Sugarcane Wax - A Par Excellent by-Product of Sugar Industry - A Review

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ABSTRACT

Sugarcane is one of the major cash crops, used for the production of sugar and ethanol. Sugarcane processing, results in many by-products like bagasse, molasses and press mud which have economic value. Also, the by-products serve to generate many value added products. Sugarcane wax is a value added product obtained by the processing of press mud. It has pharmaceutical, agricultural and industrial applications, n-Triacontanol, Policosanol, D-003 acids and waxes are some of the products derived from the Sugarcane wax. This article attempt discusses the various methods of extraction of sugarcane wax, its constituents and its characteristics and applications of the products derived from the Sugarcane Wax.

Key words: D-003 acids, Extraction, n-Triacontanol, Policosanol, Press mud, Sugarcane, Wax.

Sugarcane (Saccharum officinarum L.) is a tall perennial true grass belonging to the genus Saccharum and tribe Andropogoneae. It originated in Southeast Asia and is now cultivated in tropical and subtropical countries throughout the world for sugar and by-products. The genus Saccharum contains five important species, viz., Saccharum officinarum, Saccharum sinense, Saccharum barberi, Saccharum robustum and Saccharum spontaneum. S. officinarum was originally grown in Southeast Asia and Western India. It’s cultivation in the Indian subcontinent dates back to ca. 327 B.C. It was introduced into Egypt at around 647 A.D. and about one century later, to Spain (755 A.D.) (Chinnadurai, 2017). Since then, cultivation of sugarcane has extended to nearly all tropical and subtropical regions around the world.

Sugarcane is a C₄ crop with leaves in the form of spears, sprouting in stalks and abundant tillering in the initial phase of development (Santos et al., 2013). The plant has approximately 57% of water in its mass composition, the remainder being divided between straw, bagasse and sugar.

Worldwide, sugarcane inhabits 26.27 million ha area with a total production of 1907 million metric tons (FAO 2018). Sugarcane area and productivity differ widely from country to country. Brazil occupies the highest sugarcane-growing area (10.04 million ha) followed by India (4.73 million ha), China, Thailand, Pakistan and Mexico (Suganthi et al., 2019). Sugarcane is a versatile crop which a rich source of food (sucrose, jaggery and syrups), fiber (cellulose), fodder (green leaves and tops of cane plant), fuel and chemicals (bagasse, molasses and alcohol) and fertilizer (press mud and spent wash). The main by-products of the sugar industry which have economic value are bagasse, molasses and press mud.

In India, on an average, processing of 100 tons of sugarcane in a factory yields 10 tons of sugar, 30-34 tons of bagasse (of which 22-24 tons is used in processing and 8-10 tons is saved), 4-5 tons of molasses, 3 tons of filter mud (press mud), 120 tons of flue gases (at 180°C) and 1,500 kWh of surplus electricity (Solomon, 2011; Yadav and Solomon, 2006). The by-products of processing like bagasse, molasses, press-mud, etc., being rich in carbon compounds and minerals provide ample opportunity for production of valuable chemicals, waxes, new food/feed products and low calorie sweeteners, energy options (like cogeneration/fuel/ bio-diesel, ethanol), medicines, pesticides, etc. The objective of this paper is to bring to light the holistic idea about the Sugarcane waxes being extracted from the press mud, components and its commercial applications.

Sugarcane press mud

In the manufacture of cane sugar (Fig 1), during clarification the precipitated impurities present in the cane juice after removal by filtration, in rotary vacuum filters or by batch type filter presses forms a cake. It is also known as milk mud or press mud or filter cake. It is produced at the rate of around 3% of weight of cane in sulphitation factories and 7% in carbonation factories. Press mud/Filter cake contains about 50–70% moisture; 5–14% of crude wax and fat; 15–30% fiber, 5–15% sugar and 5–15% of crude protein, with appreciable amount Si, Ca, P₂O₅, MgO, Fe and Mn (Roufa et al., 2010).

Sugarcane wax

In Sugarcane, waxes provide protection against water loss...
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Sugarcane stalk

Cleaning and shredding

Extraction

Crushing

Bagasse

Raw Juice

Heating and liming

Press mud/ Milk mud/ Filter cake

Clarification

Clean Juice

Evaporation

Crystallization and separation

Centrifugation

Molasses

Wet raw sugar (Syrup)

Drying

Raw Sugar

Refining

(Affination, Melting, Liming, Carbonization, Decolorization, Evaporation, Crystallization, Drying, Seiving)

White Sugar Crystals

supercritical fluid extraction (SFE), ultrasonic-assisted supercritical CO$_2$ extraction (USC-CO$_2$) and accelerated solvent extraction (ASE), have been developed to reduce the time and solvent consumption of conventional extraction methods. The different extraction processes that exist for isolation of sugarcane wax from press mud are

| Methods                          | Reference                  |
|----------------------------------|-----------------------------|
| Microwave Assisted extraction (MAE) | Ganzeler et al., 1986; Eskilsson et al., 2000 |
| Ultrasonic–assisted extraction (UAE) | Sporring et al., 2005; Cardoso et al., 2013 |
| Supercritical fluid extraction (SFE) | Bowadt et al., 1995 |
| Accelerated solvent extraction (ASE) | Bjorklund et al., 2000 |

Though extraction yield is rather high, the conventional Soxhlet method presents several drawbacks such as toxicity from organic solvent, high cost of operation, solvent recovery requirement, as well as being energy-intensive operation (Lucas et al., 2006). Consequently, there is a demand for new extraction techniques that are more environmental friendly. Modern methods as alternative to Soxhlet method offer rapid and environmental friendly wax extraction concomitant with higher yield.

Conventional extraction method

Sugarcane wax is extracted with different solvents such as Toluene, Hexane and Benzene under a reflux system for 4-6 hours at a stretch. The extract is filtered under mild vacuum and the solvent used is recovered by distillation. The resultant solid mass containing wax mixtures and resins is dissolved in hot isopropyl alcohol and filtered (Fig 2). The resin portion is separated and the total wax portion is obtained, which is yellow or light cream in colour.

Microwave assisted extraction (MAE)

MAE was first reported by Ganzeler et al. 1990. Two common types of microwave-assisted extraction configuration are a closed extraction under controlled pressure and temperature and an open extractor under atmospheric pressure condition and controlled temperature at solvent boiling point. MAE enhances extraction efficiency by inducing high thermal energy via electromagnetic radiation in the range of 300 MHz to 300 GHz for heating the sample (Veggie et al., 2012).

Sugarcane wax components are extracted by exploiting their differences in solubility in different solvents and their mixtures. This is achieved by altering giving the solvent mixture ratio and controlling the temperature.

Ultrasonic–assisted extraction (UAE)

UAE is a good choice in comparison with the more traditional approaches due to its high efficiency, low energy requirements and low solvent consumption. This technique has been applied in the extraction of bioactive compounds from plants and other products (Samaram et al., 2015; Cardoso et al., 2013 and Ghitescu et al., 2015). The improvement in the extraction process on using ultrasound

Conventional extraction method

Extraction process

Conventionally, extractions use the relatively time- and solvent-consuming Soxhlet method. New extraction techniques, such as microwave-assisted extraction (MAE)
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is attributed to the destruction of the cell walls, the reduction of the particle size and the enhancement of mass transfer through the cell wall due to the collapse of bubbles produced by cavitation (Paniwnyk et al., 2001). UAE uses ultrasonic energy above 20 kHz to produce cavitation bubbles; which in turn, collapse and generate higher shear resulting in complete extraction (Chemat et al., 2017). Moreover, UAE can be used as a pre-treatment technique for botanicals to enhance extraction performance. UAE is operated at lower extraction temperature and solvent volume yielding improvement in extraction and purity.

Supercritical fluid extraction (SFE)

In SFE, carbon dioxide is used as the solvent in the majority of cases. This is an advanced technology that has a low environmental impact due to low toxicity, low cost and ease of separation from extracts [Macias Sánchez et al., 2008]. The use of CO₂ gives an added advantage in terms of quality, as extracts do not suffer excessive heating, which may destroy thermally unstable compounds. CO₂ has a very high selectivity and is a good solvent for low molecular weight and nonpolar products. In some cases, a small amount of co-solvent can be added to modify the polarity in an effort to increase the effectiveness of this solvent. The quality of the supercritical extract was found to considerably higher on using SFE due to the higher n-alcohol purity, 78.24 % (w/w) compared to organic solvent extraction yield, 22.00 % (w/w) (Lucas et al., 2007).

Accelerated solvent extraction (ASE)

Accelerated solvent extraction (ASE) or pressurized extraction (PLE) uses elevated solvent temperature and pressure in the extraction of sugarcane wax. This improves solvent solubility, diffusion rates for mass transfer into the solvent and lowers viscosity to increase solvent penetrability into the sample matrix. Extraction of sugarcane wax is done using 95% ethanol at two different temperatures (60°C and 100°C) and 2 levels of solvent flushing volume (50% and 100% volume of extraction cell). The volume of obtained extracts from filter cake is adjusted to two folds of extract volume with distilled water and kept in cold chamber (3-5°C) for 5-8 hours in order to solidify crude wax. Then the

Fig 2: Flow chart diagram for the improved process of isolation and recovery of microcrystalline wax from sugarcane press mud of the sugar industry (Source Phukan and Boruah, 1999).
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wax is separated from the extract by filtration as a white insoluble crystal due to its low solubility in ethanol at low temperature. Finally, crude wax is dried at 50°C overnight in the oven. The dried crude wax is stored at -20°C for further use. ASE is considered non-toxic, safe and low environmental impact. One study that dealt with sugarcane wax extraction using various techniques stated that ASE gave higher yield of extracted sugarcane wax than Soxhlet and SFE techniques (Chakhanbordee et al., 2016)

Sugarcane Wax constituents, characteristics and applications

n-Triacontanol

n-Triacontanol is a fatty alcohol of the molecular formula: C₃₀H₆₂O, also known as melissyl alcohol or myricyl alcohol. It is found in plant cuticle waxes and in beeswax. Triacontanol was first isolated in 1933 from alfalfa wax (Medicago sativa L.) (Chibnall et al., 1933). n-Triacontanol can also be extracted by supercritical carbon dioxide from sugarcane crude wax (de Lucas et al., 2007). Sugarcane wax contains 10–15 % n-triacontanol. After the wax has been extracted from press mud, it is esterified and the compound is further purified and fractionally crystallized using suitable solvent. CFTRI has developed a method to make pure n-triacontanol (Sontakke et al., 2018).

Applications

n-Triacontanol is a prominent plant growth promoter. It improves the growth by its effect on photosynthesis, plant metabolism (Naeem et al., 2012) and can upsurge the growth of roots, shoots and flower production (Perveen et al., 2014). It also has anti-inflammatory, anti-ulcer (Srivastava et al., 2009) and antitumor activity (Wang et al., 2015). It is found to reduce salt stress in cultivars of wheat, maize and coriander when used as foliar spray (Asadi and Batool 2017; Perveen et al., 2014 and 2017). Successful field trials have proved its efficacy for high yield in the case of a number of crops like barley, corn, paddy, maize, lettuce, cucumber, etc. Tea Research Institute, UPASI, Coimbatore has made successful field trials with n-triacontanol on tea cultivation. Yield increase to the extent of 20 to 30 % and a reduction in dormant shoots (banji) in tea plantation has been reported. One of the important factors of this compound is its effectiveness at low concentration i.e. 1 to 2 ppm. n-Triacontanol is used at the rate of 2.5 mg to 5 mg per hectare.

Policosanol

“Policosanol” is a term coined by researchers in Cuba to refer to an extract derived from sugar cane wax that was a mixture of long-chain alcohols. The Policosanol (PCO) is a mixture of long-chain aliphatic primary alcohols isolated from sugarcane wax, whose main components include octacosanol (63 %), triacontanol (13 %) and hexacosanol (6 %). It was first developed in 1991 and is presently used in more than 25 countries for cholesterol reduction, especially in Cuba and other parts of Latin America.

Applications

Policosanol (an octacosanol) has been isolated from sugarcane wax which has been found to lower the synthesis of cholesterol in the liver (which is related to the cardiac problems). This compound has been reported to increase physical stamina, repairs damaged nerve cells and even stimulates sex hormones. Policosanol has been reported to reduce platelet aggregation, endothelial damage, foam cell formation and lowering low-density lipoproteins (LDL) and increasing high-density lipoproteins (HDL) (Varady et al., 2003)

Sugarcane Wax Acids (SCWAs)

Sugarcane Wax Acids also known as D-003, is a mixture of high aliphatic primary acids (C₂₄-C₃₆) isolated and purified from sugar cane wax (Saccharum officinarum L.), that have

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**Fig 3:** Structural formula of Triacontanol (TRIA).
antioxidant, cholesterol lowering and anti-platelet properties. Its main component is octacosanoic acid, followed by triacontanoic, dotriacontanoic and tetracosanoic acids. There are also some other acids (hexacosanoic, heptacosanoic, nonacosanoic, hentriacontanoic, triacontanoic, pentatriacontanoic and hexatriacontanoic) as minor components of this mixture. Sugar cane wax acid (SCWA) or D-003 is purified after saponification of sugar cane wax post-extraction with n-hexane, ethanol and acetone.

Applications

D-003 has shown to exhibit cholesterol lowering effects in experimental and clinical studies. D-003 inhibits cholesterol synthesis prior to mevalonate formation by regulating HMGCoA reductase activity (Noa et al., 2004). D-003 also inhibits lipid peroxidation and protein oxidation, its antioxidant effects being superior as compared to those of policosanol (Castaño, et al.; Pérez et al., 2008). Also, D-003 has shown to possess bone protective effects in experimental and clinical studies. It has no toxicity over long term consumption.

Wax

Wax content in filter mud has attracted considerable interest over the years and being recovered for commercial use. It is used as a substitute for imported Carnauba wax. It is an excellent electric insulator. National Chemical Laboratory, Pune, has developed a method for preparing steroids and superior quality of wax from Filter Cake.

Carnauba wax, also called Brazil wax or palm wax, is obtained from the leaves of the carnauba palm (Copernicia prunifera). It is known as queen of waxes and in its pure state, it usually comes in the form of hard yellow-brown flakes. Because of its hypoallergenic and emollient properties as well as its shine, carnauba wax appears as an ingredient in many cosmetic formulas where it is used to thicken lipstick, eyeliner, mascara, eye shadow, foundation, deodorant, various skin care preparations, sun care preparations, etc.

Applications

As early as 1914 sugarcane wax was known to be useful as a partial substitute for beeswax in the stout, dark-colored candles of the Russian Orthodox churches. In 1918 Rindl referred to its use to a limited extent in the polish and electrical industries; for gramophone records; and as a replacement wax in general for carnauba, beeswax and montan (lignite wax extracted from brown coal) wax for edible coating applications. In its refined form it has a light yellowish colour. Due to the high melting point of 75 to 80°C sugarcane wax remains stable even on exposure to direct sunlight.

Oil from sugarcane wax is used for protection against corrosion and crude sugarcane wax is used directly for the manufacture of carbon paper. It is also used in improving the low melting/release properties of toners used in multicolour photographic copiers and printers. For this, in the core material 0.5 to 2 per cent of sugarcane wax (melting point: 60°C) is used. All the components of wax such as hard wax, oil and resin find their use as a plasticizer in tyre industry. Sugarcane refined wax is used as water proofing emulsion for particle board and textile treatment, hot melting glues, removers of a casting from fibreglass moulds and precision casting.

Food

Until the 1960s, sugar cane wax was added to the production of chewing gum as an edible wax. In this process the sugar cane wax acts as elastomer or as plasticizer and consistency regulator (Rindl, 1922). In 1943, J.W. Schiegel and L. Lang were granted a patent to flour donuts with sugar (Schlegal and Lang, 1943). The ground sugar was mixed with 0.4% of sugar cane wax. Thus, the donuts became puffy and water-repellent and kept their fresh appearance longer. Also, chocolates are thinly coated with sugarcane wax. The gloss durability improved, the melting reduced and the packing was relieved as well. In order to keep vegetables and fruits fresh or to make it look fresh emulsions from sugarcane wax mixed with other natural waxes is prepared. Vegetables or fruits are immersed in the emulsions or sprayed with wax emulsions (Warth, 1956).

CONCLUSION

The sugarcane wax and their derived products isolated from the press mud waste have a variety of applications. The potential areas of sugarcane wax include pharmaceutical preparations, agriculture use, confectionary items, processed food, industrial applications and in cosmetics industries. It is realized that there are more avenues to earn profits as there is good demand for these products in the country and also export opportunities are to be explored for fuller utilization of sugarcane crop.

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