses

Item	Average	Standard Deviation	Minimum	Maximum
Dry matter (%)	96.00	1.73	94.27	97.73
Water content (%)	5.60	0.64	4.96	6.24
Crude proteins (%)	5.45	0.21	5.24	5.65
Carbohydrates (%)	75.34	2.02	73.32	77.36
Sucrose (%)	62.50	1.33	61.17	63.83
Glucose (%)	14.38	0.07	14.31	14.45
Fructose (%)	14.39	0.11	14.28	14.50

The crude protein content of the Ivorian molasses (5.45 ± 0.21%) is higher than that of the mean mentioned in Christon and Le Dividich (1978). However, it is slightly below the average of 6.7 ± 1.8% reported for sixteen others molasses characterized worldwide (Palmonari et al. 2020). Although this protein content is of nutritional asset, it is atypical because plant materials with significant amounts of proteins are generally oilseeds, cereals and pulses with proportions of up to 20 g of pure protein per 100 g of materials. By relativizing this amount of protein to total nitrogen (N) content according to the Kjeldahl method, we realized that the studied molasses contains about 0.87% which is largely below the range of 1.4 to 2.1% of raw molasses weight (Jevtic-Mucibabic et al. 2011). Nevertheless, with this nitrogen content, the molasses studied could be reused as a cheap nitrogen source for various yeast strains in fermentation industy (Solaiman et al. 2007).

The results presented in Table 1 show that the major part of the organic matter of the molasses studied is made up of carbohydrates with a content of more than 75%. they are essentially made up of sucrose for up to 62.50% and about 28% of glucose and fructose distributed in equal proportions of 14% each. The primary use of molasses in animal feed is mainly related to its high concentration of carbohydrates, an important metabolic energy source. Thus, compared to the high cost of glucose and other commercially available sugars, this neglected by-product of the sugar industry would be a cheap alternative carbon source to exploit in various fields. Indeed, apart from traditional use to feed cattle, molasses constitutes an adequate raw material for the production of glucose and/or fructose syrups which are widely used in the food industry. Beside this, it could be used as a cheap carbon source for yeast growth in the fermentation industry (Pattanakittivorakul et al. 2019). Also, owing to its high content in fermentable sugars, it could be suggested to predominantly use molasses as raw material for bioethanol production (Dogbe et al. 2020), because it has already been estimated a high potential of bioethanol production of about 19,000 m3 per year in Côte d'Ivoire (UEMOA 2016). This approach to molasses recovery is topical and relevant because of the ever-increasing price of gas and petrol used as fossil fuels. Indeed, the energy transition would like to see a large part of fossil fuels replaced by more environmentally safe renewable energies as alcohols (Wynne and Meyer 2002; Reid et al. 2020).

Ashes and inorganics

The ash content was found to be a mean value of 16.61 ± 0.98 % of dry matters after incineration. Traces of heavy metals as lead, arsenic, cadmium and mercury with values less than 1 µg/kg were found. Potassium concentration was far higher (45,209.54 ± 34.94 mg/kg) than that of magnesium (2,108.50 ± 7.22 mg/kg), calcium (2,050 ± 10.55 mg/kg) and sodium (550.96 ± 5.11 mg/kg). Other minerals such as copper, zinc, manganese and phosphorus were also quantified in the molasses samples as shown in Table 2.

The molasses studied was found to have high mineral content dominated by potassium, which accounts for about 90% of all minerals analysed, followed by magnesium (Mg^{2+}) and calcium (Ca^{2+}) as mentioned in Table 2. Mg^{2+} is an important for over-all plant health. Specifically, this mineral contributes in enhancing plants defence by increasing the resistance of tissues to degradation by pectinolytic enzymes of bacterial soft rotting pathogens (Monilola and Abiola 2011). Mg^{2+} in the present study could contribute to the quality and organoleptic properties of the molasses. As the second most abundant cation within the body's cells after potassium, Mg^{2+} is mainly (50-65%) stored in bones where it participates with calcium (Ca^{2+}) and phosphorus (P) in the constitution of the

Table 2. Descriptive statistics of inorganic compounds content of a tropical sugarcane molasses

Item	Average	Standard Deviation	Minimum	Maximum
Ashes (%)	16.61	0.98	15.63	17.59
Sodium (Na; mg/kg)	550.96	5.11	545.85	556.07
Calcium (Ca; mg/kg)	2,050.10	10.55	2,039.55	2,060.65
Potassium (K; mg/kg)	45,209.54	34.94	45,174.60	45,244.48
Phosphorus (P; mg/kg)	260.00	2.36	257.64	262.36
Copper (Cu; mg/kg)	4.10	0.10	4.00	4.20
Iron (Fe; mg/kg)	166.07	1.15	164.92	167.22
Zinc (Zn; mg/kg)	5.74	0.09	5.65	8.83
Manganese (Mn; mg/kg)	23.34	1.44	21.90	24.78
Magnesium (Mg; mg/kg)	2,108.50	7.22	2,101.28	2,115.72
Lead (Pb; µg/kg)	0.63	0.08	0.55	0.71
Arsenic (As; µg/kg)	0.71	0.05	0.66	0.76
Cadmium (Cd; µg/kg)	0.55	0.01	0.54	0.56
Mercury (Hg; µg/kg)	0.26	0.02	0.24	0.28

skeleton (Schuchardt and Hahn 2017; Fiorentini et al. 2021). Although the total Mg content in molasses (2.11 g/kg of DM) is below the adult body value of 20 to 28 g, the new-borns body contain only 0.76 g of Mg which reaches 5 g at the age of 4 and 5 months (Romani 2011; De Baaiji et al. 2015). In this context, it is evident that the studied molasses could be used as an ingredient to supply infant foods in magnesium and, by the large, in minerals involved in the consolidation of bones.

Compared to potassium, the *Ferké* I molasses showed relatively lower rate means of phosphorus (260 mg kg^{-1} of DM), iron (166 mg kg^{-1} of DM), manganese (23.34 mg kg^{-1} of DM), zinc (5.75 mg kg^{-1} of DM) and copper (4.10 mg kg^{-1} of DM). Table 2 results give a calculated Ca/P ratio close to 7.8, thus very unbalanced because it reasonably varies between 0.1 and 0.2 for most plant foods (Christon and Le Dividich 1978). Taken individually, phosphorus could participate, along with calcium, in bone rigidity (Ciosek et al. 2021) and in supplying inorganic phosphate in phosphorylation reactions during plant metabolism (Duff et al. 1994). As iron, zinc, manganese and copper are concerned, they are "essential" elements for health (Kuo and Ehrlich 2012; Wakashin et al. 2018) whose deficiency leads to functional and physiological abnormalities in a manner analogous to a specific vitamin or hormone deficiency (Garzon et al. 2020). Taken together, the presence of all these minerals in molasses makes it a significant source that could be exploited in animal and human nutrition to help maintain physiological balance and good health.

The molasses studied contains traces of heavy metals with levels below 1 µg/kg of DM for lead, arsenic and cadmium, and below 0.3 µg/kg for mercury. When in very low concentrations, metals are essential part to maintain a number of biochemical and physiological functions in living organisms, however they become noxious when they exceed certain threshold concentrations. Reference intervals of urine and blood overview of laboratory and toxicokinetic information for these noxious cations have already been summarized in Keil et al. (2011). By considering their primary routes of deposition or elimination, we could have categorized cadmium and lead as the most dangerous elements because they can't be eliminated in urine or faeces and thus accumulates in kidneys and bones, respectively (Jaishankar et al. 2014). Heavy metal are also significant environment pollutants (Nagajyoti et al. 2010). So, in view of the alarming aspect developed above, the analysed molasses sample should be used in nanogram proportion specifically as food excipient.

Importance of molasses reuse

Molasses which constitutes the main by-product co-obtained during the process of raw sugar production could be put in good reuse. Indeed, although discarded during sugar crystallisation, the quantity of molasses obtained from the production of 1 ton of raw sugar represents a significant amount of 0.38 ton consisting in a production yield of 38% (Wang et al. 2019). In this context, molasses constitutes an important raw material which, beyond its primary applications in livestock feed (Hoste et al. 1982; DeVries and Gill 2012; De Ondarza et al. 2017) and soil fertilisation (Wynne and Meyer 2002), could be explored in various fields regarding its physicochemical characteristics described above. Indeed, it is now well accepted that the destiny and large-scale use of raw materials are largely dependent on their biochemical compositions although depending on the sugar refining process, the plant varieties and the growth soil types (Zhang et al. 2021). So, the present study has undeniably contributed in better characterization of a key tropical molasses in terms of physicochemical properties and foreseeing other perspectives of reusing in order to revitalize the sugarcane industry.

Conclusion

The present study has enabled us to broaden the potential usages of Ivorian molasses in several fields. The high compounding in simple fermentable sugars makes it an essential raw material for the fermenting industry for the production of bio alcohols and vinegars. In addition, this important source of carbohydrates energy, associated with nitrogen as well as essential mineral elements such as Fe2+, Mn^{2+}, Mg^{2+}, Ca^{2+}, K^{+} and PO_4^{3-} (to name but a few) is a considerable asset in the production of animal feed and plant fertilizers. Besides this primary use in farms and animal husbandry, Ferké I molasses can also be exploited as an ingredient in bakery products and in the supplementation of minerals for infant and pregnant mother foods.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship and/or publication of this article.

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