Product Development and Processing of Sugarcane Wax from Dissolved Air Flotation (DAF) Mud

Submitted in fulfilment of the requirements of the degree of
Master of Engineering (Chemical) in the Faculty of Engineering
and the Built Environment at the Durban University of
Technology

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2022

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Executive summary

The South African sugar industry is one of the world's leading cost competitive producers of high-quality sugar. However, this industry is currently experiencing a gradual decline due to numerous challenges such as unfavourable climate conditions, economic decline, cheap sugar imports, the Health Promotion Levy ("sugar tax"), and lack of required capital for innovation (SASA, 2022). This crisis threatens tens of thousands of jobs and hundreds of thousands of livelihoods. As a result, this study seeks to contribute to the mitigation of the crisis faced by this industry. Recently, the Illovo's Sezela furfural production plant downstream to the sugar mill was commissioned. This plant produces a waste with a sugarcane wax content of about 30% (R.D Gent, 2012), which is higher than the wax (8.3%) extracted from press mud reported by (Paturau, 1982).

The aims of this study were to assess methods of separating the wax from DAF mud, as well as a method to refine the crude wax. Furthermore, the resulting waxes were to be characterised to allow for comparison with conventional sugarcane wax as well as other plant-based waxes such as carnauba wax. Finally, a preliminary process layout was proposed, and a mass balance of the overall process presented. This serves as a basis for future equipment sizing and costing exercises.

Two methods of producing crude wax from DAF mud were compared in this study, namely a solvent extraction method and the, heating and melting method. The solvent extraction method involved dissolving DAF mud in five different solvents namely, turpentine oil, toluene, butanol, 2-butanone or ethanol. The heating and melting method involved heating the DAF mud to a melting point of crude wax and collecting the resulting wax by decanting. The crude wax yield obtainable via solvent extraction was in a range of 80 - 87.3 %, while the crude wax yield obtained via heating and melting was approximately 56%. Despite the relatively low attainable yield of crude wax via this latter method it was preferred over solvent extraction because eco-friendliness, and being more cost effective, simpler, and faster. The crude wax obtained via this method was a solid at room temperature, whilst the crude wax produced via the solvent extraction method was not in a solid at room temperature. Therefore, crude wax in a solid form is suitable for refined wax production as it can be directly treated with charcoal and a green solvent to obtain refined wax. Crude wax from the heating and melting method was used in the refining step.

Both the crude and refined wax were characterized for their physico-chemical properties. Results show that crude wax produced by heating and melting method has an acid value of 155 ± 2.2 (mg KOH/g wax), saponification value of 227 ± 10 (mg KOH/g wax), % FFA of 78 ± 1, ester value of 72 ± 10 (mg KOH/g wax), Iodine number of 53 ± 5 (g I_2/100 g), unsaponifiable matter (%) of

21.5 ± 2, melting point (°C) of 76 ± 2, density (g/cm^3) of 0.850 – 0.882 (at temperatures between 25 and 80 °C) and refractive index (26°C) of 1.4923.

Crude wax was further treated with activated charcoal and ethanol to obtain refined wax, at a crude wax: ethanol: activated charcoal ratio of 1:04:02. After crude wax was refined, it was then characterised for its physical and chemical properties. Refined wax characterization results showed that it has an acid value of 23 ± 3 (mg KOH/g wax), saponification value of 59 ± 7 (mg KOH/g wax), % FFA of 12 ± 1, ester value of 35 ± 7 (mg KOH/g wax), Iodine number of 44 ± 8 (g I_2/100 g), melting point (°C) of 75 ± 2, density (g/cm^3) of 0.787 – 0.814 (at temperatures between 25 and 80 °C) and refractive index (26°C) of 1.4867.

The GC-MS analysis revealed that, similar to crude wax, refined wax predominantly consists of five main classes of compounds namely, fatty acids, alkanes, alcohols, aldehydes, and esters. Fatty acids contributed about 50% to the total composition for both crude and refined wax samples. Furthermore, both crude and refined wax samples were found to contain policosanol, which can be used to support the evidence of the applicability of sugarcane wax derived from Illovo's Sezela DAF mud in various applications such as pharmaceuticals industry. In preparation for the scale up of the process a process layout was proposed and a process flow sheet for the whole process and subsequent mass balances derived. Mass balances will be useful in equipment sizing and overall project costing which is part of the future work and beyond the scope of this study.

It was concluded that the crude sugarcane wax obtained from DAF mud is quite different from that obtained from filter mud. However, the ester number is in the range given in the literature for filter mud-derived sugarcane wax. The iodine number of the DAF mud-derived raw wax is much higher than that of the conventional filter mud-derived wax. The unsaponifiable matter was lower and the melting point is in the range reported for filter mud-based crude wax. The DAF mud-derived refined wax of this study is compared to different wax fractions derived from conventional filter mud-based waxes. The saponification value lies within the ranges of "hard wax" and "refined wax". The iodine number and the melting point of the refined wax from DAF mud lie within the ranges of "soft wax" and "hard wax", respectively.

Furthermore, the DAF mud-derived refined wax' properties was found to resemble those of candelilla wax rather than carnauba wax, with the acid and saponification values as well as iodine number being in the same ranges. The melting point is 2-4°C higher than that specified for candelilla wax. Future studies should evaluate the economic feasibility of the process by costing the overall project, investing in the equipment to produce a completely eco-friendly refined sugarcane wax.

Preface

The experimental work described in this dissertation was performed at the University of KwaZulu-Natal in the College of Agriculture, Engineering and Science (CAES) at the Department of Chemical Engineering, Howard College Campus, and in the School of Chemistry and Physics, Howard College, Durban, from September 2020 to July 2021, under the supervision of Professors Annegret Stark and Sammy Lewis Kiambi.

This study is the original work by the author and has not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others it is duly acknowledged in the text.

Declaration

I, **Sandile Mtolo**, declare that

(i) The research reported in this thesis, except where otherwise indicated, is my original work.

(ii) This thesis has not been submitted for any degree or examination at any other university.

(iii) This thesis does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.

(iv) This thesis does not contain other persons' writing, unless specifically acknowledged as being sourced from other researchers. Where other written sources have been quoted, then:

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Candidate: Mr S.M Mtolo

Signature: Date:25 November 2021

As supervisors of the aforementioned candidate, we do agree to the submission of this dissertation.

Supervisor: Prof. S.L. Kiambi
Signature:………………………… Date:……………………….

Co-supervisor: Prof Anne Stark
Signature:………………………… Date: 31-03-2023

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I, **Sandile M. Mtolo** and **Prof. Sammy L. Kiambi** (Supervisor) and **Prof. Anne Stark** (Co-supervisor), do declare that in respect of the following dissertation/thesis:

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Acknowledgements

Honour and glory to Omnipotent God for the opportunity and gift of life. He has granted me the opportunity of carrying out this work from start to finish, through all the challenges. He made it possible for this work to become a great success.

I would like to express my gratitude towards my project supervisors. Firstly, I would like to thank Prof. Annegret Stark (co-supervisor) for believing in me and giving me a chance to undertake this project through many challenges faced. I would also like to appreciate her for the unconditional support (academically and financially) that she has given me during my project. I am truly thankful, and I appreciate her efforts and inputs in improving the standard and quality of this work. Moreover, I would like to thank her for availing the SARChI Research Chair / National Research Foundation bursary to pursue my master's degree and cover the cost incurred. I could have never made it without her; I am out of words to express my gratitude towards her. Secondly, I would also like to thank my supervisor Prof. L. Sammy Kiambi for his continuous support, availability, his inputs in making sure this work becomes a success. Furthermore, I would like to thank Charles Kruger (Downstream Optimisation Manager at Illovo Sugar Africa) and Illovo's support staff for providing us with their waste biomass (DAF mud) and allowing us to use it for experimental purposes of this thesis. I would also like to give special thanks to Mr Warwick Thompson for providing technical support.

Special thanks to Dr Edwin Mombeshora for his ideas and guidance in the beginning of this project. Moreover, I would like to thank Mr Edward Marondedze for his very useful insight and help regarding this thesis. I would also like to extend my gratitude to the UKZN Chemical Engineering technicians (Ms Xoli Hadebe, Mrs Thobe Mfokeng) for their patience, hard work and continuous support in assisting with the GC-MS and technical instrumentation. I would also like to thank the Durban University of Technology school of Engineering and Built Environment for allowing me to use their computer labs. I thankfully acknowledge the support received from the workshop technicians, my fellow colleagues in our research group.

The financial assistance of the National Research Foundation (NRF) towards this research is hereby acknowledged (under grant no. 115465, SMRI/NRF SARChI Research Chair for Sugarcane Biorefining). Opinions expressed and conclusions arrived at, are those of the author and are not necessarily to be attributed to the NRF. Lastly, I would also thank TUFM, my family and friends for amazing support from the start to the finish of this project. I thank you.

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List of abbreviations

Abbreviation	**Explanation**
AV	Acid value
CAGR	Compound Annual growth rate
CED	Cumulative energy demand
CEPCI	Chemical Engineering Plant Cost Index
CW	Crude Wax
DAF	Dissolved Air Flotation
EHS	Environmental , Health and Safety
FFA	Free Fatty Acid
FTWEP	Fischer Tropsch Wax Expansion Project
GDP	Gross Domestic Product
HPL	Health Promotion Levy
IV/IN	Iodine number/number
KOH	Potassium Hydroxide
Mp	Melting Point
PCE	Total Purchase Cost of major Equipment
PPC	Total Physical Plant Cost
RW	Refined Wax
SACU	South African Custom Union
SASA	South African Sugar Association
SD	Standard deviations
SFE	Supercritical Fluid Extraction
SV	Saponification value
SW	Sugarcane Wax
US	Unsaponifiables
USDA	United States Department of Agriculture

List of symbols

Symbol	Description	Units
$\mathbf{T_0}$	Outlet temperature	K
$\mathbf{m_{content}^{in}}$	Moisture content in	kg/kg solids
$\mathbf{m_{content}^{in}}$	Moisture content out	kg/kg solids
$\mathbf{C_p}$	Specific heat capacity	kJ/kg-K
$\dot{\mathbf{m}}$	Mass	kg
$\mathbf{F13w}$	Mass flowrate of wax in F13	kg/s
$\mathbf{x6w}$	Mass fraction of wax in F6	dimensionless
$\boldsymbol{\rho}$	Density	kg/m^3
$\boldsymbol{\mu}$	Viscosity	Pa.s

1 Introduction

1.1 Background

Sugarcane wax extraction began over centuries ago in the United States by a scientist named Avequin (Ray, 2003), and other countries also followed later with this sugarcane wax process. However, most of the industries ceased production due to high competition from fossil-based waxes that were dominant at the time. As a result, the extraction of wax from sugarcane was deemed uneconomical. Nowadays, there is a renewed interest in sugarcane wax globally, especially for the European markets, with more interest coming from the cosmetic and pharmaceutical industries (Forecast ltd, 2020).

The production of sugarcane wax from a sugar production waste stream has commenced in South Africa. Illovo's Sezela's furfural downstream plant produces a unique type of wax. The uniqueness of this wax comes from a unique feedstock, Dissolved Air Flotation (DAF) mud which is a waste stream derived from a furfural production process that only exists in one sugar mill in the world. The wax extraction strategies from Illovo's DAF mud and full industrial utilization of the associated by-products from sugar cane are still an active research area that have the potential to reduce the current market price of the wax. This unique wax from a unique stream is what inspired this study. Before developing a process scheme, the wax that can be obtained from DAF mud had to be characterised, and preliminary economic considerations of running the process conducted. It is thought that sugarcane wax can serve high-value markets and satisfy their product demand in the future. Findings in this study are based on the experimental data obtained from validated laboratory experiments. The information gathered was then used to scale up the process to perform mass balances on the overall process. The mass balance may be used in future studies to evaluate the economic process parameters to determine the overall feasibility of the proposed process, which is beyond the scope of this study.

1.2 Significance of the study

The South African sugar industry is currently facing a gradual decline. This industry has since struggled to reach its maximum production peak of 2002/3. This is due to several factors, such as the economic recession, unfavourable climatic conditions, the decline of small-scale sugarcane farming, economic decline, outdated technology, and lack of required capital (Hattingh, 2019). It is reported that annual sugar production in South Africa has declined by nearly 25%, from 2.75 million to 2.1 million tons per annum, over the past 20 years (Ngcobo, 2020). The number of sugarcane farmers has declined by 60% during this period, and sugar industry related jobs are estimated to have reduced by 45% (Ngcobo, 2020).The crisis faced by the South African sugar industry threatens tens of thousands of jobs and hundreds of thousands of livelihoods. This research seeks to develop a new product contributing to the South African Sugarcane Value Chain Master Plan to 2030 (SASA, 2022) to help mitigate the challenges faced by the sugar industry of South Africa.

This will be achieved by the valorisation of Illovo's Sezela furfural downstream plant waste stream. This stream contains DAF mud which can be used as a biomass from which sugarcane wax (SW) can be extracted. SW has a wide range of applications in different industries such as the pharmaceutical industry, cosmetic industry, lubricants, coatings and adhesives amongst others (Singh, 1964). This study focuses on the future application of SW in high-value markets such as the pharmaceutical industry and cosmetics, as a substitute for carnauba wax.

Carnauba wax is currently dominating the wax market. The drawbacks of this wax are that it is produced in only one place in the world, i.e., from the leaves of the Brazilian carnauba palm tree. Moreover, it is seasonal thus, making it more expensive. This research project seeks to develop a unique method to obtain and process SW from a unique biomass DAF mud. Findings in this research will then allow companies to deduce whether SW can be used as an alternative to carnauba wax.

Furthermore, findings in this study will directly benefit the currently declining South Africa's sugar industry by creating a diversified revenue streams for sugar producers, and in turn create new job opportunities while contributing to sustainable growth. Moreover, creation of the diversified and globally competitive transformed sugarcane-based value chains will benefit SASA (South African Sugar Association), and help to contribute to South Africa's economic and social development, society, and environment.

1.3 Scope of the project

In the recent years, there has been increasing demand for non-fossil-based products. It is predicted that this demand will continue to increase in the foreseeable future (MarketsandMarkets, 2019). In view of this situation, the present study seeks to find an alternative to the currently existing non-fossil market dominating waxes such as carnauba wax. This study was focused on developing a method of attaining and processing sugarcane wax from DAF mud. The produced SW was subsequently characterized for its physical and chemical properties. SW properties were compared to carnauba and other plant based wax properties to deduce whether SW can be used an alternative. Physical and chemical properties studied in SW include: moisture content, acid values, saponification values, iodine numbers, unsaponifiable matter, density, refractive index, melting point and its chemical composition. The physicochemical properties of SW were heavily dependent on the operating conditions under which the wax was extracted and purified. Thus, operating conditions were optimized in order to produce competitively high-quality SW.

It is important to note that findings of this study were specifically based on DAF mud from Illovo's Sezela downstream plant. Thus, the scope of the study was limited to South Africa and more specifically to DAF mud of Illovo Sezela.

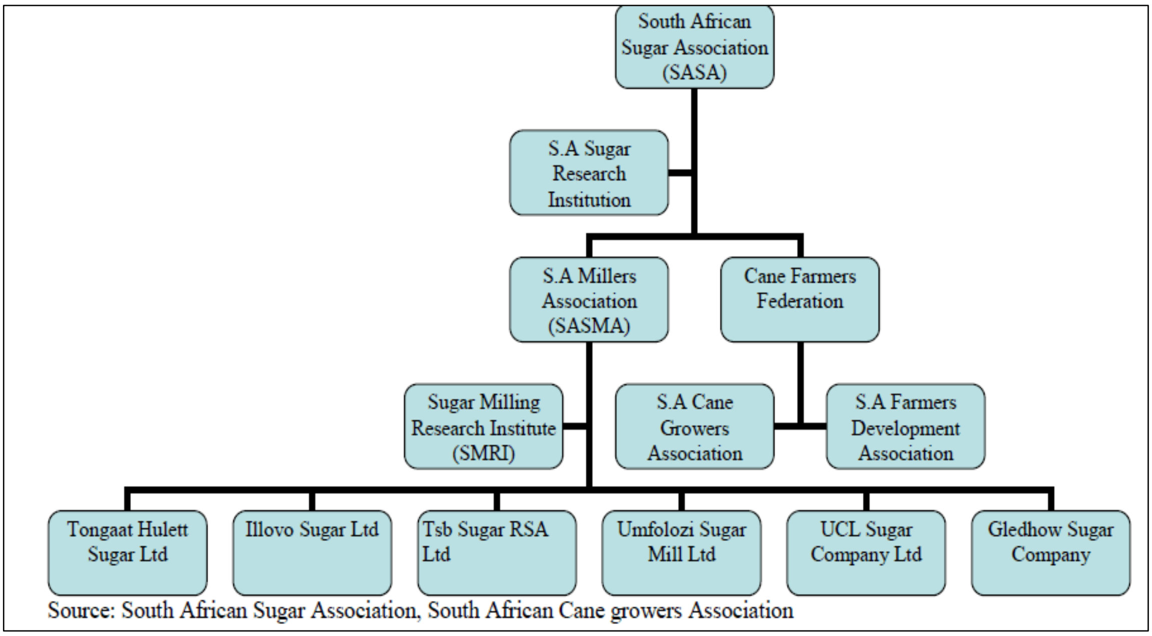
2 Literature review

2.1 General introduction

According to the South African Sugar Association (SASA), the sugar industry of South Africa is one of the world's leading cost-competitive producers of high-quality sugar. The contribution of this industry to the country's gross domestic product (GDP) is undeniable and it makes an enormous contribution to employment, especially in rural areas, sustainable development, and the national economy. It is a diverse industry having agricultural activities that deal with the cultivation and processing of sugarcane. The industry also manufactures a range of by- products including molasses, syrups, raw and refined sugar and specialized sugars (SASA, 2022).

2.2 The South African sugar industry

The South African sugar industry consists of six sugar milling companies; name, Tongaat Hulett Sugar Ltd, Illovo Sugar Ltd, Tsb Sugar RSA Ltd, Gledhow Sugar Company, Umfolozi Sugar Mill Ltd, and UCL Company Ltd. There is 14 sugar mills in operation for sugar production (USDA, 2022). Every season, the industry produces an average estimate of 2.2 million tons of sugar. Approximately, 60% of the sugar produced is marketed in the South African Customs Union (SACU). The remaining portion is exported to other countries in Africa, Asia, and the Middle East (SASA, 2022)/ The structure of the South African Sugar industry is shown in Figure 2- 1: The structure of the South African sugar industr.



Source: South African Sugar Association, South African Cane growers Association

Figure 2- 1: The structure of the South African sugar industry (SASA, 2022).

Sugarcane in South Africa is grown in two provinces, namely Kwa-Zulu Natal and Mpumalanga. Large-scale farmers supply 75% of sugarcane, while the small-scale farmers and sugar estates supply a portion of the remaining 25%. There are close to 21,500 sugarcane growers in South Africa that are registered, and there are 20,200 small scale growers and approximately 1,300 large scale growers (USDA, 2022).

This sharp division in numbers indicates the vitality of this industry from a socio-economic perspective. Sugarcane cultivating season is approximately 8-9 months in South Africa. Sugar is cut from the harvesting sites and transported to the mill for milling during the harvesting season. Diversity is key in terms of product and production output in today's highly integrated sugar mill operations. The main objective of a sugar mill is to produce the main product, sugar. Apart from sugar, the mills produce a range of other value-added products such as ethyl alcohol, furfural, bagasse, and molasses (SASA, 2022). The sugar produced (white and brown) is used locally for consumption and the other is sent to the export market. The figure below depicts the statistical figures for South African sugar cane production over two decades (USDA, 2022).

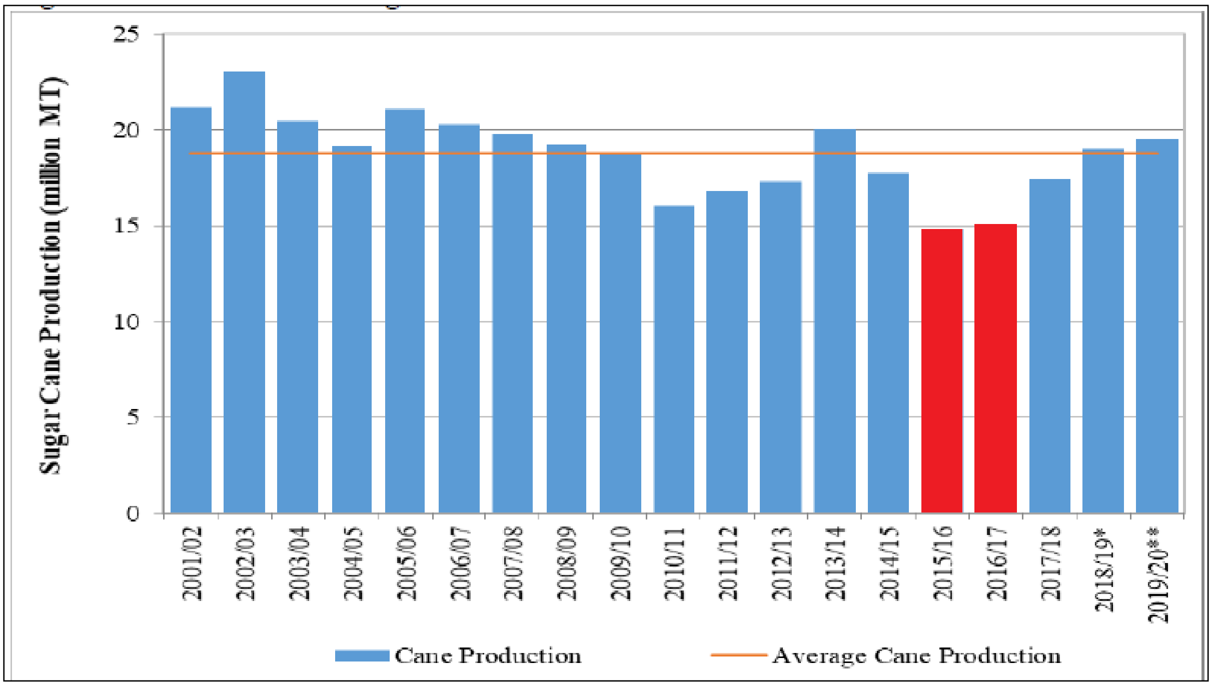


Figure 2- 2: South African sugarcane production over the years (SASA, 2022).

South African sugar industry is currently experiencing a gradual decline due to numerous challenges. The decline in sugar production between the 2008/9 seasons is attributed to the economic recession. The drastic decrease in the production from 2014/15 to 2016/17 is attributed to several factors, including unfavourable climatic conditions, economic decline, obsolete technology, and lack of required capital (SASA, 2022). This industry has since struggled to reach its maximum peak of 2002/3.

The decline of small-scale sugarcane farmers has been remarkable over the past years. The number of small-scale farmers has declined from around 50 000 in the early 2000s to just below 20 000 as of recently (Hattingh, 2019). This has a detrimental effect on several rural households as they no longer have a source of income from farming sugarcane and consequently lost their jobs. The South African Farmers Development Association (SAFDA) cited challenges faced by all farmers and attributed the decline of their numbers to various reasons. These reasons include low sugar prices, lack of funding, little or no access to finance and, high input costs such as fertilizers (Hattingh, 2019). The local sugar industry is also challenged by the Health Promotion Levy (HPL) on sugar beverages. The health promotion levy has reduced sales in the local market to an estimated 250 000 tons in local annual sugar consumption (Hattingh, 2019). It is predicted that the sugar demand will drop significantly, as drink bottlers have reformulated their products to avoid the sugar tax using artificial and chemical sweeteners (S. Mchunu, 2019). It has been reported that sectors that are not affected by the sugar tax have voluntarily started reducing sugar on their products and replacing it with artificial sweeteners. This has a potential to create a huge competition on the use and demand of artificial sweeteners in South Africa (USDA, 2022). Figure 2-3 illustrates South Africa's imports and exports figures for sweeteners.

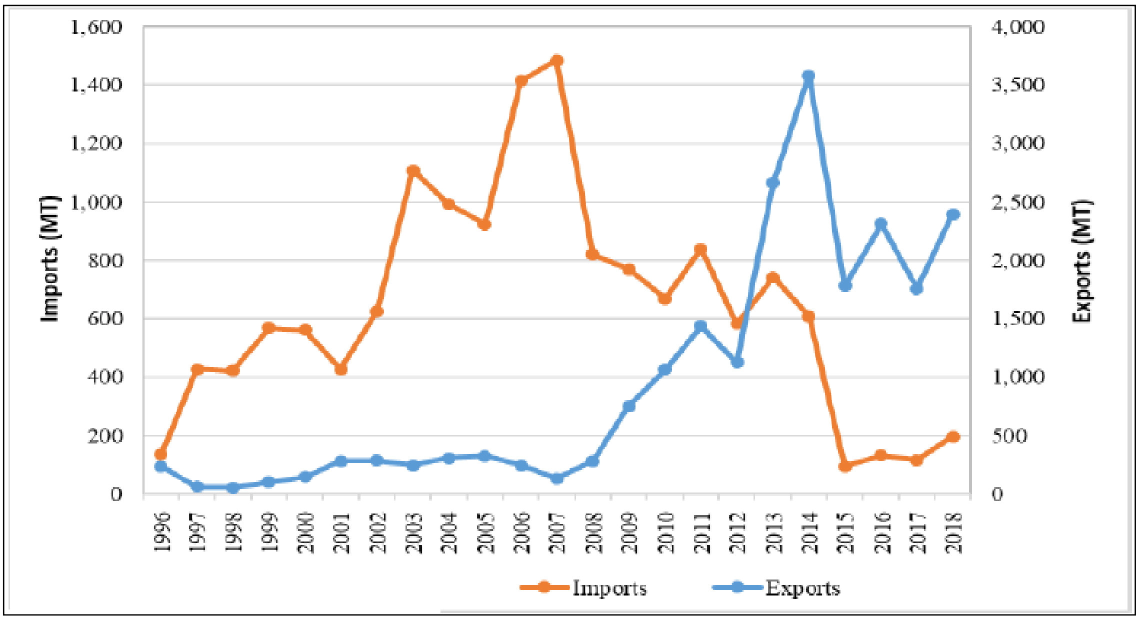


Figure 2- 3: Imports and exports of sweetening substances to and from South Africa (SASA, 2022).

The figure above illustrates that South Africa is currently a net exporter. The South African sugar market and the industry is therefore strongly affected by the world sugar price. The world sugar price is quoted in US dollars, which fluctuates regularly. More importantly, the world sugar price is distorted, due to massive governmental subsidies. For example, Brazil, the number one producer of sugar in the world, receives an annual subsidy of an estimated 2.5 billion USD. This gives Brazil a massive advantage over its competitors and the prices are in turn distorted (Hayes, 2013). Brazil's subsidization has assisted the country to gain approximately 50% market share of global sugar exports. Subsidized countries produce sugar at a very low cost, which then allows market prices to fall below the actual market price, resulting in distortion. The negative effects of subsidization are experienced by other sugar-producing countries with little or no subsidization, e.g., South Africa. Subsidization results in cheaper import costs and this negatively affect the South African sugar industry as it encourages the import of cheaper foreign sugar in South Africa. Most companies that rely on huge quantities of sugar e.g., Cadbury, Coca-Cola, etc.

hence opt to importing sugar rather than purchasing it locally. This is caused by the insufficient level of import tariffs on sugar imposed by the government.

Climate is another factor that impacts sugarcane production. Sugarcane requires sunny, warm and frost-free weather areas for it to thrive. Mostly, it grows best in a tropical or subtropical climate with at least 60 mm of annual rainfall. The optimum growth temperature is between 20°C to 35° C with optimal growth temperature for germination cutting ranges from 32° C to 38° C. Sugarcane also grows best in a high humidity environment, and in places with high exposure to sunlight. The major cane growing provinces in South Africa, Kwa-Zulu Natal (KZN) and Mpumalanga (MP) fall under subtropical regions which are more susceptible to drought. About 95% of sugarcane production in KZN relies on rain with few irrigated areas. MP on the other hand relies 100% on irrigation systems for sugar production (USDA, 2022). The scarcity of water has caused a decline in cane growth rate and caused a poor seasonal performance between the 2016/17 seasons, as shown in figure 2- 2.

In summary, the sugarcane industry is currently facing adversity due to all the factors mentioned in this section. These factors have negatively affected the sustainability and survival of both the local and international sugarcane market, thus, new product development is imperative to help revive this industry, especially within South Africa where product beneficiation is a potential recovery mechanism. In an attempt to come up with new strategies, this thesis investigates a potential process of producing sugarcane wax from a unique stream of Illovo's Sezela furfural downstream effluent. The use of this stream as a feedstock does not affect sugar production output and the operation of the mill, as this is a waste stream. Sugarcane wax attained from this stream has a commercial potential for the South African sugar industry and global market to substitute the supply of the currently existing and market dominant carnauba wax.

2.3 Sugarcane wax

Sugar cane wax refers to a whitish to yellowish coating on the surface of the sugar cane, that has historically been extracted and separated from press mud during the crushing and processing of the cane juice. Its main applications are in cosmetics and the pharmaceutical industry to name a few. Therefore, it can be considered as an alternative to expensive carnauba wax (Inarkar & Lele, 2012).

2.3.1 The botany of sugarcane

The sugarcane plant consists of the following main parts; the stalk, leaf, and root system. Figure 2- 4: Section view through cane stalk apex shows the sugarcane stalk parts labelled.

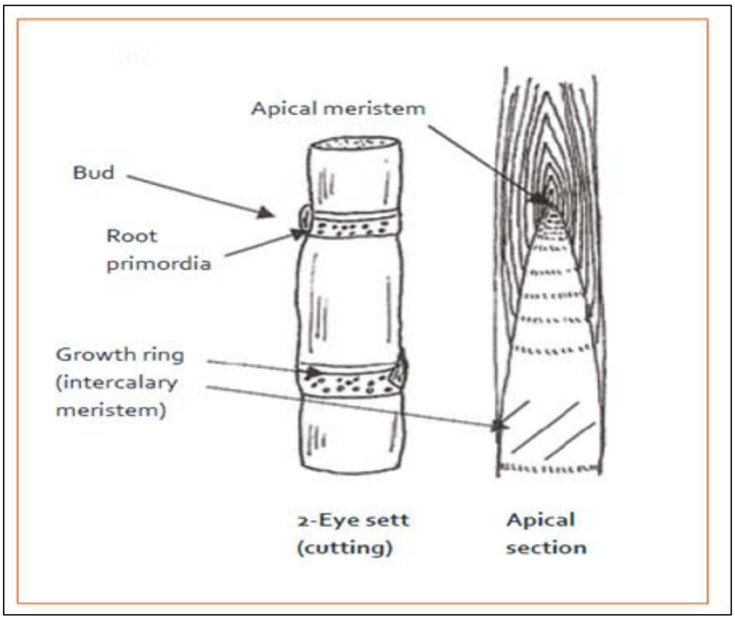


Figure 2- 4: Section view through cane stalk apex (Australia Limited & of Agriculture and Fisheries, 2016).

Stem cuttings having buds normally spread sugarcane. On germination, the bud produces a primary stalk. Each stalk consists of nodes, with a bud, one or more rows of root buds, and a growth ring, separated by internodal storage tissue. Internodes are the sugar-storage organs of the plant. They differ in length from less than 10 mm to about over 300 mm according to age and growing conditions. Sugarcane stalks normally reach up to 3 m in height in the normal growing season (Australia Limited & of Agriculture and Fisheries, 2016). SW is mainly found in cane nodes as a whitish coating that serves to protect the plant against water loss during evapotranspiration (Paturau, 1982).

2.3.2 Historical background of sugarcane wax

Sugarcane has been grown as a commercial crop for several centuries. However, sugarcane wax (whitish deposit found in sugarcane stalk) did not draw the attention of chemists until the year 1840 (Ray, 2003). During this year, a chemist by the name of Avequin of New Orleans in the United States isolated and purified sugarcane wax and named it "cerosin" from cera meaning wax (Ray, 2003). Removal of the whitish deposit found on the cane stalk was achieved by scrapping it off.

S. Wijnberg patented the wax extraction method from press mud in 1909, and this became the primary method of extracting cane wax from press mud (Paturau, 1982). Press mud, also sometimes referred to as filter cake or filter mud is of no value and a by- product formed during sugar production. It contains an appreciable amount of wax that settles in it during the clarification stage in sugar production (Ray, 2003).

The first commercial plant for wax extraction from filter cake was established at Durban, Natal in South Africa in the year 1916 (Ray, 2003). By 1924, this plant was producing around 6 000 tons of cane wax per annum (Paturau, 1982). Wax produced by this plant was used for the production of candles for the Russian Orthodox Church. Already in 1928, this plant was forced to shut down due to various difficulties encountered, the Russian revolution, and the associated war against the church (Karocki Media, 2020). In the same year, 1928, Java was also producing sugarcane wax from press mud. Crude cane wax produced in Java was exported to Greece for the manufacture of candles. However, the recovery of sugarcane wax in Java was also discontinued due to the devaluation of Greek currency (S.C (Ray, 2003).

Three other plants were producing wax from press mud, one in Australia, and two in Cuba. The Australian plant faced economic challenges and lost its viability in 1960 (Ray, 2003).. The reason for most plants to shutdown was due to high input costs associated with wax extraction from press filter cake (Paturau, 1982) , low recovery of hard-refined wax compared to carnauba wax, low solvent recovery, and low demand for SW at that time, thus, carnauba wax was a preference for many industries (Ray, 2003). In order to obtain the so-called “hard wax”, also known as “refined wax”, which has comparable properties to carnauba wax, fats and oils need to be removed from the crude sugarcane wax. This was proving very costly, and crude and refined wax qualities produced from press mud were not meeting the specifications for commercial use (Ray, 2003).

In Cuba, commercial production of SW started in the 1940s. There was a pilot wax refining plant in operation since 1982 producing refined wax approximately 15-20 tonnes/year (Ray, 2003). A new plant with a capacity of 500 tonnes/year of refined sugarcane wax was scheduled to begin operation in 1990, but faced economic challenges (Ray, 2003). India also established its wax processing plant in 1947 and this plant was shut down due to economic failure in 1980 (Ray, 2003).

As mentioned earlier, SW was initially produced for candles in church. However, with the latest technologies and research conducted thus far, it has been reported that sugarcane wax has numerous applications in sectors like pharmaceuticals (policosanol to be discussed later), cosmetic industry, industrial and food applications (Singh, 1964). Even though there exist numerous patented information on sugarcane wax, chemical properties and various methods of extraction, there is limited information available on the SW market.

2.3.3 Composition of sugarcane wax

SW is the term used to refer to the lipids contained in sugarcane. Within these lipids, are hard (waxy) lipids and soft (fatty) lipids. Both these lipids combined form about 0.18% of the cane weight. The composition of the wax material varies for each cane stalk depending on the geographic origin of the sugarcane cultivar and on the sugarcane maturity level (Weerawatanakorn et al., 2016) .The concentration of crude wax from press mud from four Indian sugar mills was between 6.20-11.00% (Saleh-e-In et al., 2012). The crude wax content extracted from press mud from Jamaica and Barbados was about 11.3% and 14.7% on dry mud basis, respectively (Ray, 2003).

Crude wax is made of soft wax and hard wax and is normally obtained by extraction from press mud. The crude wax contains approximately 30-45% soft wax (fatty lipids). Soft wax consists of glycerides of fatty acids (oleic, palmitic, stearic acid), resin acids, sterols of phytosterol class, chlorophyll, and pectins. The hard wax (waxy lipids) contributes toward the other 55-70% of the crude wax and is of commercial interest within the natural wax market. Crude wax contains about 58% unsaponifiables, which in turn contains 20% sterols (80% β-sitosterol and 20% stigmasterol) (Paturau, 1982). In research conducted in the 1970s, it was reported that SW from filter cake contained 38.5% sitosterol, 37.1% stigmasterol, and 24.4% compesterol (Mitchell, 1979). Table 2.1 depicts the literature values of soft wax (fatty lipids) and hard wax (waxy lipids) obtained by different authors. It is important to note that the properties of sugar cane wax may vary depending on the geographical origin and other factors (Ray, 2003).

Table 2 - 1: The sugarcane wax properties from various literature

Wax fraction	**SV (mg KOH/g)**	**AV (mg KOH/g)**	**IN (g/100g)**	**Mp. (°C)**	**US%**	**reference**
Crude wax	60 -135	15 - 23	26 - 31.5	66 -78	43.7	(Ray, 2003)
Crude wax	102.59 - 103.01	26.9-27.7	6.72-6.82			(Saleh-e-In et al., 2012)
Hard wax	65-77	23-28	13-29	79		(Paturau, 1982)
Soft wax	144-156	24-26	49-85		23-59	(Paturau, 1982)
Soft wax	188.50	31.50			33.5	(Mitchell, 1979)
Refined wax	65 -77	23 - 28	13 - 29	79		(Ray, 2003)

SV: saponification value, AV: acid value, IV: iodine number, US: unsaponifiables, Mp.: melting point

Therefore, from Table 2 – 1, it can be concluded that the physio-chemical properties of cane wax are highly dependent on the extraction method employed and the origin of cane wax biomass. Table 2 - 2 depicts the density and refractive index values of sugarcane wax obtained from different literature.

Table 2 - 2: Density and refractive index literature values for crude wax

Wax fraction	Density(g/cm^3)	Refractive index	reference
Crude wax	0.961 – 0.979	1.510	(CAMEO, 2020)
Crude wax	0.80-0.85		(DEUREX, 2021)
Crude wax		1.5028 – 1.5033	(Saleh-e-In et al., 2012)

2.3.4 Factors influencing the content of sugarcane wax in press mud

The quantity of SW present in press mud depends upon various factors. These factors could be the climate under which the sugar cane is grown, farmed, and harvested, the method and efficiency of clarification during mud settling, the variability of sugarcane ground, water temperature during maceration i.e., whether cane is burned or not, and the severity of conditions employed during the milling process. The severity of conditions employed might be a major controlling factor for the wax content, since it would control the amount of wax extracted in the juice, and so the amount left in the press mud (Ray, 2003). These factors also influence the content of SW in DAF mud as they do in press mud.

2.3.5 Benefits of sugarcane wax

SW is one of the most sustainable waxes as it is produced entirely from sugar cane, which is a purely natural and renewable natural product. Due to this, SW is perfectly suitable for sustainable formulations since the wax is biodegradable and compostable (DEUREX, 2021). The conventional biomass feedstock (press mud) from which SW originates is produced as a by- product of the sugar production process. Likewise, the biomass feedstock of this thesis is DAF mud, which is a waste stream from the reaction of bagasse with steam through hydrolysis to form furfural. Thus, in both instances, there are no other further natural or artificial resources used in the production of sugarcane wax. The production of SW may significantly increase the added value of sugar cane plants. Furthermore, there are less seasonal fluctuations in availability of SW compared to carnauba wax.

2.3.6 Sugarcane wax production and refining

Different methods have been reported for the production of SW using press mud as a conventional feedstock.

2.3.6.1 Press mud as a conventional wax feedstock

A simplified sugar process flow diagram for a typical sugar mill is depicted in figure 2 -5. As seen in the diagram, during the crushing stage, the juice is extracted from sugarcane and the fibre that remains is sent to the exit stream in the form of bagasse. The bagasse (by-product) is fed to the boilers for steam and electricity generation. Once the juice is extracted, it is sent to a clarifier where solids separation occurs under the influence of density. During this stage, the heavier (fibrous material) is removed as clarifier/press mud. The lights (juice) are sent to the evaporator, then the crystallizer, and finally to the drier to form the desired sugar product.

Press mud has been considered as a low economic value by-product that is normally used by farmers in the cane fields as a natural fertilizer (Diaz, 2016). However, from this mud, about 40% of the overall wax content of sugarcane has been recovered as crude wax after solvent extraction, and the remainder exits the process with the bagasse.

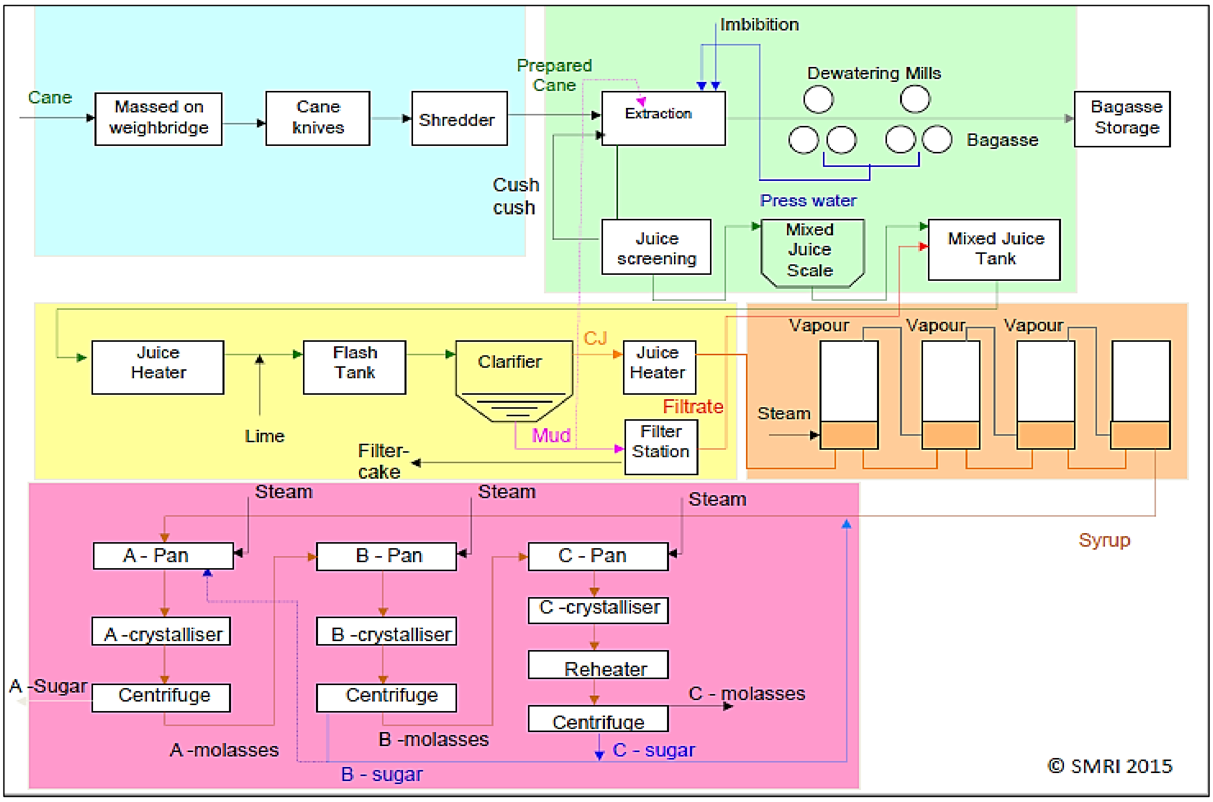


Figure 2- 5: Flow diagram of a typical sugar mill (Sugar Milling Research Institute (SMRI), 2015)

Press mud can be either drum dried or air-dried. However, the latter method is preferred since it is more cost effective. Air-dried press mud contains between 6-15% crude wax (Paturau, 1982), (Saleh-e-In, 2012), (Ray, 2003), thus, the wax content of press mud is higher than that of sugarcane. In former times, the obtained crude wax was processed further for fractionation into dark hard wax (70%) and soft wax (30%). The amount of refined SW is dependent on the initial amount of crude wax present.

The basic composition of press mud and sugarcane varies greatly due to on such factors mentioned in section 2.3.4. This leads to the variation of the chemical composition of press mud in different sugar mills. The final content of refined wax from press mud is normally low, averaging at 4.4% (Saleh-e-In, 2012).

2.3.6.2 Conventional solvents used to extract sugarcane wax from press mud

According to literature, two methods have been employed in the extraction of crude wax from press mud. The first method makes use of two solvents, the first solvent being a hydrocarbon such as benzene, hexane etc. The second step involves the extraction of fatty substances contained in the crude wax by a selective solvent such as acetone, followed by the chilling and filtering of the slurry. The main function of the second solvent is to facilitate re-dissolution, precipitation, and filtration of the hard wax by chilling. The entrainment that consists of soft wax is separated by solvent evaporation (Paturau, 1982). The second method makes use of a single solvent, such as petroleum solvents or spirits. These petroleum spirits help in removing the soft wax in the cold. The obtained hard wax is further refined by de-ashing using hydrochloric acid (HCl). In this process, the crude hard wax is melted in water followed by the addition of HCl. HCl is added until the wax is separated from the water as it floats at the top. The refined hard wax is then washed several times with water, and then cooled until it hardens. After the cooling process, it is heated until all the water in it is evaporated (Paturau, 1982). A bleaching or purification stage is normally added to the process based on the application the wax will be used for. Conventional extraction solvents such as hexane are now prohibited in the manufacture of waxes for applications such as cosmetics, food, and pharmaceuticals. According to (Yousefi et al., 2017), hexane has toxic effects on both humans and animals-

Wilder invented a method for the purification of wax both from fatty and resinous matter in 1945. This method consisted of melting the crude wax at 85-90°C. The molten crude wax was poured into a fat solvent maintained at 35°C with agitation. The hard wax was filtered after 15 minutes of further stirring. To improve the pouring qualities of the molten crude wax, aromatic solvents such as benzene, toluene or xylene were added (Ray, 2003).

Swanson further purified wax that was already free from soft fatty matter with a fat solvent (ether, methyl ethyl ketone, acetone, hexane or heptane) and heated the mixture (100°C) under pressure (200 mmHg), hence dissolving parts of the wax and leaving a resinous hard wax matter behind. The hard-wax fraction that instantaneously formed because of precipitation was removed by filtration (Ray, 2003).

Goepfert devised a method whereby a pure wax may be directly obtained from filter press mud using only one solvent. In this invention, crude wax from press mud was extracted with hot isopropyl acetate. Then, on cooling the filtered solution, hard wax that crystallized and was separated from the soft fatty materials remaining in solution by filtration. However, the drawbacks to this method is that the solvent used is an ester, which is susceptible to hydrolysis during extraction.

Since all the previous mentioned methods have drawbacks, this thesis will investigate an alternative method to produce a solvent-free crude SW and eco-friendly refined SW using a non- toxic green solvent.

2.3.6.3 Conventional refining of crude wax

Crude SW is not entirely desirable in its form due to the presence of impurities in it. Thus, it is refined to remove impurities and to give wax a lighter colour. Refining of crude wax was traditionally achieved by de-ashing with HCl (Paturau, 1982). This is necessary because crude wax contained lime used in the sugarcane juice clarification step. In this process, crude wax was melted in water followed by the addition of acid until wax rises to the surface resulting in a sharp division of wax layer and liquid layer. After phase separation, the wax was washed numerous times in boiling water, and then cooled until it hardens. Water was drained off and the residue dried. The molten crude wax was then contacted with solvents such as acetone, methyl ethyl ketone, ethyl alcohol, petroleum ether etc., in which the fatty acids are readily soluble and in which the wax is almost insoluble (Paturau, 1982). Refined wax was then bleached with the help of sulfuric acid. During the bleaching process, air was blown through the bleaching liquor to keep the temperatures within the safe limits and to facilitate bleaching by agitation (Paturau, 1982).

2.4 Proposed alternative unique feedstock (DAF mud) to produce sugarcane wax

Recently, it was discovered that at Illovo's Sezela furfural production plant downstream, a waste stream is available, which is rich in wax. This stream is generated by a Dissolved Air Flotation (DAF) unit. This stream is economically attractive as its wax content is as high as 30% ((R.D Gent, 2012), while the conventional feedstock press mud wax content is between 6 and 15% (Paturau, 1982), (Saleh-e-In et al., 2012), (Ray, 2003). The economic potential of this stream comes from its uniqueness and the fact that it has never been valorised. Figure 2-5 depicts the process flow diagram for Illovo's Sezela mill furfural production plant.

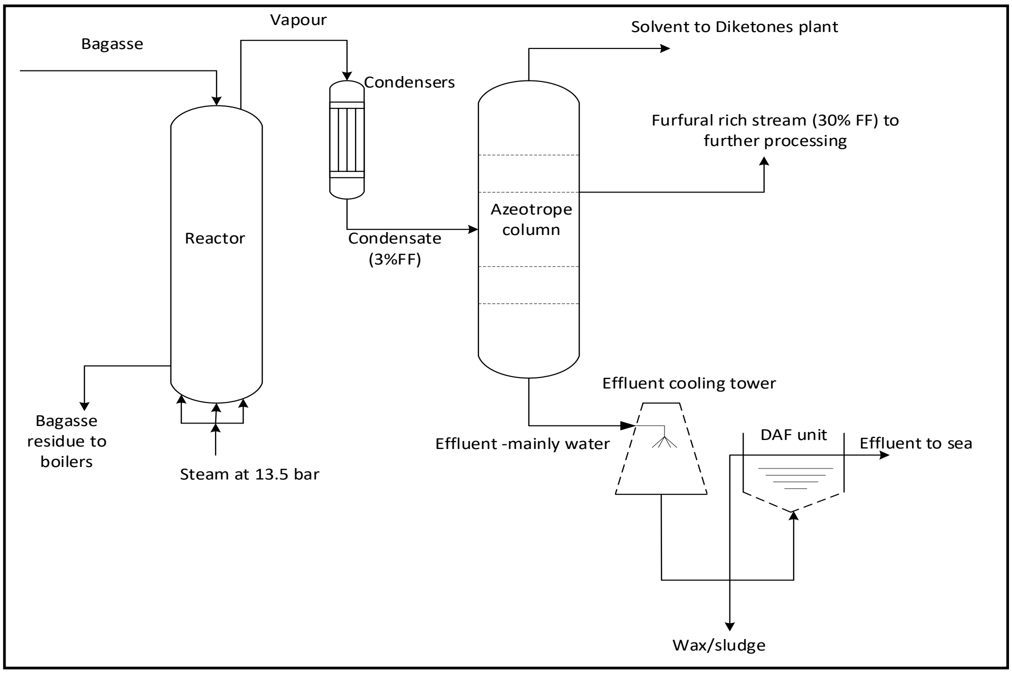


Figure 2- 6: Process resulting in DAF mud waste from Illovo Sezela, Pty Ltd (Gent, 2012).

In the furfural process, bagasse is reacted at high pressures and temperatures with steam, turning hemicellulose contained in bagasse to furfural. The remaining bagasse residue is sent to the boilers to fuel the furfural plant and the sugar mill. The vapour is condensed and sent to an azeotrope column where the furfural-rich lights are removed and the heavies such as waste water and fine particulate matter exits the bottom of the column to the cooling tower. The cooling tower effluent is then sent to the Dissolved Air Flotation unit where solids and wax are separated from the water. The wax /sludge stream shown in the diagram is normally sent back to the fields as a low-grade fertilizer, or to landfills at the cost of the sugar mill. In this project DAF mud will be used to produce sugarcane wax.

2.5 Solvent selection considerations for sustainable processes

Since the process of obtaining wax from DAF mud will entail the use of a solvent, some consideration is given in the following to the selection of sustainable solvents. The 12 Principles of Green Chemistry and Engineering require the selected solvent to at least satisfy the following principles (Hargreaves, 2008):

- Use less hazardous chemical substances.
- The use of safer or innocuous auxiliary agents.
- Reduce energy demands.
- Use renewable raw materials; choose reagents that will reduce the possibility of accidents.
- These principles can be translated to three factors are used to define a sustainable solvent, namely Environmental, Health, and Safety (EHS), the Cumulative Energy Demand (CED) (Byrne et al., 2016); and source and availability of a solvent.
- EHS considers factors that affect human health and safety as well as factors that affect the environment. These factors are listed below:
- Safety - Flammability, Boiling Point, Flash Point, Conductivity.
- Health – Toxicity, Skin Effects, Carcinogenic and Mutagenic Effects, Vapour Pressure.
- Environment - Volatility, Odour, Global Warming Potential (GWP).

The CED considers the energy that will be involved in the production of the solvent and the energy that will be recovered or required during disposal or recovery, respectively. Solvent source and availability aspects consider whether the solvent is available from a renewable resource, and even more beneficially, from sugarcane. Examples include bio-ethanol, bio- methanol, and bio-acetic acid and their derivative esters etc.

Solvent selection guides have been introduced in the chemical industries that use a ‘traffic light’ method to easily identify suitable solvents. Various categories are indicated, using green (good), yellow (okay), and red (bad). Pfizer (Alfonsi et al., 2008) created the first recognized solvent selection guide using the simple ‘traffic light’ approach. Sanofi (Prat et al., 2013) and GalaxoSmithKline (GSK) (Henderson et al., 2011) developed separate guides using both the traffic light method in addition to scores from one to ten to remove ambiguity, to describe the effects of solvents.

The Pfizer guide is more sensitive towards Health and Safety, while the GSK guide examines the environmental factors. The GSK guide is more informative and included more factors during its development, thus, it is normally selected as the most suitable guide to make decisions on selecting a sustainable solvent. The factors considered take into account both EHS and CED, as well as flammability and explosion, reactivity and life cycle. Table 2-3 demonstrates the GSK solvent selection table on the example of solvents used in this thesis.

Table 2 - 3: GSK solvent selection guide 2009

Classification	Solvent	Cas number	Melting point °C	Boiling Point °C	Waste	Environmental	Health	Flammability & Explosion	Reactivity/ Stability	Life Cycle score	Legislation Flag	EHS Red Flag
Alcohol	1-Butanol	71-36-3	-89	118	5	7	5	8	9	5		
	Ethanol	64-17-5	-114	78	3	8	8	6	9	9		
Ketone	2-butanone	78-93-3	-87	80	3	7	8	4	8	3		
Aromatic	Toluene	108-88-3	-95	111	6	3	4	4	10	7	3	
Hydrocarbon	Turpentine oil	8006-64-2	-55	154	3	2	4	3	9	7		

Table 2 - 4: Colour grading scale

*Colour purity (Scale 1 to 5) [1: Less pure (less white), 5: Purer (whiter)

Colour	▨	▨	▨	▨	
Number scale	1	2	3	4	5

2.6 Characterization methods of sugarcane wax

In quality control, several parameters such as acid value (free fatty acids present as a result of fatty ester hydrolysis), saponification and ester values, iodine number (degree of unsaturation), unsaponifiable matter content, melting point, refractive index and density are key parameters of interest as they determine the shelf-life quality and hence the economic value of waxes, as well as their application areas.

2.6.1 Acid value and percentage free fatty acid (%FFA)

Definition: The acid value is defined as the number of milligrams of potassium hydroxide required to neutralize the free acid in 1 g of fat or oil (Spitz, 2016). It measures the free fatty acids (FFA) present in the fat or oil (Spitz, 2016).

Principle: Acid value is a common technique used to determine the amount of carboxylic acid in the fat or oil sample. An increased amount of free fatty acids in a sample of fat indicates hydrolysis of triglycerides. In edible fats and oils, an increase in the amount of FFA indicates inadequate processing and storage conditions (Spitz, 2016). As waxes rancidify, triglycerides are converted into fatty acids and glycerol, resulting in the increase in acid value. For the sugarcane waxes, this is a useful and quick method to determine the amount of acids and compare it with the existing commercial waxes such as carnauba wax.

$$\mathrm{RCOOH} + \mathrm{KOH} \longrightarrow \mathrm{RCOO^{-}\,K^{+}} + \mathrm{H_2O}$$

After the titrations of the wax sample against standardized KOH, the following equation can be used to determine the acid value:

$$\text{Acid value} = \frac{V_{\mathrm{KOH\ x\ N\ x\ MM_{KOH}}}}{\mathrm{W}} \tag{2.1}$$

Where: VKOH = Volume of 0.1 M standardized KOH solution used (ml); N = Normality of KOH solution (from standardization with KHP); W = Weight of fat sample (g); MMKOH = Molar mass of KOH.

The acid value can be used to estimate the amount of free fatty acids in a sample by assuming that the average molar mass of the free acids is equivalent to that of oleic acid as approximation for the great number of different carboxylic acid possibly present in the sample. The free fatty acid (%) content is expressed as oleic acid equivalent, as shown in equation

$$\mathrm{FFA(\%)} = \frac{Titre(mL) \times N \times MWoleic\ acid}{10 \times \mathrm{W}} \tag{2.2}$$

Where: Titre = volume of KOH (cm3) dispensed during titration; N = Normality of KOH; MWOleic acid = Molecular weight of oleic acid; W = weight of the sample

Challenges associated with acid value determination: The method used to determine acid value in the wax is based on a titration of the sample in ethanol using phenolphthalein as indicator. However, shortcomings of this and similar methods are the use of organic solvents (volume and toxicity), the heat needed to facilitate the reaction, solubility of the wax in solvent, and the possibility of error to detect the color change of the indicator when analysing colored samples. There are some non-titration methods designed to overcome these disadvantages e.g. the GC-MS method. Nevertheless, the titration method remains the most preferred since it does not require the use of expensive equipment (Libretext, 2020).

2.6.2 Saponification value

Definition: The saponification value is the number of milligrams of KOH required to neutralize the fatty acids resulting from the complete hydrolysis and saponification of 1g of fat (Spitz, 2016).

Principle: The saponification value indirectly indicates the character of the fats and oils present in the fat or wax. Triglycerides or (fatty acid esters) undergo hydrolysis to produce glycerol and soap (potassium salts of fatty acids) on refluxing with alkali. At the same time, all free carboxylic acids present in the wax are neutralised. Hence, it is used to determine the sum of free and glycerol-bound fatty acid constituents of a wax.

Reaction:

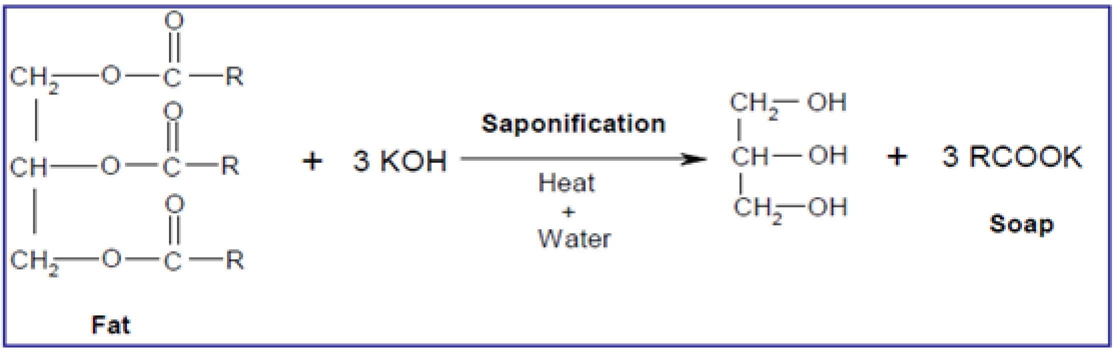


Figure 2- 7: Saponification value reaction scheme (Spitz, 2016).

The difference between the blank and the test reading gives the number of millilitres of KOH required to saponify 1.0 g fat or wax.

$$\text{Saponification value} = \frac{V_{(b-w)HCl} \text{ x } N \text{ x } MM_{KOH}}{W} \tag{2.3}$$

Where: Vw = Titre of HCl for a fat sample (ml); Vb = Titre of HCl for blank (ml); N = Normality factor of KOH (determined by standardized KOH solution with KHP); W = Weight of sample (g)

Challenges associated with saponification value determination: The saponification value can be affected mainly by the effect of three parameters, i.e. ethanolic KOH content, reaction temperature, and reaction time. These should be carefully monitored and explored for the optimum saponification. Furthermore, shortcomings of determining the saponification value can also occur during titration which uses organic solvents, and also the possibility of error in detecting the color change when analyzing colored samples. The saponification value can also be estimated using gas chromatography data on fatty acid composition.

2.6.3 Ester value

The ester value is defined as the number of milligrams of potassium hydroxide required to saponify the esters present in 1 g of the substance (Patterson, 2015). It is determined as the difference between the saponification and acid values and is expressed in milligrams of potassium hydroxide (Patterson, 2015).

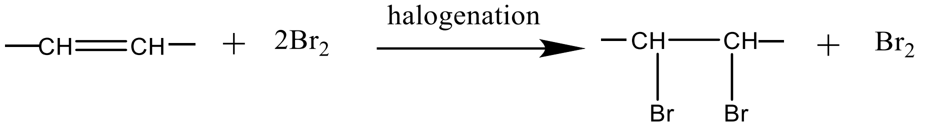
$$\text{Ester Value} = \text{Saponification value} - \text{Acid value} \qquad (2.4)$$

2.6.4 Iodine number

Definition: The iodine number is defined as the number of grams of iodine absorbed per 100 g of fat or wax (Spitz, 2016). It is used to determine the degree of unsaturation in the fat sample, and used as a measure of the unsaturated bonds present in the fat, i.e. a low iodine number indicates few unsaturated bonds (Spitz, 2016).

Principle and reaction: A known amount of bromine solution is added to a fixed weight of a fat or wax sample.

Principle and reaction: A known amount of bromine solution is added to a fixed weight of a fat or wax sample.



$$-CH=CH- + 2Br_2 \xrightarrow{\text{halogenation}} -CH(Br)-CH(Br)- + Br_2$$

The excess bromine not used up by the unsaturated bonds liberates an equal number of moles of iodine from potassium iodide.

$$Br_2 + KI \longrightarrow 2KBr + I_2$$

The liberated iodine is then titrated with a standard solution of sodium thiosulfate.

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

The reaction mixture is kept in the dark and the titration is carried out as quickly as possible since halogens are oxidized in the light.

$$Iodine\ number = \frac{Nx(B-T)\ x\ 12.69}{w} \qquad (2.5)$$

Where: B = Volume of thiosulfate used for sample (mL); T = Volume of thiosulfate used for the blank (mL); W = Weight of the fat sample (g); N = Normality of sodium thiosulfate (0.1N standardized by potassium iodate solution).

The sample titration (T) gives of the amount of iodine left in the solution after halogenation process. The titration of a blank (B) gives a measure of the total amount of halogenating reagent present initially. A subtraction of the values (B) from (T) indicates the quantity of reagent utilized in the halogenation.

Challenges associated with iodine number determination: In determining the iodine numbers, one of the major limitations is that halogens does not react stoichiometrically with conjugated double bonds (Spitz, 2016). The titration technique shortfalls are also applicable in this method.

2.6.5 Unsaponifiable matter

The unsaponifiable matter refers to the substances that are neither fats, oils (triglycerides) nor carboxylic acids. After hydrolysis and saponification of all fats and free fatty acids, the unsaponifiable matter can be extracted with diethyl ether from the aqueous solution. It constitutes of mainly of hydrocarbons, sterols and aliphatic alcohols of high molecular mass (F. Yildiz, 2016). Hence, unsaponifiable matter consists of the non-hydrolysable components of the fatty substance (Expascience, 2020). There are several key factors that determine the quality and composition of unsaponifiables, such as the origin of the biomass, storage and treatment of the biomass prior to fat extraction, method used in the extraction and refining process, and how the unsaponifiables are separated and purified (Expascience, 2020).

The equation to calculate the percentage unsaponifiable matter is:

$$\%\ \text{Unsponifable matter} = \left(\frac{\text{final constant mass (g)}}{\text{initial mass weighed (g)}}\right) * 100\% \qquad (2.6)$$

Challenges associated with the determination of unsaponifiable matter: In determining the unsaponifiable matter, parameters such as temperature of the water bath, refluxing time, concentration of KOH/ethanol solution, and oven temperature can cause shortfalls in determining the unsaponifiable matter.

2.6.6 Melting point

The melting point of a substance refers to temperature at which the solid and liquid forms of a pure substance can exist in equilibrium (Gordon, 2003). The melting point is measured with a designated apparatus depending on the sample being studied. Normally the apparatus is calibrated and checked to ensure that it meets the certain tolerances, for example; a STUART SMP11 is calibrated to make sure it meets the following tolerances: 60°C+/-0.5°C; 100°C+/- 0.5°C; 200°C+/-1.0°C. A check on the accuracy of the temperature readings is performed by measuring the melting point of a certified reference standard (CSR). CSRs are chemicals of high purity that have been tested and certified by standards laboratories. A list of suitable melting point CRSs are provided by The World Health Organisation (WHO) (Cole-Parmer, 2021).In general, the apparatus is calibrated by measuring the melting point of the CSRs. If the measured value deviates from the nominal value of the CSR, the apparatus is serviced by a qualified technician, otherwise, the melting point measurement commences.

Shortfalls associated with melting point measurements: If the sample is not solid, melting point analysis becomes impossible using standard melting point determination instruments. The melting point depends on pressure and usually reported at standard pressure. However, for qualitative identification analysis, there are now more specific and accurate analyses that exist, although they are typically much more expensive (Spitz, 2016)

2.6.7 Density

Density of a material refers to the mass of a unit volume of a substance (American Chemical Society, 2021). The mass of atoms, their size, and how they are arranged determine the density of a substance (American Chemical Society, 2021).

$$\rho\ (density)\left(\frac{g}{cm^3}\right) = \frac{mass\ (g)}{volume(cm^3)} \qquad (2.7)$$

There are various techniques in existence for measuring the density of waxes. Some density measurement techniques rely on the measurement of either the mass or volume of the fluid, while others rely on measurements of the mass of a fixed volume of the material (American Chemical Society, 2021). The density of a liquid is measured using a device such as a pycnometer or density cup. The attained density measurement depends on a reference or standard working fluid, such as water, using an analytical balance. Pycnometers are used for measuring and comparing densities of liquids, while density cups are used for pastes and solids.

To get the unknown density of the fluid, one needs to first measure the weight of the empty density cup. The density cup is then weighed when filled with the reference fluid (water) of known density. It also weighed again when filled with the tested fluid of unknown density. These weights are used to work out the density of the fluid. A calibrated oven is usually used to achieve temperature control in the case of determining density as a function of temperature. In this study, densities of SW (both crude wax and refined wax) are determined through use of metal density cups.

Shortfalls associated with density measurements: Density measurements using pycnometers may be affected by the GC temperature, inaccuracy in sample or density cup weighing and sample heating time. Monitoring of these parameters is essential to avoid experimental errors.

2.6.8 Refractometry

The refractive index is defined as the velocity of light in vacuum relative to the velocity of light in a given medium. It measures the bending of a ray of light when passing from one medium into another. The refractive index is also equal to the velocity of light of a given wavelength in empty space divided by its velocity in a substance (American Chemical Society, 2021).

The wavelength of the light wave changes as it crosses the phase boundary. During the process, the wave is deformed based on the angle of incidence and refraction. Snell's Law (2.8) best describes the relationship between the angle of incidence and angle of refraction

$$\frac{\sin\alpha}{\sin\beta} = \frac{n_1}{n_2} \tag{2.8}$$

Where α and β are the angles of incidence and refraction, respectively, while $n1$ and $n2$ are the refractive indices of the given media.

In this study, the optical properties of the SW were determined through measurement of refractive index, and the refractive index data is used for quality control purposes in characterizing the wax.

Shortfalls associated with refractometry measurements: the refractive index is affected by two parameters, temperature and the speed of light. Refractive index values are usually determined at standard room temperature. A higher temperature means a light will travel faster in the medium since the liquid becomes less dense and less viscous. This results in a smaller value for the refractive index due to a smaller ratio and vice versa. The relationship between the refractive index varies and the wavelength is directly proportional or linear because different wavelengths interfere to different extents with the atoms of the medium. Monochromatic light is normally used to prevent dispersion of light into different colours (UTSC, 2021).

2.6.9 Gas Chromatography-Mass Spectroscopy (GC-MS) analysis

GC-MS is used to study liquid, gaseous or solid samples. It consists of a gas chromatograph, where the sample is vaporized into the gas phase and separated into its various components using a capillary column coated with a static phase. An inert gas such nitrogen or helium is used to propel the components. Each compound is eluded from the column at a different time based on its boiling point and polarity, and this results in the separation of components of the mixture. The final steps of the process are ion detection and analysis, with fragmented ions appearing as a function of their mass-to-charge ratios. Using extensive commercially available libraries of mass spectra such as NIST, unknown compounds and target analytes can be identified and quantified (Thermofisher, 2020).

2.7 Commercial waxes

Waxes are chemical substances made up primarily of long aliphatic alkyl chains, though aromatic compounds can sometimes be found. There are numerous commercial waxes in the market serving different and specific purposes.

2.7.1 Background

The term wax originates from the Anglo –Saxon word "weax" meaning beeswax. Wax consists of a layer of fatty components and they are normally found on the surface of a plant leaves, insect body, and animal skins (Tinto et al., 2017). They are hydrophobic substances of medium chain length that are solid at room temperature (Banerjee, 2014). Waxes consist of lipids (sterols, fatty acids, and glycerides) and long-chained molecule alkanes. In general, they have various functional groups such as ketones, aldehydes, fatty acids, amides, aromatics, alcohols, and unsaturated bonds (Banerjee, 2014).

Waxes can be categorized as natural waxes (including fossil-based natural waxes, such as plant and animal waxes), and synthetic waxes (such as Fischer-Tropsch wax). Natural waxes are normally obtained from their feedstock using extraction or distillation methods, while synthetic waxes are normally obtained by polymerization of molecules (Banerjee, 2014). Natural waxes can be classified as either renewable or non-renewable. Renewable waxes can be modified chemically by methods such as hydrogenation and re-esterification (Tinto et al., 2017). The non-renewable (fossil-based) waxes are the mineral waxes that are obtained from shale oil, brown coal, peat deposits, or lignite. These waxes may be crude or refined, e.g. petroleum, and montan (Tinto et al., 2017). Some waxes may be chemically treated to make the wax suitable for a particular application.

2.7.2 Application of waxes

Waxes possess a special property that makes them applicable to a wide range of industries. They find most of their applications due to their texturing, oiling, gelling, and viscosity-increasing properties (Tinto et al., 2017). Their application has increased in the past, and this comes with intensive research and discovery of new compounds that are present in different waxes. For example, sugarcane and other plant waxes have been found to contain policosanol, a generic term for long chain alcohols with 24-34 carbon atoms, which is applicable in the pharmaceutical industry. Other wax applications include: oil binding in shoe polish and lipsticks, release performance in bakery and plastics, lubrication in pencils, metalworking, and pharma matrices, water repellent in industrial coatings, dispersion in mascara and toners, scratch resistance in car polish and inks, plasticizing in hot-melts and chewing gum and binding properties in ceramic and cosmetic powders. Some of the properties of commercial waxes are listed in table 2 - 5.

Table 2 - 5: Properties of some available commercial waxes (Tinto et al., 2017).

Wax	**Source**	**Iodine number**	**Saponification Number**	**Acid value**	**Melting point (˚C)**	**Ref. Index**	**Spec. Gravity**	**Use**
Plant waxes								
Bayberry wax	Myrica cerifera	2.9-3.9	205-217	3.5	40-49	1.436	0.977-0.995	soap making, candles, natural insect repellent
Candelilla wax	Euphorbia antisyphilitica; Pedilanthus pavinia	14-37	35-86	12-20	67-71	1.456	0.950-0.990	leather dressing, polishes, sealing wax, paper sizing, metal casting
Carnauba wax	Corypha cerifera	7.2-13.5	75-95	0.4- 9.7	83-86	1.467-1.472	0.990-0.999	floor waxes, polishes, metal casting, printing inks, carbon paper
Ceresin wax	purified ozocerite				61-78		0.91-0.92	candles, sizing, floor polish, waterproofing; leather dressing.
Japan wax	Rhus verniciflua; Rhus succedanea	4.5-12.6	206.5-237.5	6-209	53		0.97-0.99	candles, floor waxes, crayons, adhesive, metal casting
Chinese Rhux wax	Extracted from the fruit peel of Rhus Verniciflua Stokes	5-18	205-225	<30	48-55			Cosmetic industry, Foodstuff industry, and pencil making industry
Rice wax	Extracted from rice bran oil		80-95	<10	78-82			Brightening agent, Cosmetic industry, Foodstuff industry
Animal wax								
Lanolin (wool wax)	Ovis aries	15-47	80-127	5.6-22.0	36-43	1.478-1.482	0.932-0.946	emollient, leather dressing, rust preventative
Beeswax	*Apis mellifica*	6-11	84-103	16-24	63-70	1.440-1.449	0.955-0.966	candles, polishes, adhesives, plasticizer, paint binder (encaustic)
Spermaceti	*Physeter macrocephalus*	3.0-4.4	120-136	2.0-5.2	40-50	1.4330-1.440	0.905-0.945	ointments, candles, soap, surgery, leather dressing
Synthetic wax								
Fischer-Tropsch wax	*Synthesis gas*	Varies	Varies	Varies	Varies	Varies	Varies	Waterproofing, inking, bitumen modification, polishes and textile, polymer processing
Poly-Olefin Waxes	*produced by polymerizing the olefin ethylene.*	Varies	Varies	Varies	Varies	Varies	Varies	used for blow moulded or rotationally moulded components
Fossil based natural waxes								
Montan wax	*Lignin and peat*	16-20	74-127	30-70	76-130	1.010-1.030		polishes, phonograph records, adhesives, sizing, candles, carbon paper
Paraffin wax	Petroleum	0	0	0	47-75	1.442-1.448	0.880-0.925	floor wax, waterproofing textiles and paper, leather dressing, rust preventative
Microcrystalline	Petroleum	0	0	0	60-93	1.441	0.915-0.941	polish producing clear, non-sticky finish.

2.7.3 Industrial wax market

2.7.3.1 Global markets

In 2018, the industrial wax market was valued at 9.8 billion USD and is projected to reach 14.3 billion USD by 2026, registering a compound annual growth rate (CAGR) of 4.8% during 2018-2026 (MarketsandMarkets, 2019). The increasing applications of industrial waxes and growing demand from candle application are the main drivers of the market. Figure 2-7 illustrates the industrial wax market share by application in 2019.

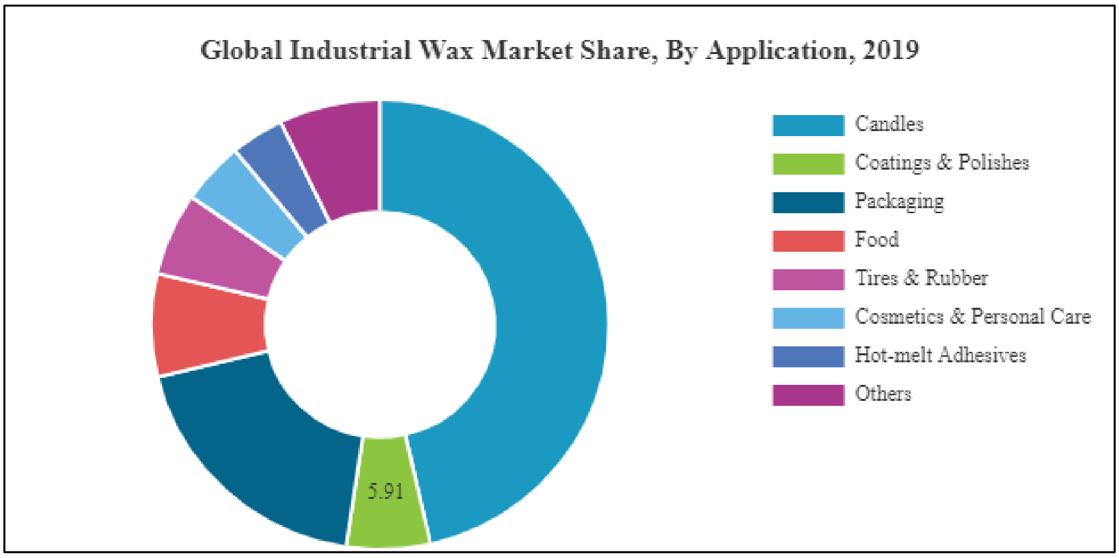


Figure 2- 8: Industrial wax market share by application 2019 (MarketsandMarkets, 2019).

Fossil-based waxes dominate industrial wax applications. The waxes are mostly applicable in candle making, coating of commercial products, and packaging. Moreover, these waxes are considered extensively safe and thus, they are widely used in the cosmetic industry and are derived from various processes of crude oil refining. On the other hand, petroleum wax is widely used as an ingredient for polishes including; floors, furniture, and cars due to its high gloss characteristics (MarketsandMarkets, 2019). The tire and rubber industries that is growing at a high rate are expected to drive the demand for industrial waxes. This is because of their wide applicability to tires and rubbers to protect them from cracking, and ultraviolet light. In 2017, Asia Pacific accounted for the largest share in the industrial wax market. China, Japan, and India are the countries that were leading the market in candle making, packaging, coating & polishes, as well as tire and rubbers. The current monetary value of a carnauba wax is $7.41 /kg (Rajpal, 2023). This is costly as the price excludes shipping and other import associated costs. Thus, it is imperative to look for other alternatives such as SW, and optimize the production process to become competitive with current benchmarks.

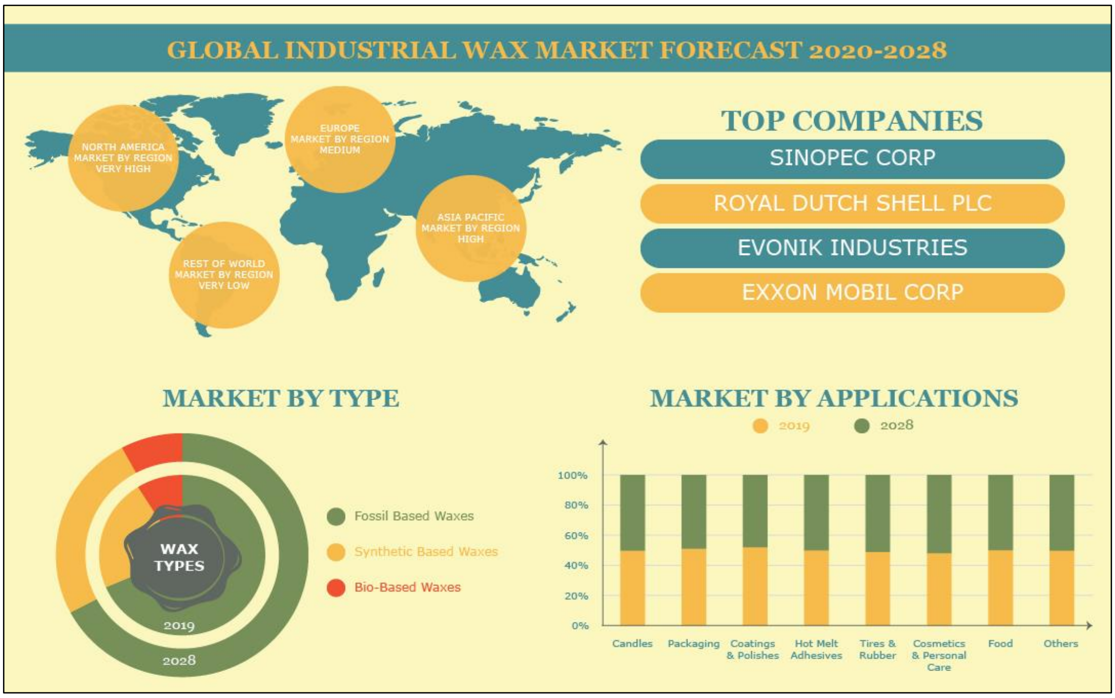


Figure 2- 9: Global industrial wax market forecast, 2020-2028 (Inkwood Research, 2021)

The market is largely driven by the rising demand for applications such as candles, tire & rubber, and coating & polishes. Candle application accounts the largest share in the industry and it is predicted to account for a larger share even in the future. The cosmetic industry is also growing and is expected to be a huge market driver in the market.

The supply of fossil-based paraffin waxes has been shrinking (MarketsandMarkets, 2019). This is attributed to base oil manufacturers shifting their focus from waxes to comparatively more profitable base oil options. The shrinking supply of fossil-based waxes is expected to be the restraining factor for the wax market, it is also expected to increase the gap between supply and demand (MarketsandMarkets, 2019). This will create a growing demand for non-conventional waxes such as sugarcane wax, which is a bio-based wax. Bio-based waxes are most favoured in food packaging, cosmetics, and personal care applications. The growth of the industrial wax market is also influenced by the growing cosmetic industry.

In 2017, global demand for industrial wax was 5,329.8 kilotons and is expected to be growing at a CAGR of 3.8% between 2018-2026. Fossil-based waxes account for around 81% of wax demand, most of which is for paraffin waxes (MarketsandMarkets, 2019). The total supply of paraffin waxes has been impacted by the recent shutdowns of group I base oil plants, and capacity reductions. Balancing supply and demand is one of the challenges in the industrial wax market

2.7.3.2 Key players

The leading players in the industrial wax market are Sinopec (China), Royal Dutch Shell (Netherlands), Exxon Mobil (US), Petroleo Brasileiro (Brazil), Sasol (South Africa), International Group (Canada), HCl (China), The Blayson Group (UK), Numaligarh Refinery (India) and Oil Co. Lukoil PJSC (Russia). These players adopted developments, in terms of new product launches, and agreements as one of their strategies for their key growth from 2013 to 2016. These strategies have assisted them to increase their wax producing capacity and a wide range of customers (MarketsandMarkets, 2019).

2.7.3.3 Recent developments

Sasol inaugurated the full completion of its Fischer Tropsch Wax Expansion Project (FTWEP) in March 2017. This expansion is one of several major capital investments the company has made in South Africa. Phase-2 began operation in March 2017. In January 2016, Sinopec commenced constructing its R&D centre in Saudi Arabia. The centre is expected to focus on technology research, serve as a technology promotion centre as well as a senior personnel training centre of Sinopec (MarketsandMarkets, 2019) .Sugarcane wax market trends

According to the market data forecast of September 2020, the global sugarcane wax market was calculated to be $ 42.8 million in 2018 and is predicted to gather a CAGR of 3.87% to arrive at $ 55.7 million in 2025 (Forecast ltd, 2020).The cane wax industry expansion is driven by the presence of the established pharmaceutical industry, the increase of the aged population, and an increase in the number of people with cardiac-related diseases.

According to the Market data forecast, sugarcane wax production is difficult and economically intensive. Thus, economic production seems to be feasible in the main growing countries such as Brazil, India, China, Thailand, Pakistan, and Mexico (Forecast ltd, 2020). The escalated consumption of confectionery gums and chocolate goods in the developing economies is predicted to drive the call for sugarcane wax during the forecast period. Socio-economic factors such as rapid urbanization, population expansion, and rising per capita disposable income stimulate industry expansion in developing countries. The dominant players in the global sugarcane wax market are Deurex AG (Germany), Cerax (South Africa), Origen Chemicals (South Africa), Huzhou Shengtao Biotech LLC (China), and Godavari Biorefineries (India) (MarketsandMarkets, 2019).

2.8 Mass balance of the proposed process for future economic evaluation

For every plant designed, an economic evaluation is of importance as it assists in deciding on the financial feasibility of the plant. A project is deemed economically feasible when it is proving to be more profitable than other competing projects (Felder, 2005). The following steps are followed to accomplish the economic evaluation of the process:

- Preparation of a process flow diagram
- Calculation of mass and energy balances
- Sizing of major equipment
- Estimation of the capital cost
- Estimating of production cost
- Estimation of the return on investments (ROI)

However, sizing of major equipment, estimation of the capital cost, estimating of production cost and estimation of the return on investments (ROI) were beyond the scope of this study, and may be included in the future work.

Calculation of mass balances

Material and energy balances are based on the first law of thermodynamics known as the conservation law. This law states that, energy can neither be created nor destroyed, only altered in form. It requires that the materials entering any process must either accumulate or leave the process (Felder, 2005).

Input +source = output +sink+ accumulation (Felder, 2005). (2.9)

Balances of particular entities are made around a bounded region called a system. A key factor in the effective formulation of material and energy balances is a proper notation for equipment and streams.

2.9 Conclusions of the literature review and research questions

The literature review has shown that there is a market demand for renewable waxes. Sugarcane wax is one such example, and it is available from a local sugar mill, where it currently accumulates as waste. However, the DAF mud derived wax has undergone the severe conditions of the furfural production, where bagasse is treated with steam at high temperatures and pressures. Three research questions hence arise:

1. Is it possible to produce sugarcane wax from DAF mud of Illovo's Sezela furfural downstream waste treatment? And if so:
2. What are the characteristics of this wax, when compared to conventional sugarcane wax or alternatives, such as carnauba or candelilla wax?

The literature review has also shown that plant-derived waxes contain commercially important compounds such as policosanol. The third research question is hence:

3. Is there any evidence to suggest the presence of policosanol in DAF mud derived sugarcane wax?

2.10 Aims and objectives

The aims of this study were to assess methods of separating the wax from DAF mud, as well as a method to refine the resulting crude wax. Furthermore, the resulting waxes were characterised to allow for comparison with conventional sugarcane wax as well as other plant-based waxes. Finally, mass balances were performed on the overall process for future preliminary project costing exercise to be conducted.

To meet the aims of the project, the following set of objectives had to be addressed,

- Development of a suitable method for producing SW from DAF mud, using a laboratory-based approach. Two approaches were to be taken into account, namely one employing a solvent extraction, and the other one using a combination of heating, melting and decantation.
- Development of a suitable method for the production of refined wax.
- Investigation of the physical and chemical properties (acid value, saponification and ester value, iodine number, density, refractive index, melting point and unsaponifiable matter) of the obtained waxes and comparison to existing commercial waxes, in particular carnauba wax.

- Preparation of a process flowsheet for a proposed process, undertaking mass balances on the overall process as part of a preliminary economic assessment of newly developed process.

2.11 Outline of the dissertation

The introduction and background relating to the current study have been described in Chapter 1. The literature review including the detailed project's aims and objectives has been discussed in Chapter 2. Chapter 3 provides a concise description of the experimental procedures that were undertaken while exploring and investigating the objectives. In Chapter 4, the results that were derived from the various experiments conducted are presented and discussed. Finally, Chapter 5 contains the conclusions, recommendations and future outlook relating to the current study.

3 Experimental

The experimental methodology followed for the attainment of SW from DAF mud is described in this chapter. The handling and characterization of the DAF mud followed specific and well-established protocols to accurately establish certain properties of interest such as acid values, saponification values and ester values amongst others. Density, refractive index, and viscosity of SW were also determined, along with the composition of SW by means of GC-MS

3.1 Materials

Crude DAF mud was collected from Illovo Sugar (Pty) Ltd T/A Sezela Sugar Mill, SA. The samples were stored in 20 L plastic buckets at room temperature. Prior to storage, the samples were drained off any excess water. This was done to thoroughly remove all the visibly excess water that's not part of the actual crude DAF mud. The commercial chemicals used in this study were used as received from the respective suppliers. Table 3-1 shows a comprehensive list of all the chemicals used in the study.

Table 3 - 1: List of chemicals used

Name	**Formula**	**Supplier**	**%Purity/Concentration**
Water (Deionized)	H_2O	UKZN Chemical Engineering Lab	
Turpentine oil	$C_{10}H_{16}$	Honeywell	99.98
Butan-1-ol	$C_4H_{10}O$	Merck	97.00
Ethanol (absolute)	C_2H_5OH	Honeywell	99.98
2-butanone	C_4H_8O	Merck	99.98
Toluene	C_7H_8	Merck	>97.00
Potassium hydrogen phthalate (KHP)	$C_8H_5KO_4$	Merck	99.5
potassium hydroxide pellets	KOH	Merck	>85.00
Hydrochloric acid solutions	HCl	Merck	37.00
Phenolphthalein indicator	$C_{20}H_{14}O_4$	Merck	0.5 g L^{-1}
Activated charcoal	C	Merck / NT Laboratory Supplies	100
Starch powder	$(C_6H_{10}O_5)_n$	Merck	99.80
Sodium thiosulphate pentahydrate solution	$Na_2S_2O_3 \cdot 5H_2O$	Merck	98.00
Chloroform	$CHCl_3$	Merck	99.40
Potassium iodide	KI	Merck	99.00

3.2 Water content in DAF mud

To determine the water content of DAF mud, DAF mud was weighed into a pre-weighed glass beaker and dried in an oven at 50 °C. The mass of the beaker was recorded after every 24 hours until it became constant. Three separate samples were measured in triplicate each. Assuming that the mass loss was strictly due to water alone, the moisture content was then calculated using equation 3.1.

$$\text{Mass loss (\%)} = (\text{Mass of original sample} - \text{Mass of the dried sample})/(\text{Mass of original sample}) \times 100 \qquad (3.1)$$

3.3 Crude wax production from DAF mud

There are two methods used in this project to obtain crude wax from DAF mud. These methods are solvent extraction, and heating and melting method. The purpose of producing crude wax is to remove fine particulate matter from the DAF mud. The removal of fine particulate matter assists in improving the quality of the produced wax, reduces wax contamination by removing impurities and reduces pollution.

3.3.1 Solvent extraction method

Preliminary experiments were carried out with four solvents (butanol, toluene, turpentine oil and 2-butanone) to determine the solubility of crude wax at room temperature of 25°C. The basis of selecting the set points e.g. solid to liquid ratio was based on visual inspection and trial and error. The set points were set such as to avoid adding too much sample to a small amount of solvent, forming a supersaturated solution and vice versa. In each case, about 2.0 g of dried DAF mud was dissolved in 10 cm^3 of a solvent in a 100 cm^3 glass beaker for a period of 24 hours. The miscibility of crude wax in each solvent was evaluated after a complete 24 h interval. At the ratio of 1:5, dried DAF mud samples were not fully submerged in the solvent. Thus, a solvent volume was increased to make a solid to liquid ratio of 1:10. Figures 3-1 and 3-2 depicts the miscibility of crude wax in four solvents. Crude wax was completely miscible in toluene and partially miscible in other three solvents (2-butanone, turpentine oil and butan-1-ol). The bottom layer, which is dark brown, is the dried DAF mud solution consisting of solids and crude wax. This solid to liquid ratio (1:10) was applied in the solvent extraction method described in this section.

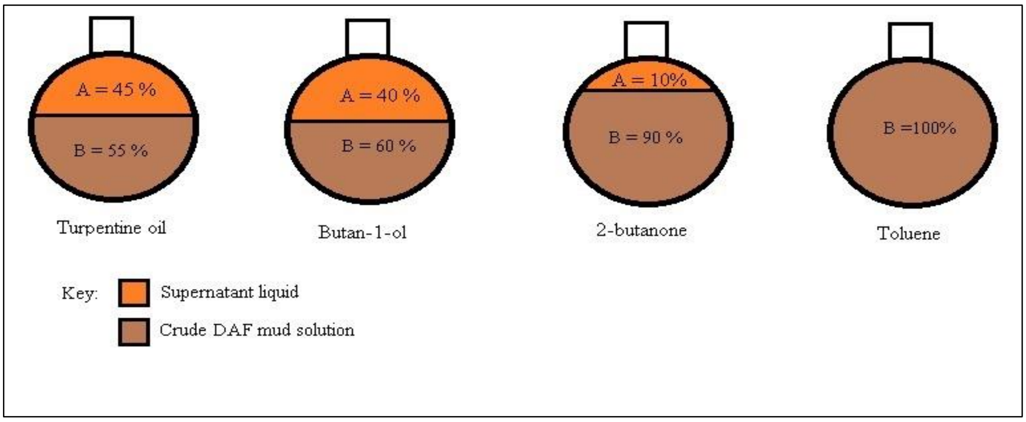
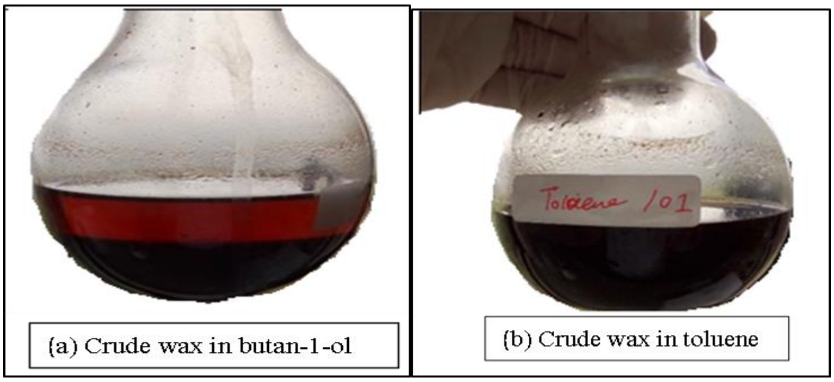


Figure 3- 1: Miscibility of crude wax dissolved in different solvents. The letter A represents the approximate percentage of the observed supernatant liquid, while letter B represents the approximate percentage of crude wax solution and residue.



(a) Crude wax in butan-1-ol

(b) Crude wax in toluene

Figure 3- 2: Observations of miscibility of crude wax in different solvents

Crude wax was extracted from dried DAF mud using either of four different solvents (butanol, toluene, 2-butanone and turpentine oil). In each case, about 10 g of DAF mud (oven dried at 50 ^{o}C) was weighed and mixed with a solvent in a 250 ml flask. By visual inspection, this sample mass was sufficient in this flask volume so it wouldn’t require more additional solvent. The mixture was swirled and shaken for thorough mixing and allowed to stand at room temperature for a period of 6h. Thereafter, the mixture was filtered using a Buchner flask. The solids left on the filter paper were weighed out and the filtrate was transferred back to the flask. The yield of crude wax was determined by subtracting the mass of solids from the initial mass of DAF mud, and consequently dividing this difference with the total mass of DAF mud initially used. The equation for crude wax yield is given in the Appendix A3 on dry basis as. The volume of the mixture in the flask was filled up to 100 cm^3 by addition of additional fresh solvent. This crude wax containing solution was then homogenized by shaking, and consequently used determine physicochemical properties such as acid value, saponification value, iodine number, and the composition of DAF mud.

3.3.2 Heating and melting method

To obtain crude wax by this method, about 1.5 kg dried DAF mud was weighed into a 8 dm^3 aluminium/stainless steel vessel and was heated at 70 °C on a hot plate to homogenise the DAF mud by melting. Thereafter, the DAF mud was left to cool and solidify. The crude DAF mud was then weighed out into three 500 ml beakers yielding batch one (SM-01-T-CWY), two (SM-02-T-CWY), and three (SM-03-T-CWY), respectively. The masses of dried DAF mud were fixed at about 100g in the beakers. The variation of dried DAF mud masses i.e. 1.5 kg and 100g was due to different container volume sizes (8L and 0.5L). The idea was to observe if the obtainable yield would be approximately the same or not.

Preliminary oven experiments have shown that the crude wax in DAF mud starts to melt at an oven temperature of 65^{o}C. Furthermore, literature review has shown that crude wax from press mud has a melting point range of 66 -78 ^{o}C (Ray, 2003), while that of a targeted carnauba wax is ranging from 83-86 ^{o}C (Tinto et al., 2017). 85 ^{o}C was treated as the limiting upper bound temperature; heating beyond this temperature might end up altering the chemical properties of the desired wax. Thus, it was a good start to treat each batch at temperatures between 65 and 85^{o}C in an oven, where the wax melted and collected as the top layer. In the bottom, the fine particulate matter accumulated. The wax was separated by decanting the molten raw wax into separate beakers. Raw data for this set of experiments is listed in table A3-3. The crude wax yield on dry basis was then calculated using the initial mass of dried DAF mud and the final mass of crude wax obtained after decanting the waxy material as shown in Appendix A3.

Figure 3- 3: Crude wax obtain via heating and melting method

Figure 3-3 depicts the crude wax obtained via decanting of waxy material after heating of DAF mud and melting of the crude wax in it. The crude wax obtained via this method is a solid at room temperature, whilst the crude wax produced via the solvent extraction method was not in a solid at room temperature. Therefore, crude wax in a solid form is suitable for refined wax production as it can be directly treated with charcoal and a green solvent to obtain refined wax. Furthermore, crude wax obtained via heat and melt method is more environmentally friendly as it is it does not require the use of solvent. Thus, considering all these factors, it made sense to proceed with refining crude wax produced via heating and melt method. This technique is less laborious, time saving, energy saving and solvent saving. Crude wax from the heating and melting method was used in the refining step, as detailed in section 3.4.

3.4 Refining of crude wax

The proposed method for refining crude wax included treatment of crude wax (from the heating and melting method) with activated charcoal and a solvent that not only will dissolve the wax, but also is sustainable.

3.4.1 Selection of a suitable solvent

Solvent selection guidelines provided by Pfizer, GSK, and Sanofi (see section 2.5) were used to determine the most sustainable solvent. Since the effect of a solvent's properties on the refining using activated charcoal (in terms of yields, and resulting wax properties) is unknown, a wide range of solvents was initially selected to contain examples of alcohols, ketones, aromatics and hydrocarbon. Table 3-2 shows the selected solvents and their solvent selection guideline ratings.

Table 3 - 2: Solvent selection guidelines provided by Pfizer, GSK, and Sanofi

Class	Solvent	Pfizer rating	GSK rating	Sanofi rating
Alcohols	Butan-1-ol	Preferred	Few issues	Recommended
	Ethanol	Preferred	Some issues	Recommended
Ketones	2-butanone (MEK)	Preferred	Major issues	Recommended
Aromatics	Toluene	Usable	Some issues	Substitution advisable
Hydrocarbon	Turpentine oil	Usable	Some issues	Substitution advisable

The important variables that were considered in selecting the most sustainable solvent were the ratings and the cost of the solvent. Butanol and ethanol both have similar properties as they have the same functional group. According to the guidelines shown in table 3-2, ethanol and butanol are the most preferred solvents. After careful consideration, ethanol was included in the study on the production of refined wax. This came after reviewing its properties in terms of safety, cost and recyclability. Additionally, ethanol is produced by the local sugar industry, hence securing availability.

Although less preferred, 2-butanone, toluene and turpentine oil were also included in this study to see the effect of solvents of different polarities, and hence solvent properties. It is important to note that crude wax can be obtained (as demonstrated in this thesis) via solvent free technique (heating and melting), which makes the production of crude wax in this thesis a very environmentally friendly method. Furthermore, refined wax is produced using a green solvent. The final decision on the most preferable solvent was based on the eco-friendliness of the solvent in this thesis. It should be noted that the use of supercritical fluid extraction (SFE) with CO_2 may offer an even greener alternative, and has demonstrated many advantages such as improved selectivity, higher extraction yields, better fractionation capabilities, and lower environmental impacts (Sánchez-Camargo, 2014). However, this method was beyond the scope of this study due to instrumentation limitations and costs involved

3.4.2 Purification with activated charcoal

Figure 3 -4 depicts an image of dried DAF mud and molten crude wax obtained from the heating and melting method (right). It is evident that the crude wax is very dark in colour.

Figure 3- 4: Dried DAF mud (left) and molten crude wax (right)

In order to obtain a saleable product, a refining step must be included to achieve a white or slightly yellow product. Refining of crude wax was achieved by adding a known mass of crude wax in a known volume of a solvent using a systematic approach to determine the required amount of activated charcoal. After dissolution of the crude wax in the given solvent, a proportional amount of activated charcoal was added to form a slurry. The slurry was homogenised by means of mechanical agitation using handheld wooden rod at 70°C for 30 minutes. It was then transferred to a filter press (MIT Certified Stainless Steel 304 and 3CR12 filter press, 300Dia x 300mm High – 23.4 Litre), operating at a pressure of 4 bar for another 30 minutes to separate the refined wax from the filter cake. The filtrate was collected in 500 g buckets and sent to a rotary evaporator to remove the solvent. The yield of the refined wax was determined after drying the solvent.

A one-variable-at-a-time approach was chosen to determine the optimum ratio of crude wax/solvent/charcoal by visual inspection of the resulting wax as well as the yield. In each case, the key variable was a mass of charcoal to crude wax mass since that determined the desired color purity. The viscosity of slurry that formed determined the volume of solvent needed to be added in each case. If the slurry was more viscous, more solvent was added until it was well mixed and homogenized by means of mechanical agitation using hand held wooden rod, and vice versa. This was a trial and error method and it focused more on the obtainable yield and the color purity of the desired refined wax. The final optimal ratios were selected after a targeted color purity and the corresponding higher yield of refined wax was obtained using a green solvent. The mixing ratios were altered as shown in table 3-3. Characterisation of the refined wax is described for wax produced with ethanol, at a crude wax: ethanol: activated charcoal ratio of 1:04:02.

Table 3 - 3: Optimization of process parameters for purification of crude wax

Entry	**Solvent**	**crude wax mass /g**	**Volumeof solvent /cm^3**	**Mass of charcoal /g**	**Ratios (CW/ Solvent/ Charcoal)**	**Final mass (g) Refined wax**
1	Butan-1-ol	20.744	100	20.038	1:05:01	12.992
2	Butan-1-ol	20.021	150	40.163	1:08:02	13.101
3	Butan-1-ol	10.298	100	40.815	1:10:04	6.911
4	Butan-1-ol	10.748	50	19.818	1:05:02	6.789
5	2-Butanone	20.706	100	20.304	1:05:01	7.012
6	2-Butanone	20.576	150	40.853	1:08:02	8.665
7	Toluene	10.799	50	20.822	1:05:02	4.752
8	Toluene	20.472	150	40.618	1:08:02	9.542
9	Toluene	20.125	150	40.175	1:08:02	8.963
10	Ethanol	20.141	80	40.522	1:04:02	13.116
11	Ethanol	5.154	40	10.994	1:08:02	2.897
12	Ethanol	10.668	100	40.117	1:10:04	5.899

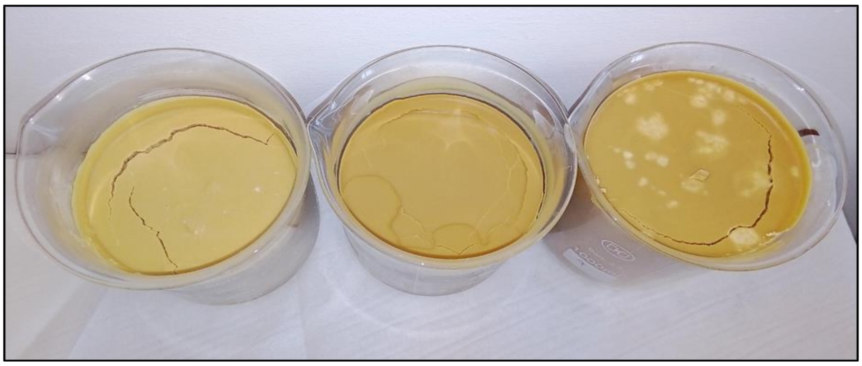


Figure 3- 5: Refined wax samples using ethanol

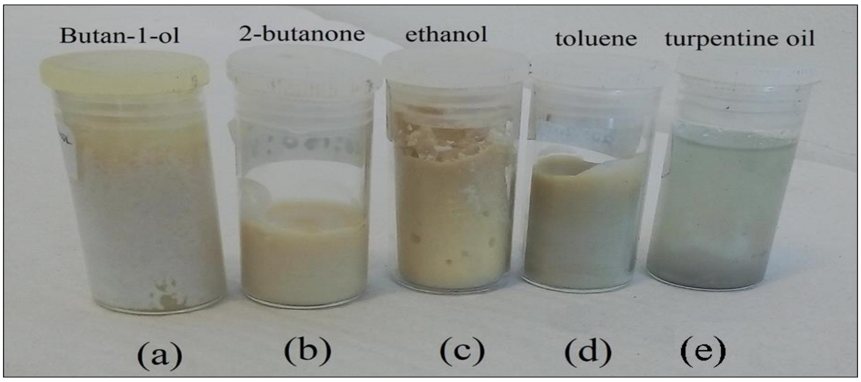


Figure 3- 6: Refined wax samples using various solvents

3.5 Preparation of standard solutions

For all titrations, a 50 mL class A burette graduated at 0.1 ml with a tolerance of ±0.05 ml was used. Solutions of KHP, KOH and HCl were prepared gravimetrically. These solutions were standardized by means of titrimetric analysis. All titrations were conducted in triplicate and average titre volumes were used for the respective calculations. When the standards were depleted, fresh standards were made up following the same method.

3.5.1 Preparation of 0.1 M KHP solution

A 0.1010M solution of KHP was prepared by dissolving 5.185 g of 99.5% KHP in deionized water in a 250 cm^3 volumetric flask. The flask was swirled to dissolve KPH and then filled to the mark with deionized water. This 0.101 M solution was used to standardise the 0.1 M KOH solution.

3.5.2 Preparation of 0.1 M KOH solution

A 0.1 M solution of KOH was prepared by dissolving 6.601 g of >85% pure KOH pellets in 250 cm^3 of deionized water in a 1000 cm^3 flask. The flask was swirled until KOH pellets were completely dissolved and then filled to the mark with deionized water.

3.5.3 Standardization of 0.1 M KOH solution

KOH solution was standardized by titrating 10.0 cm^3 of 0.1010 M KHP with an approximately

0.1 M solution of KOH in the presence of phenolphthalein indicator. The final concentration of standard KOH solution was 0.1133 M. Table A1-1 depicts the standardization raw data used.

3.5.4 Preparation of 0.1 M HCl solution

Approximately 0.1 M solution of HCl was made by measuring 8.30 ml of 37 % HCl and adding it to a 500 cm^3 of water in a 1000 cm^3 volumetric flask. The flask was swirled to mix and then filled to the mark with deionized water.

3.5.5 Standardization of 0.1 M HCl solution

HCl solution was standardized by titrating 10.0 cm^3 of the approximately 0.1 M HCl solution with 0.1133 M KOH in the presence of phenolphthalein indicator. See appendix A1; table A1-2. The final concentration of the standardized HCl was 0.1085 M.

3.5.6 Preparation of 0.1 M alcoholic KOH solution

To prepare an approximately 0.1 M ethanoic KOH solution, 1.6620 g of KOH pellets were dissolved in 100 cm^3 of absolute ethanol in a 250 cm^3 volumetric flask. The flask was swirled to mix the contents and then filled to the mark with absolute ethanol.

3.5.7 Standardization of 0.1 M alcoholic KOH solution

The alcoholic KOH was standardized by titrating 10 cm^3 aliquots of 0.1 M ethanoic KOH solution with the standardized 0.1085 M HCl solution. Raw data used for standardization of this ethanoic KOH solution is available in Appendix A1, Table A1-3.

3.5.8 Preparation of 10% potassium iodide solution

A 10 % potassium iodide (KI) solution was prepared by dissolving 10.09 g of this chemical in100 ml of distilled water in 250 ml conical flask and the contents covered with foil paper and kept in the dark.

3.5.9 Preparation of 0.1 M sodium thiosulfate solution

An approximately 0.1 M solution of sodium thiosulfate pentahydrate, ($Na_2S_2O_3.5H_2O$) solution was prepared by dissolving 24.8000 g of $Na_2S_2O_3.5H_2O$ in 500 cm^3 of freshly degassed, deionized water. The flask was swirled to dissolve the contents and then filled to the mark with the degassed and deionized water.

3.5.10 Standardization of 0.1 M sodium thiosulfate solution

Approximately 2.0 g of dried finely ground ($K_2Cr_2O_7$) potassium dichromate was accurately weighed and quantitatively transferred to a glass plate to dry in the oven at 100 ^{0}C for 6 hours. About 0.2g of the finely ground ($K_2Cr_2O_7$) potassium dichromate was transferred to each of the three 250 ml conical flasks. Subsequently, 25 ml of distilled water, 5 ml HCl and 20ml of KI were added to the flask. The contents were carefully mixed by vigorous shaking until they were thoroughly mixed. The top of the flask was covered with foil paper and the contents were kept in the dark for 30 minutes. After 30 minutes was complete, 100 ml of distilled water was added to the contents. This was titrated against the previously prepared 0.1 M sodium thiosulfate solution until the pale-yellow straw colour has almost disappeared indicating the first endpoint. About 2 ml of starch indicator solution was then added after the yellow straw colour has almost disappeared, and the contents were further titrated against the 0.1 M sodium thiosulfate solution until the dark blue colour just disappear.

The normality of sodium thiosulfate was calculated as follows,

$$\mathrm{N} = 20.394\left(\frac{\mathrm{W}}{\mathrm{V}}\right) \qquad (3.1)$$

Where N = Normality of sodium thiosulfate solution

W = weight of dried finely ground ($K_2Cr_2O_7$) potassium dichromate used (g)

V = Volume of sodium thiosulfate solution used (ml)

The standardised thiosulfate solution had a final concentration of 0.1040 M.

3.6 Acid values of neutral solvents

The solvents (butanol, toluene, turpentine oil, ethanol, and 2-butanone) used in all experiments in this thesis are known as neutral solvents. Nevertheless, they may contain acid impurities which could interfere with the analysis of the wax. Their acid values were hence determined. In each case, a 10.0 cm^3 aliquot of the solvent was titrated with 0.1133 M KOH in the presence of phenolphthalein indicator, using a 25 ml burette with a precision of 0.05 mL. Titrations were conducted in triplicate. The raw data for this set of experiments listed in Appendix A2, table A2-1 shows that the solvents' acid content was below or close to the limit of detection, which was deemed to be 0.05 ml (one drop). Table 3-4 depicts the results expressed as acid values for the five solvents.

Table 3 - 4: Acid values for solvents

Solvent	**Experimental acid value/mg KOH g^{-1} solvent**	**Reported acid value/mg KOH g^{-1} solvent**
Toluene	0.0457	0.0110
n-Butanol	0.0506	0.0450
2-Butanone	0.0489	0.0280
Ethanol	0.0499	0.1000
Turpentine	0.0375	Np*

Np* ~ Not provided

The results indicated that the concentration of acid impurities in the solvents used are very low, and will hence not interfere in the acid value determination of the wax samples. It was hence deemed not necessary to correct the wax acid values.

3.7 Characterization of waxes

In general, wax is characterised by the acid value, saponification value, ester value and iodine number. In the following, the characterisation of crude wax samples obtained by either the extraction, or the heating and melting methods, as well as refined wax, is presented.

Characterisation of the refined wax is described for wax produced with ethanol, at a crude wax: ethanol: activated charcoal ratio of 1:04:02. Furthermore, the experimental details for the determination of unsaponifiable matter, the melting point, density, refractive index, as well as gas chromatography coupled with mass spectrometry are given

3.7.1 Acid value

For samples from the extraction method, the acid value was determined by pipetting out the replicates of 10 cm^3 aliquots out of the diluted solution and titrated against 0.1133 M KOH. Each solvent was titrated four times. For samples from the heating and melting method, as well as refined wax, the acid value was determined by dissolving approximately 0.25 g of the crude wax in 25.0 cm^3 of each of the following solvents: butanol, toluene, 2-butanone, and turpentine oil. The mixture was then titrated with 0.1133 M KOH in the presence of phenolphthalein indicator. All samples were analysed in triplicate. The acid value was calculated using equation (2.1) and the amount of free fatty acids (oleic acid equivalent) FFA (%) was calculated using equation equation (2.2)

3.7.2 Saponification value

To determine the saponification value of crude wax from the extraction method, 10 cm^3 aliquots of the diluted solutions were pipetted into a 250 cm^3 round-bottomed flask followed by the addition of 20 ml of 0.1018 M alcoholic KOH. The contents were mixed and transferred to a three-necked round bottom flask connected to a reflux system. The contents were then refluxed at 80 ˚^{o}C for 1 hour. Six times 5 cm^3 aliquots were pipetted from the cooled solution and titrated against 0.1085 M HCl standard solution. The blank sample was created by mixing 10 cm^3 of the solvent and 20 cm^3 of 0.1018 M alcoholic KOH solution. The blank run was similarly treated. Saponification values for crude wax from the extraction method were calculated from the raw data information provided in Appendix A4 and A5, Table A4-2 and A5-2.

To determine the saponification value of crude wax obtained by the heating and melting method, approximately 0.25 g of the crude wax was dissolved in 5.0 cm^3 of absolute ethanol in a 250 cm^3 round-bottomed flask. 25.0 cm^3 o^{f} 0.1018 M alcoholic KOH was added to the flask.

To determine the saponification value of refined wax, approximately 1.00 g of the crude wax was dissolved in 20.0 cm^3 of absolute ethanol in a 250 cm^3 round-bottomed flask. 30.0 cm^3 o^{f} 0.1018 M alcoholic KOH was added to the flask. The remainder of the procedure was followed as described above, and 10.0 cm^3 aliquots were titrated with HCl. Raw data is given in appendix A1; table A1-2 Titrations were repeated trice for three different batches.

3.7.3 Ester value

Since the saponification value determines both the free acids and esters in a mixture, the ester value is obtained by subtracting the acid values from the saponification values.

3.7.4 Iodine number

The iodine number was determined for the crude wax produced through heating and melting, and for the refined wax. To determine the iodine number, the wax sample was prepared by adding

0.25 g of wax in a flask containing 10.0 cm^3 of chloroform. 25.0 cm^3 of Hanus solution was then added to the flask and the flask stoppered carefully with foil. The flask was placed in a dark cupboard for 30 minutes. The flask was removed from the dark after 30 minutes and 20 cm^3 of 10% KI solution and 100 $cm^3$of distilled water were added to it. The resulting solution was titrated with 0.1 M Na_2S_2O3. Three batches each of the crude wax and refined wax were titrated in triplicate. Raw data can be found in Appendix A5 and A6 , table A5 –3 and table A6 - 3.

3.7.5 Unsaponifiable matter

The unsaponifiable matter was determined by placing 5.0 g of crude wax in a round-bottom flask with a reflux condenser. 35.0 cm^3 of 0.5 M KOH solution was added to the flask and heated under reflux for 1 h. After 1h, the mixture was transferred to a 250 cm^3 separating funnel. Three samples of crude wax derived from the heating and melting method were extracted using 3 × 50 cm^3 portions of diethyl ether. All ether extracts were later combined and filtered under vacuum. The filtrate was washed with 20 cm^3 portions of water until a neutral pH value was reached for the water phase. The ether phase was quantitatively transferred to a weighed flask and the ether was separated from the crude wax on a rotary evaporator. Thereafter, the flask was left to stand in an oven at 75 $^{\circ}$°C and was weighed periodically until the weight was constant. The amount of material in the flask was calculated and expressed as percentage of the accurately weighed crude wax, which represents the percentage unsaponifiable matter. The percentage unsaponifiable matter was determined by equation (2.6) as described in section 2.6.5. For each sample, the experiments were conducted in duplicate.

3.7.6 Melting point of sugarcane wax

The STUART SMP11 used for the determination of the melting points of waxes. It was calibrated and checked to ensure that it meets the following tolerances: 60°C+/-0.5°C; 100°C+/-0.5°C; 200°C+/-1.0°C. Calibration of the STUART SMP11 was accomplished by measuring the melting points of the two CSRs i.e. vanillin (83°C) and benzil (96°C).. The melting point of these substances were measured three times for verification purposes and the results are displayed on table 3-5.

Table 3 - 5: Calibration of STUART SMP11

Melting point °C	Vanillin	Benzil
Run 1	83 °C	96 °C
Run 2	83 °C	95 °C
Run 3	83 °C	96 °C
Average	83 °C	95 °C
Standard deviation	0.00	0.57

After noting that the melting point of the CSRs are precise and triplicate runs had a very low standard deviation, melting points measurements of both crude and refined wax commenced. A small amount of sugarcane wax was placed in the end of a 1. 9 mm diameter glass capillary tube while ensuring that its other end is entirely closed. The capillary tube was filled with the wax sample up to 2-3 mm. The capillary tube was inserted in the apparatus to get the melting point.

3.7.7 Density of sugarcane wax

The density of sugarcane wax was determined at different temperatures (25, 30, 50, 60, 70, and 80 ˚C) using BYK-Gardner midget cup steel density cups (shown in figure 3-7) specifically designed for the determination of densities of pastes and waxes. These cups are cylindrically shapee with a large opening in the lid to allow for an ease filling, emptying, and cleaning. The stainless-steel covers are tightly fitted and have an upward slope to a small hole in the centre to allow excess sample material to be expelled without entrapping air bubbles.

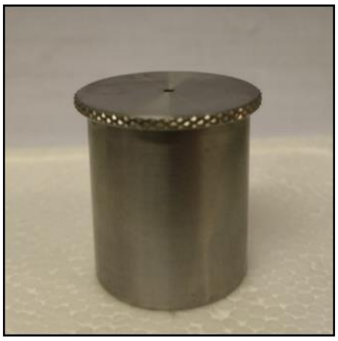


Figure 3- 7: BYK-Gardner density cup

Molten SW was gently added to the density cup, avoiding the formation of air bubbles. The density cup was then allowed to cool. Further wax was added until full and the top lid tightly closed. Any excess wax expelling over the small top hole was scraped off using a spatula and all the outer surfaces of the density cup were thoroughly cleaned. The density cup was then weighed to get the mass of the loaded cup, and the mass of the wax was calculated by subtracting the mass of the empty cup. As a reference, the density of water was also determined using the same density cup under the same conditions. In each case, 6 replicates were analyzed. To obtain the densities at various temperatures, the cups were placed in a GC oven operated at the respective temperature, and allowed to equilibrate. Excess wax leaving the cup through the hole in the lid was wiped off, and the cup then weighted

3.7.8 Refractive index of sugarcane wax

The refractive index of sugarcane wax was measured with an Atago RX-5000i automatic refractometer at room temperature (26 ˚C). This instrument has a resolution and measurement uncertainty of 0.00001 and ±0.00004 respectively. For the measurement of refractive index of sugarcane wax, approximately 0.1 g was dissolved in 5.0 cm^3 of toluene. The refractive index of SW wax was determined by subtracting the refractive index of toluene from the obtained measurement.

3.7.9 Gas Chromatography-Mass Spectroscopy (GC-MS) Analysis

To verify the presence of policosanol in both crude wax and refined wax, the crude wax obtained by the heating and melting method, as well as the refined wax were characterized by means of GC-MS. However, it is important to note that GC-MS can also be used for the verification of acid values and iodine numbers. The analysis was conducted by means of a SHIMADZU GC-MS QP2010 on a Restek RTX-5MS capillary column (30 cm × 0.25 cm × 0.25 cm). The total flow of hydrogen, the carrier gas through the column, was 1.3 cm^3 min^{-1}. A split ratio of 50 was used for all analyses. In each case, 200.0 mg of SW was dissolved in 5 ml of toluene. Exactly 2.0 µL of the solution was injected for analysis. The purge flow and total flow were 3 cm^3/min and 69.3 cm^3/min, respectively. The oven temperature was set to 50 °C and it was maintained at that temperature for 1 minute. The oven temperature was raised by 50 °C intervals at a heating rate of 8 °C min^{-1}. The final oven temperature was 280 °C and it was maintained for 15 minutes. An ion source temperature was 230°C and the interface temperature was 250 °C with a solvent cut time of 3.6 minutes. Run time was 44.75 minutes with an initial mass to charge ration of 50 m/z and final mass to charge ration of 800 m/z. The identification of the various components contained within the SW was achieved by comparison of experimental data with GC-MS NIST library database.

4 Results and Discussion

The experimental work started by determining the water content of drained DAF mud, as well as the time required to dry it. The dried DAF mud was used in the production of crude wax. For this purpose, two methods were used. The first one entailed the dissolution of the wax components using a selection of solvents, and filtration to remove fine particulate matter. The properties of the wax dissolved in the solvents were determined.

In the second method, the dried DAF mud was heated and melted, and then decanted from the fine particulate matter. The properties of the resulting wax were characterised.

In order to refine crude wax, the crude wax obtained from the heating and melting method was dissolved in a selection of solvents, and then treated with activated charcoal. The properties of the resulting waxes were then determined. The study was concluded by performing a mass balance on the proposed process for future preliminary costing exercise based on the data obtained.

4.1.1 Water content in DAF mud

DAF mud was dried at 50 °C until a constant mass was measured (Figure 4-1). DAF mud had to be dried to reduce the probability of microbial growth. The amount of water removed from the mud was assumed to be directly related to the loss of water rather than other volatiles It can be stated that the drying time should be around 30 hours, if a temperature of 50°C is used. The overall deviation of the water content, obtained from nine drying experiments is 2.1%, indicating that the DAF mud sample is very homogenous, and has an average water content of 57.1% (Appendix A3).

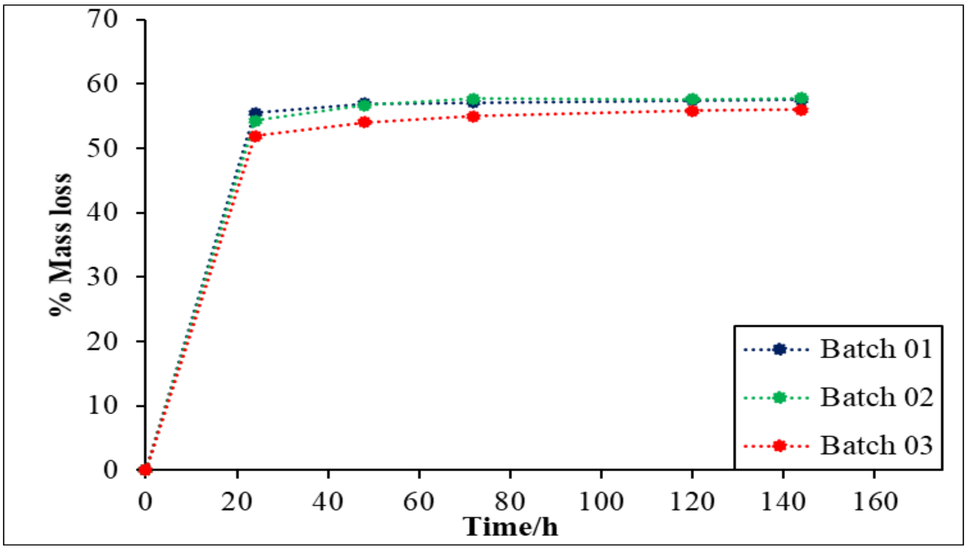


Figure 4- 1: Mass percentage loss of water in DAF mud versus time

4.2 Crude wax production from DAF mud

4.2.1 Solvent extraction method

In the solvent extraction method, wax was separated from fine particulate matter by dissolution and filtration. Brown solutions were formed. Figure 4- 2 shows that the crude wax yield was similar for all solvents, with a maximum average crude wax yield (87.3%) obtained using butanol. The minimum yield (81.0%) was obtained when turpentine oil was used for extraction. Toluene and 2- butanone had average crude wax yields of about 85%. The maximum standard deviation between three titrations of the same solvent was 1.7%. From the results, it can be concluded that turpentine oil dissolves the least of wax the components compared to the other three solvents.

Overall, on average, undried DAF mud comprises hence of 57.1% water, 5.4% fibre and 37.5% crude wax. The wax content of DAF mud is hence much higher than the one reported of press mud (6-15%) (Saleh-e- In, 2012) (Ray, 2003). This is promising as the low wax content of press mud affected the economic viability of the conventional sugarcane wax production process.

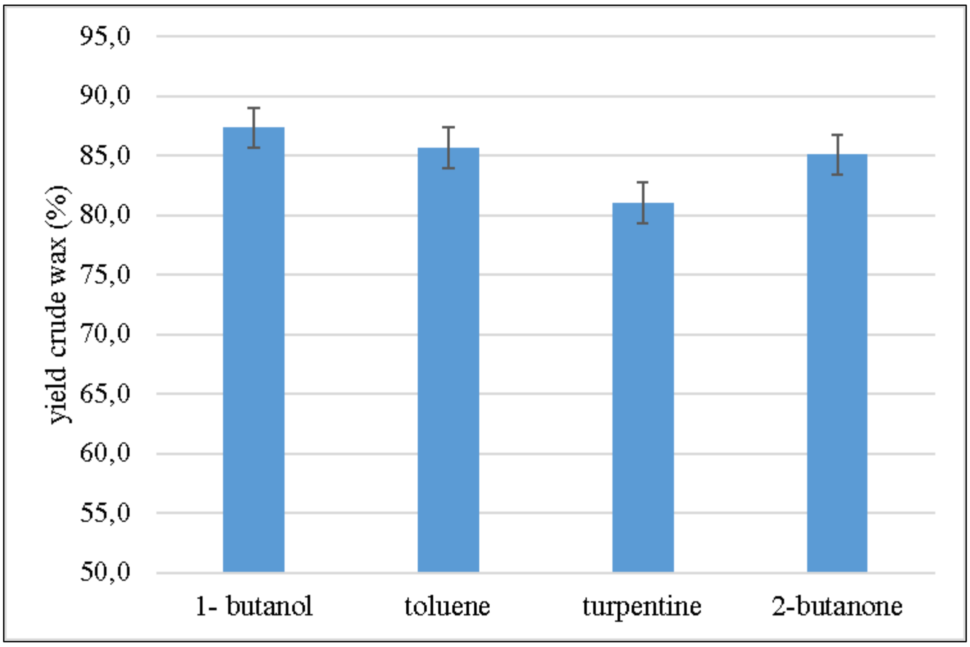


Figure 4- 2: Crude wax yield via solvent extraction.

Maximum standard deviation between three titrations of the same solvent is 1.7%.

4.2.2 Heating and melting method

Crude wax was obtained from dried DAF mud at different temperatures in the ranges of 65 – 85 °C, as described in section 3.3.2. Operating temperatures above 85 °C were avoided as this could have negatively affected the integrity of SW. The results of three experiments conducted at the same temperature deviated by 0.9-3.8%, indicating good repeatability. As shown in figure 4- 3, the maximum attainable yield of crude wax was 56 % at 80 °C. This yield, relative to dried DAF mud, is somewhat lower than the yield obtained from the solvent extraction method (80-87.3%). This is explainable by the fact that the residue, which was discarded, contained some wax still. Nevertheless, the separation from the residue is sufficiently good, so that the use of a solvent as in section 4.2.1 may not be warranted. In the literature, crude wax yields are only reported for sugar mill recoveries, which cannot be directly compared to the DAF mud of this study, which results from a different process. Nevertheless, it can be stated that this yield is higher than the crude wax yield (6.20-11.00%) extracted from press mud reported by (Saleh-e-In et al., 2012).

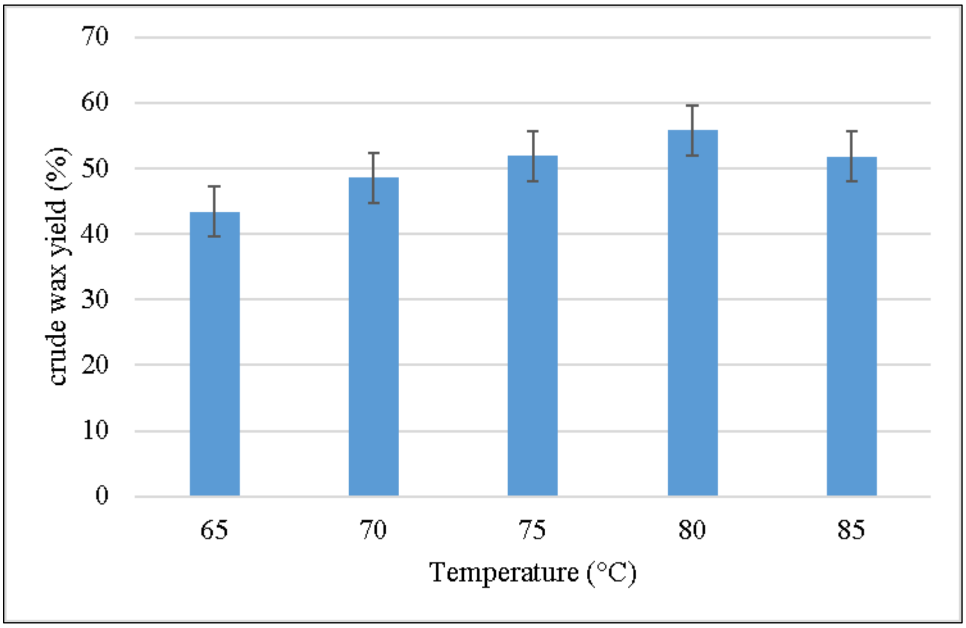


Figure 4- 3: Crude wax yield as function of melting temperature; heating and melting method (average values of three experiments; error bars are given as the maximum standard deviation between three experiments from the same batch, i.e. 3.8%)

4.2.3 Refining of crude wax

Crude wax obtained from the heating and melting method was treated with activated charcoal using different solvents. The ratio of crude wax mass to solvent volume and activated charcoal mass was investigated i.e. Crude wax (g): Solvent (ml): Activated charcoal (g), to find optimum ratios to produce refined wax. Table 4-1 shows the ratios as well as the yields obtained.

Table 4- 1: Ratios of crude wax, solvent and charcoal investigated for the refining of crude wax, as well as yields obtained.

Entry	**Solvent**	**Ratios(CW/ Solvent/ Charcoal)**	**Yield (%) Refined wax**	**Mean**	**Standard deviations (%)**
1	Butan-1-ol	1:05:01	62.6		
2	Butan-1-ol	1:05:02	63.2		
3	Butan-1-ol	1:08:02	65.4*		
4	Butan-1-ol	1:10:04	67.1		
				64.58	9.28
5	2-Butanone	1:05:01	33.9		
6	2-Butanone	1:08:02	42.1*		
				38.00	8.72
7	Toluene	1:05:02	44.0		
8	Toluene	1:08:02	46.6		
9	Toluene	1:08:02	44.5*		
				45.03	8.22
10	Ethanol	1:04:02	65.1*		
11	Ethanol	1:08:02	56.2		
12	Ethanol	1:10:04	55.3		
				58.87	9.39

The * refers to samples shown in Figure 4-4. The basis of selecting optimum ratios is explained in section 3.4.2.

Using 1-butanol, the amounts of solvent and activated charcoal relative to the crude wax were altered, and the effect on the yield determined. Increasing the amount of charcoal had a marginal effect on the yield (entries 1 and 2). Increasing the solvent volume (entries 2 and 3) also improved the yield somewhat. The highest yield was found at a crude wax/ solvent / charcoal ratio of 1:10:04 for butanol.

For selected ratios, other solvents were also tested. 2-Butanone (entries 5 and 6) and toluene (entries 7-9) gave much lower yields than butanol, irrespective of the ratio. Experiments with turpentine were conducted, but unfortunately the samples were lost before the yield could be determined. Ethanol, on the other hand, gave high yields, especially at a low solvent and activated charcoal ratio (entries 10-11). Low solvent and charcoal ratios are favourable as they decrease the overall cost of the process.

Figure 4-4 shows an image of refined wax samples obtained using various solvents and activated charcoal ratios as indicated by the * in Table 4-1.

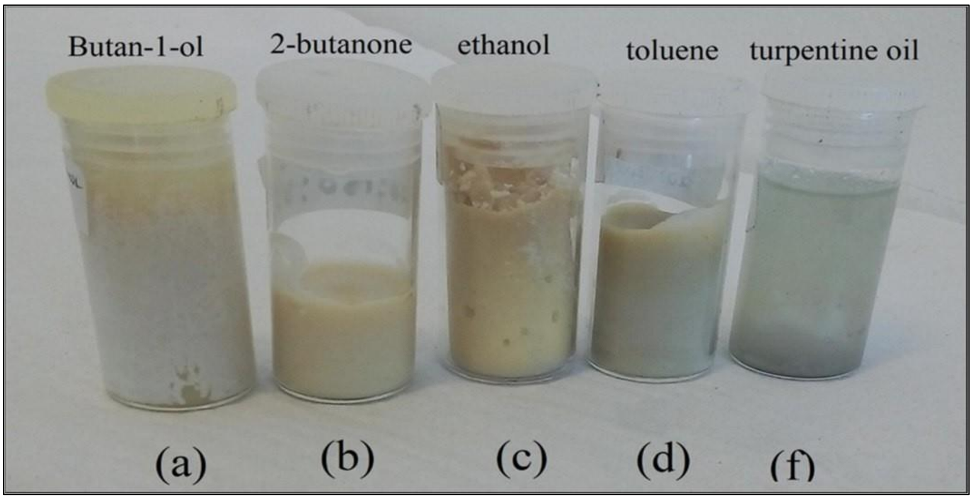


Figure 4- 4: Refined wax samples using various solvents

In summary, the highest yield obtained in the refining stage from crude wax is hence 65%, which can be obtained using either 1-butanol or ethanol. Overall, the composition of drained DAF mud is 57.1% water, 5.4% fibre and 37.5% wax. The yields of crude wax are 87.3% and 56% for the solvent extraction and melting and heating methods, respectively. The yield of refined wax from crude wax is 65%. Hence, the overall yield of refined wax from DAF mud for the solvent extraction method is 21.4%, while that for the heating and melting method is 15.9%. Both methods hence have a higher yield than that reported for refined wax from filter mud from the sugar mill, which is 4.4% (Saleh-e-In et al., 2012).

4.3 Characterization of crude wax from solvent extraction method

The acid value of crude wax from DAF mud was determined by procedure outlined in section 3.7.1.

4.3.1 Acid value and free acid percentage

The acid values as well as the contribution of free fatty acids (FFA %) (expressed as oleic acid equivalent) were calculated from the data provided in appendix A4 (table A4-1).

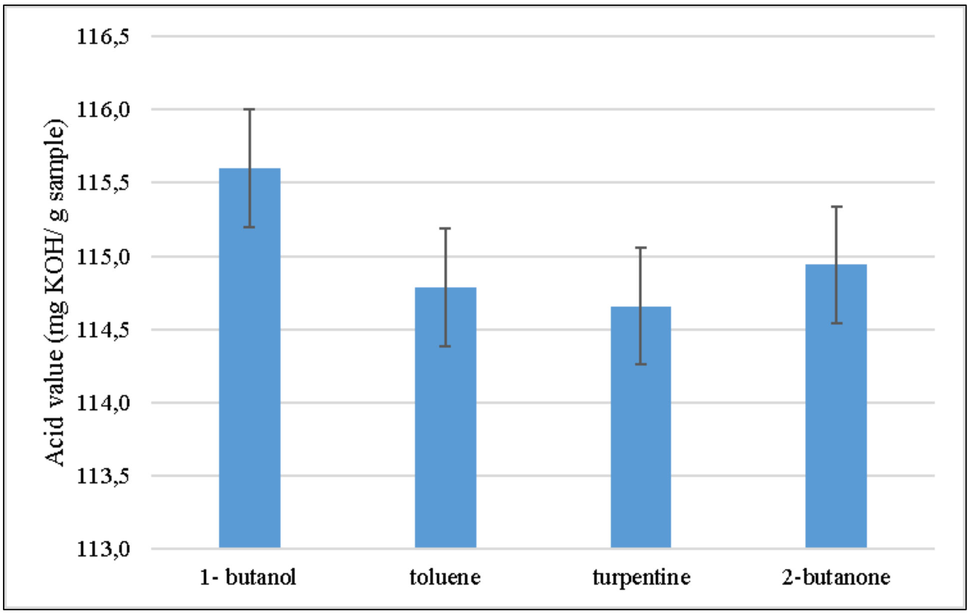


Figure 4- 5: Acid values for crude wax extracted from DAF mud.

Values are given as average of 3 measurements per solvent. The error bar (±0.4 mg KOH/ g sample) represents one drop of titre.

Figure 4 -5 depicts the acid values for the crude wax extracted with four different solvents namely; butan-1-ol, toluene, turpentine oil and 2-butanone. It can be seen that the acid values of the crude wax extracted with different solvents ranges from (114.7 – 115.6) mg KOH/ g crude wax, i.e. the acid values in of wax in different solvents varied only marginally The error bars in the figure is equivalent to one drop of titre. This is higher than the maximum standard deviation between three titrations of the same sample (0.24 mg KOH/g).These acid values are high compared to published literature values of crude wax extracted from press mud discussed in section 2.3.3 shown in table 2-1. The high acid values can be attributed to the severe processing conditions that leads to hydrolysis of fats to free acids during the steam explosion process to make furfural from the hemicellulose within bagasse from which the DAF mud is derived from.

Figure 4- 6 depicts the amount of free fatty acids (oleic acid equivalent) in the extracted crude wax. The FFA % (oleic acid equivalent) ranges from (57.7 – 58.2 %) (See Figure 4- 6). As for the acid value, the differences between the waxes obtained by extraction using different solvents are marginal only.

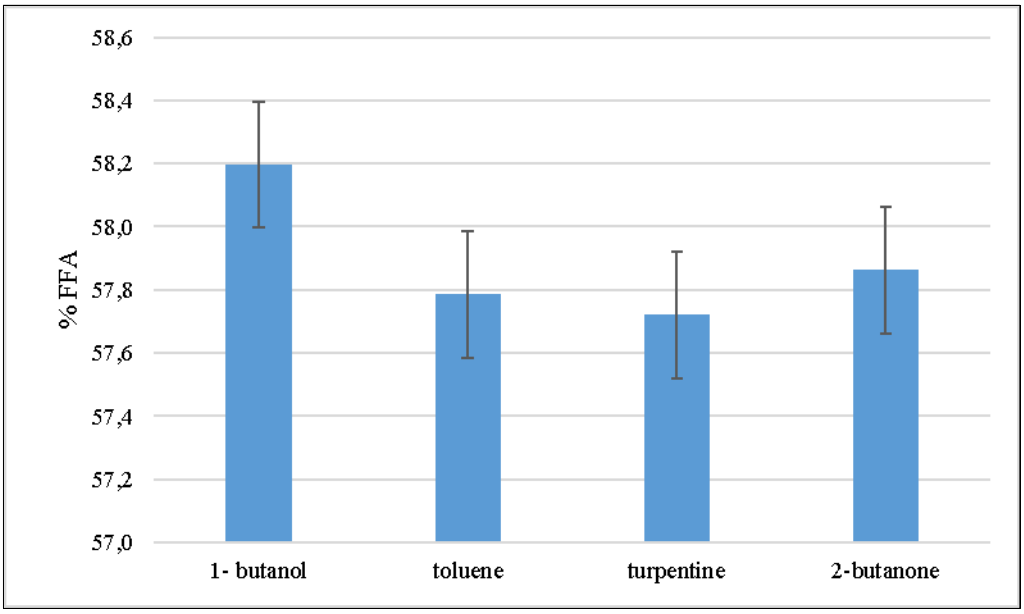


Figure 4- 6: FFA % (oleic acid equivalent) for crude wax extracted from DAF mud.

Values are given as average of 3 measurements per solvent. The error bar (±0.2%) represents one drop of titre.

To sum up, the experimental crude wax acid values range between 114.7 – 115.6 mg KOH/ g crude wax. This range is higher than the crude wax acid values from literature reported by (Ray, 2003) (15 -23 mg KOH g^{-1} crude wax) and (Saleh-e-In et al., 2012) (26.7 – 27.7 mg KOH g^{-1} crude wax). In addition, very little influence of the polarity of the extracting solvent on the crude wax acid composition was found. When expressed in oleic acid equivalents, it can be stated that over half of the wax is comprised of free fatty acids when expressed as oleic acid equivalents.

4.3.2 Saponification value

Saponification values were calculated from the raw data provided in Appendix A4, table A4-2 and method is outlined in section 3.7.2.

Figure 4-7 shows the average saponification values for crude wax extracted from dried DAF mud using four different solvents (butan-1-ol, toluene, turpentine oil and 2-butanone). The saponification values for crude wax obtained from extraction by butan-1-ol, toluene, turpentine oil and 2-butanone are, 116.6, 106.9, 119.3 and 118.4 mg KOH g^{-1} crude wax, respectively, with the maximum standard deviation of 23 mg KOH/g between three titrations of the same sample. Statistically, the differences between the saponification values in different solvents is insignificant, and the average is 113 mg KOH/g wax. The effect of the polarity of the extracting solvent can hence not be discussed. These low saponification values are indicative of a low number of triglycerides present.

The experimental saponification values are consistent with literature values reported by (Ray, 2003), (Saleh-e-In et al., 2012) and (Paturau, 1982) as displayed in table 2-1.

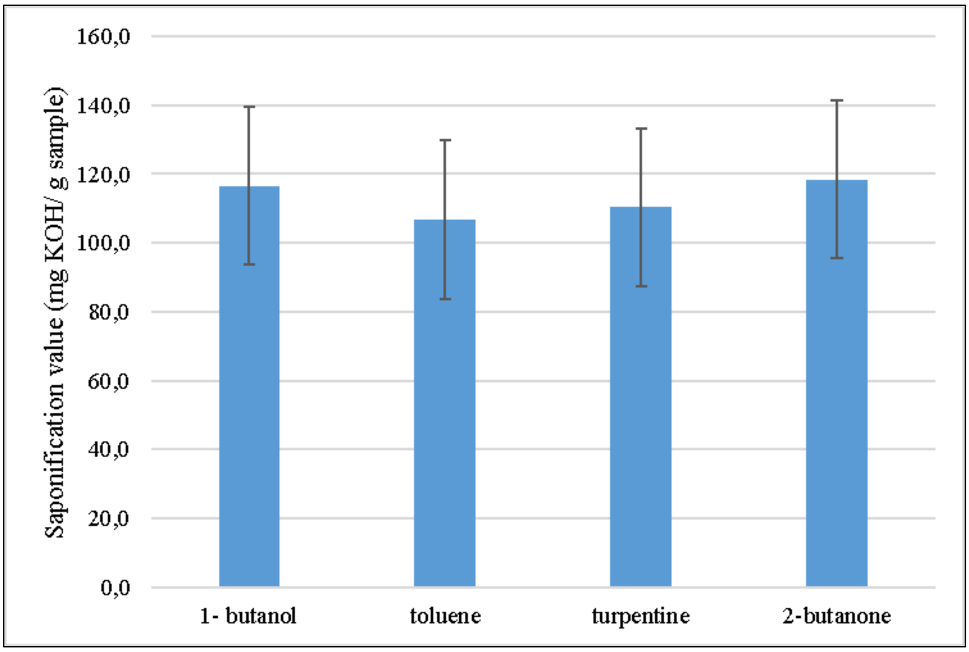


Figure 4- 7: Saponification values for crude wax extracted from DAF mud.

Values are given as average of 3 measurements per solvent. The standard deviation shown is the maximum deviation of ±23 mg KOH/g between three titrations of the same sample.

4.3.3 Ester value

The ester value obtained after extraction of dried DAF mud with different solvents was determined as the difference between the corrected acid values and saponification values. Due to the relatively large error of the titrations for the saponification value, the standard deviation of the ester value is very large as well. It is hence not surprising to find negative ester values. However, it can be stated that the amount of ester in a crude wax sample obtained by the extraction method is very low. The esters were also verified or validated by the GC-MS, as they were found present in the refined wax produced from crude wax, which is produced from DAF mud. The n-hexadenoic acid and its butyl and, 9, 12-octadecadienoic acid and its butyl ester were verified by the GC-MS in refined wax.

Table 4- 2: Showing ester values of crude wax extracted from DAF mud

Solvent	**Acid value (mg KOH / g crudewax)**	**Saponification value (mg KOH /g crude wax)**	**Ester value (mg KOH / g crude wax)**
butanol	115.6 ± 0.4	116.6±23	1.0±23
toluene	114.8 ±0.4	106.9±23	-7.9±23
turpentine	114.9±0.4	110.3±23	-4.6±23
2-butanone	114.9±0.4	118.4±23	3.5±23

4.4 Characterization of crude wax from heating and melting method

Crude wax obtained via heating and melting method was characterised for physical and chemical properties such as acid values, free fatty acid content, saponification values, ester value, iodine numbers.

4.4.1 Acid value and free acid percentage

Crude wax acid values were determined using the method described in section 3.7.1.

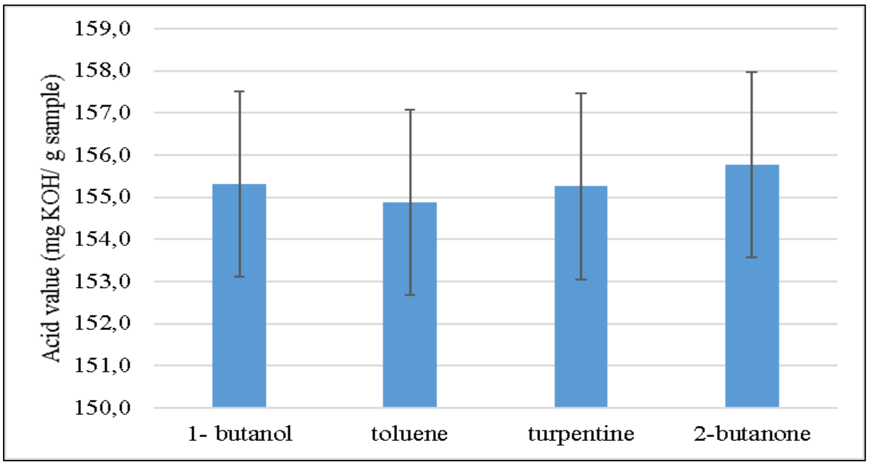


Figure 4- 8: Acid values for crude wax from heating and melting

Values are given as average of 3 measurements per solvent. The error bar (±2.2 mg KOH/g) is the average standard deviation of all samples from the mean.

Figure 4 – 8 depicts the average acid values obtained by dissolving a known mass of crude wax sample in different solvents followed by titration with a KOH standard solution of a known concentration. It is observed that the crude wax obtained by heating and melting method had a high average acid value of 155.3 mg KOH/ g crude wax, irrespective of the solvent used. It is interesting to note that the acid value of wax obtained by melting and decanting is higher than that from solvent extraction (115 mg KOH/g wax). While the reason for this is not known, it may be reasoned that further hydrolysis of triglycerides takes place during the heating process in the melting of the DAF mud.

The acid values are higher than the acid values reported by(Ray, 2003) for crude wax extracted from press mud (15 to 23 mg KOH/ g crude wax). In addition, they are also higher than the acid values reported by (Saleh-e-In et al., 2012) which were ranging from 26.9 to 27.7 mg KOH/ g crude wax. The high experimental acid values obtained in this study indicates a high amount of acids in the crude wax due to the formation of fatty acids caused by hydrolysis. The difference in experimental and reported values can be attributed to the factors influencing the content of sugarcane wax in DAF mud as discussed in section 2.3.4. The corresponding average %FFA (oleic acid equivalent) is 78.2% FFA. This value indicates a high amount of free fatty acids present in the crude wax sample. This is not surprising as DAF mud from which the crude wax was derived from is produced under relatively severe process conditions resulting in acid hydrolysis.

4.4.2 Saponification value

The average saponification value for crude wax obtained by the melting method, from 3 different batches of DAF mud, is 227 mg KOH/g, with a standard deviation of 10 mg KOH/g.

The saponification value represents all saponificable matter (free carboxylic acids and triglycerides). These are much higher than the reported values of 60 - 134 mg KOH/g crude wax obtained by (Ray, 2003) from crude wax extracted from press mud, indicating that in the bagasse steam explosion, non- saponificable matter may have been removed from the wax fraction.

4.4.3 Ester value

The ester value was calculated by subtracting the average crude wax acid value from the average saponification value. The calculated ester value was 72 ±10 mg KOH/ g crude wax. This indicates that although the wax has been subjected to high temperatures and pressures during the bagasse steam explosion, not all esters were cleaved.

4.4.4 Iodine number

The iodine number obtained for crude wax ranges three batches* from 45 – 58 g I_2/ 100 g of crude wax with an average value of 53 g I_2/ 100 crude wax (see figure 4 – 9) and a standard deviation of 5 g I_2/100g. One way ANOVA at a confidence level of 0.05 resulted in a F-value of 8.6, indicating that the differences are statistically significant overall. More precisely, the ANOVA between two batches gave that while the difference in iodine value of batch 1 and 3 as well as 2 and 3 are statistically insignificant, for batch 1 and 2 it is significant, as also shown in the error bars. It can be stated that the difference in the iodine number between the three different batches is statistically significant.

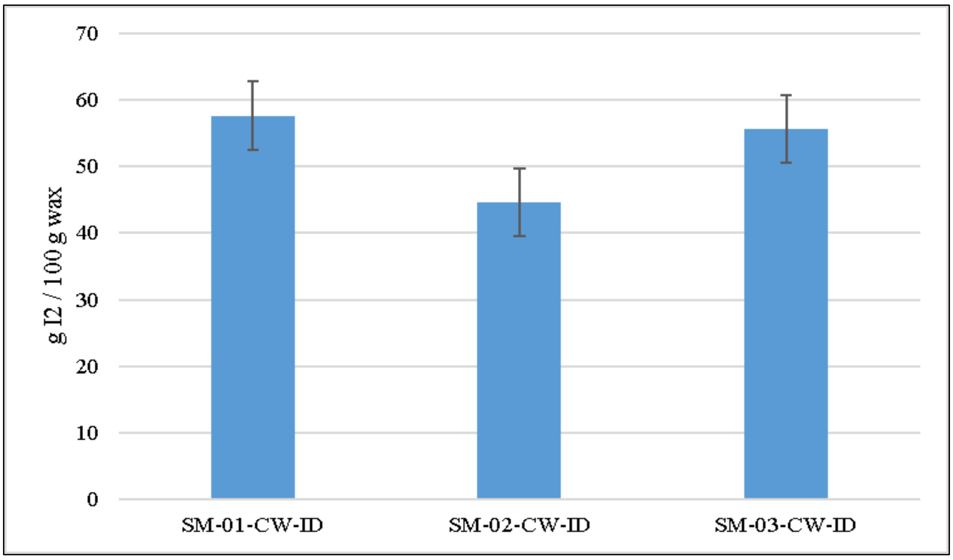


Figure 4- 9: Iodine numbers for crude wax obtained via heating and melting method

Error bars (± 5 g I_2/100 g wax) represent the maximum standard deviation of triplicate measurements of the same batch.

*SM=Sandile Mtolo, 01=Sample 1, CW = Crude wax, ID= Iodine number

The experimental crude wax iodine number is high compared to reported values. For example, (Ray, 2003) reported iodine numbers ranging from 26 to 32 g/ 100g crude wax for crude wax extracted from press mud, whilst (Saleh-e-In et al., 2012) obtained iodine numbers ranging from 6.77 to 6.82 g/ 100 g crude wax for crude wax extracted from press mud. The high experimental iodine numbers obtained indicate the presence of many unsaturated bonds in the crude wax samples.

One could assume that the unsaturated bonds are only present in the carboxylic acid moieties, and not in other organic molecules that constitute unsaponifiable matter. In this case, the comparison of the mol KOH required to saponify the sample (0.4 mol/100 g wax) and the mol I_2 required to halogenate the double bonds (0.2 mol/100g wax) indicates that about half the carboxylic acid moieties (either free fatty acids or those bound as triglyceride) are in fact monounsaturated.

4.4.5 Unsaponifiable matter

The average of the unsaponified matter for three batches of crude wax derived from the heating and melting method was calculated to be 21.5% with a standard deviation of 2%. The raw data is compiled in Appendix A5, Table A5 -4. This average amount of unsaponifiable matter is lower than the amount of unsaponifiables (58%) reported by (Paturau, 1982). The crude wax studied by (Paturau, 1982) was obtained from press mud via solvent extraction. The difference can be attributed to the processing conditions as discussed in section 2.3.4.

4.4.6 Melting point

The melting points of the three crude wax sample batches (SM-01-CW-MP, SM-02-CW-MP, and SM- 03-CW-MP) were determined by the method discussed in section 3.7.6. The melting points of crude wax for the three samples were 76 °C, 78 °°C, and 74 °°C, respectively with an average of 76 °°C and a standard deviation of 2 °C.

Table 4- 3: Melting point measurement of crude wax obtained from the heating and melting method.

Melting point °C	**Crude wax**
Batch 1	76 °C
Batch 2	78 °C
Batch 3	74 °C
Average	76 °C
Standard deviation	2.00

The obtained values agree with the literature values of 66 - 78 °° C reported by (Ray, 2003), 79 °C reported by (Paturau, 1982).

4.4.7 Density

Density measurement was conducted using the method in section 3.7.7. Density cups were used to get the density range of sugarcane wax at various temperatures.

Density measurements were limited to within the temperature range of 25 - 80 °C due to apparatus used and temperature boundary limit such as the melting point of sugarcane wax. Figure 4 - 10 depicts the density of crude wax as a function of temperature. The standard deviation in the data is indicated as error bar, showing the highest standard deviation obtained between two measurements at the same temperature. The one way ANOVA analysis indicated that at a confidence level of 0.05, the difference in density values over the temperature range were insignificant. As such, the "kink" in the data cannot be discussed with certainty. However, it could be indicative of the onset of melting and the wax

Furthermore, it can be stated that the crude wax density is inversely proportional to an increasing temperature. The density of crude wax ranges from 0.850 – 0.882 g/ cm^3. The density of crude wax (0.850 – 0.882 g/ cm^3) obtained, is comparable to crude wax densities of 0.80-0.85 g/ cm^3 reported by existing crude sugarcane wax industries such as DEUREX (2021).

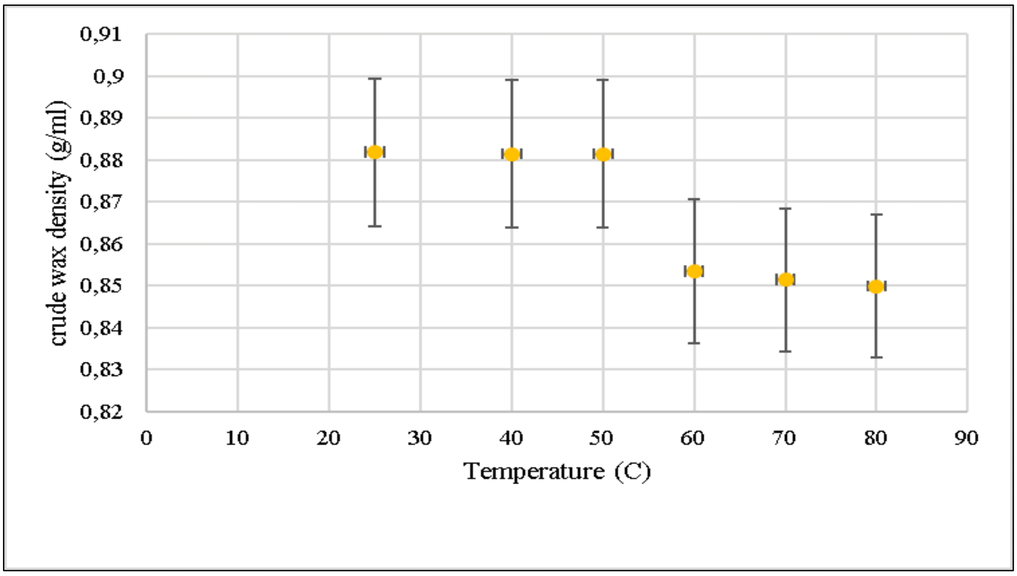


Figure 4- 10: Density of crude wax at various temperatures

4.4.8 Refractive index

Refractive index is a common quality standard measure for pharmaceutical or chemical products. The refractive index measurements were conducted as described in section in section 3.16. The refractive index for crude wax was 1.4923, which indicates the purity and long chain unsaturated fatty acid in the wax. The crude wax refractive index is comparable to literature values published by (Saleh-e-In et al., 2012) of 1.5028 – 1.5033, and to the value of 1.510 published by CAMEO (2020).

4.4.9 Qualitative composition (GC-MS Analysis)

Crude wax was subjected to the GC-MS analysis for characterization. Figure 4 -11 shows the chromatograph and peak report for the compounds present in crude wax along with their retention time and percent composition. The major components are shown as high peaks. Crude wax was found to predominately consist of five main classes of compounds namely, fatty acids, alkanes, alcohols, aldehydes, and esters. The n-hexadenoic acid /palmitic acid (43.78%) and 9, 12-octadecadienoic acid (ZZ) (7.39%) (linoleic acid) were the major identified fatty acids in the wax samples, both contributing to about 50 % of total composition. Although a GC calibration would be required to quantify the components, it can be stated that the composition is in line with the high acid values found in this study. Furthermore, with hexadecanoic acid being the main carboxylic acid, the %FFA would be better expressed as hexadecenoic rather than the standard oleic acid equivalent, taking into account its lower molecular weight of 254.4 g/mol. Also, certain unsaturated carboxylic acids were identified by GC-MS, substantiating the results of the iodine number.

N-hexadanoic acid has its major applications in artificial flavouring for the manufacturing of its esters (Chemicalbook, 2017). It is also widely used as a food additive and emollient or surfactant in cosmetics (Berman, 2000). Linoleic acid has a number of health benefits, including anticarcinogenic and antiatherogenic activities, and the ability to enhance growth promotion and reduce body fat (Fenaroli, 1976).The main goal of the GC-MS analysis for SW samples was to verify the presence of policosanol. However, it can also be used for the verification of acid values and iodine numbers Policosanol compounds are applicable in the pharmaceuticals as they are known to have effective cardio protective properties (Inarkar & Lele, 2012). Policosanol compounds were found (as their alkane or aldehyde homologues) to be present in crude wax (retention times > 27 min.) (see figure 4-12). These compounds can be expected to be contained in the unsaponificable matter fraction, as they would pass into the diethyl ether phase. The carboxylic acids and their derivative constitute 61%, while the unsaponificable matter components make up 39% in this GC-MS analysis.

In conclusion, the GC-MS analysis of crude wax found that the wax consists predominately of five main classes of compounds namely, fatty acids, alkanes, alcohols, aldehydes, and esters. Fatty acids contributed about 50% to the total composition for both crude and refined wax samples. Furthermore, both crude and refined wax samples were found to contain policosanol, which can be used to support the evidence of the applicability of sugarcane waxes in the pharmaceutical industry.

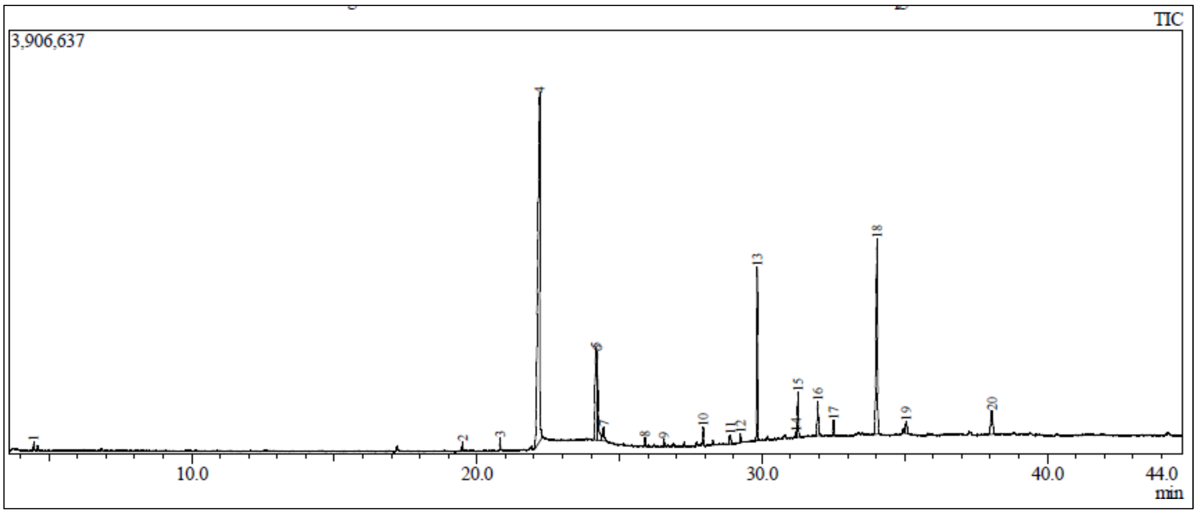
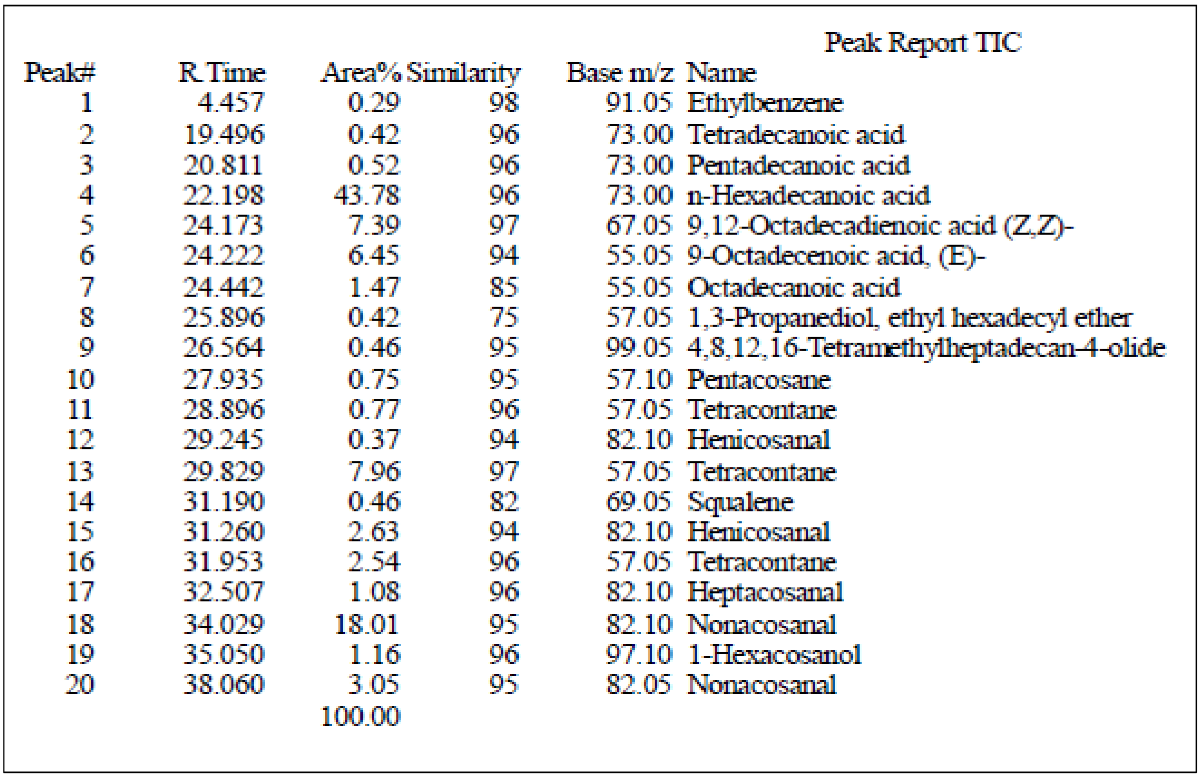


Figure 4- 11: GC-MS chromatogram of crude sugarcane wax



Peak Report TIC

Peak#	R.Time	Area%	Similarity	Base m/z	Name
1	4.457	0.29	98	91.05	Ethylbenzene
2	19.496	0.42	96	73.00	Tetradecanoic acid
3	20.811	0.52	96	73.00	Pentadecanoic acid
4	22.198	43.78	96	73.00	n-Hexadecanoic acid
5	24.173	7.39	97	67.05	9,12-Octadecadienoic acid (Z,Z)-
6	24.222	6.45	94	55.05	9-Octadecenoic acid, (E)-
7	24.442	1.47	85	55.05	Octadecanoic acid
8	25.896	0.42	75	57.05	1,3-Propanediol, ethyl hexadecyl ether
9	26.564	0.46	95	99.05	4,8,12,16-Tetramethylheptadecan-4-olide
10	27.935	0.75	95	57.10	Pentacosane
11	28.896	0.77	96	57.05	Tetracontane
12	29.245	0.37	94	82.10	Henicosanal
13	29.829	7.96	97	57.05	Tetracontane
14	31.190	0.46	82	69.05	Squalene
15	31.260	2.63	94	82.10	Henicosanal
16	31.953	2.54	96	57.05	Tetracontane
17	32.507	1.08	96	82.10	Heptacosanal
18	34.029	18.01	95	82.10	Nonacosanal
19	35.050	1.16	96	97.10	1-Hexacosanol
20	38.060	3.05	95	82.05	Nonacosanal
		100.00			

Figure 4- 12: GC-MS peak report on the composition of crude sugarcane wax

4.4.10 Summary

Table 4-4 summarises the chemical properties of the crude wax obtained through the heating and melting method. It is interesting to note that the FFA%, which assumes that the carboxylic acids present are similar in molecular weight to oleic acid, is somewhat overestimated: Added together with the percentage unsaponifiable matter, close to 100% are reached, without taking into account the esters present. Hence, the average molecular mass of the carboxylic acids must be lower than that of oleic acid (as also discussed in section 4.4.9). It should be noted that the error bars are large in the graphs plotted for the heating-melting method. These large error bars are indicative of large uncertainties, i.e. the concentration of the values the average was calculated on is low, and thus that the average value is uncertain.

Table 4- 4: Chemical properties of DAF mud-derived crude wax, produced by the heating and melting method.

	Crude wax
Acid value (mg KOH/g wax)	155 ± 2.2
Saponification value (mg KOH/g wax)	227 ± 10
% FFA	78 ± 1
Ester value (mg KOH/g wax)	72 ± 10
Iodine number (g I_2/100 g)	53 ± 5
Unsaponifiable matter (%)	21.5 ± 2
Melting point (°C)	76 ± 2
Density (g/cm^3) between 20-80°C	0.850 – 0.882
Refractive index (26°C)	1.4923

4.5 Characterization of refined wax

The experimental details for refining of crude was discussed in section 3.4.2. After crude wax has been refined, it was then characterised for physical and chemical properties as discussed in section 3.7. Refined wax from experiments using ethanol and charcoal, at a crude wax: ethanol: activated charcoal ratio of 1:04:02 was used.

4.5.1 Acid value and free acid percentage

The acid value of the refined wax was determined by titration, as described in Section 3.7.1. For that purpose, the refined wax was dissolved in different solvents. Three batches of refined wax were titrated each, in triplicate.

Table 4- 5 depicts the acid values for individual batches of refined wax and their averages. As previously observed, the acid values obtained are independent of the solvent used. The overall

average is 23.6 ± 3 mg KOH/g of refined wax, and these are comparable to literature values published by (Ray, 2003), (23 – 28 mg KOH / g refined wax).

When compared to the crude wax obtained by solvent extraction or by the heating and melting method, which resulted in 115 and 155 mg KOH/g crude wax, it is obvious that the treatment with activated charcoal has reduced the amount of free fatty acids in the wax. This is due to the high affinity of polar carboxylic acids towards the surface of activated charcoal.

Table 4- 5: Refined wax acid values and free fatty acid percentage. (Values are given as average of 3 measurements per solvent, with an error of ±3 mg KOH/g)

Solvent	**Average acid value** (mg KOH/ g refined wax)	**FFA (%)**
Butan-1-ol	24.7 ± 3	12.4 ± 0.6
Toluene	21.2 ± 3	10.7 ± 0.6
Turpentine	23.8 ± 3	12.0 ± 0.6
2-butanone	24.7 ± 3	12.4 ± 0.6

The average FFAs (oleic acid equivalent) are also shown in figure 4-13, with an average value of 11.9% ± 1.6%.

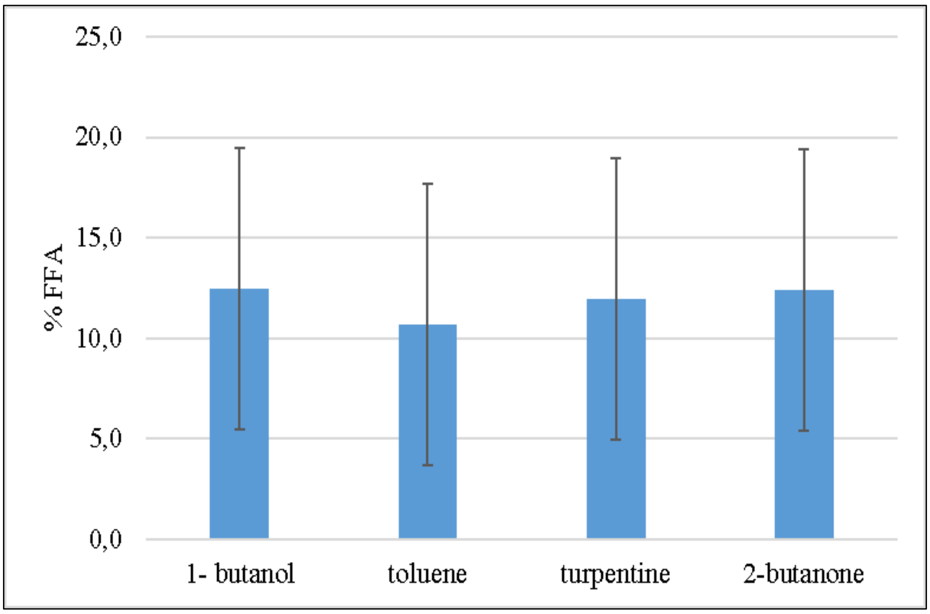


Figure 4- 13: FFA (%) (Oleic acid equivalent) for refined wax. Values are given as average of 3 measurements per solvent.

4.5.2 Saponification value

The saponification values were determined for three different batches of refined wax from ethanol, and the results are displayed in figure 4-14.

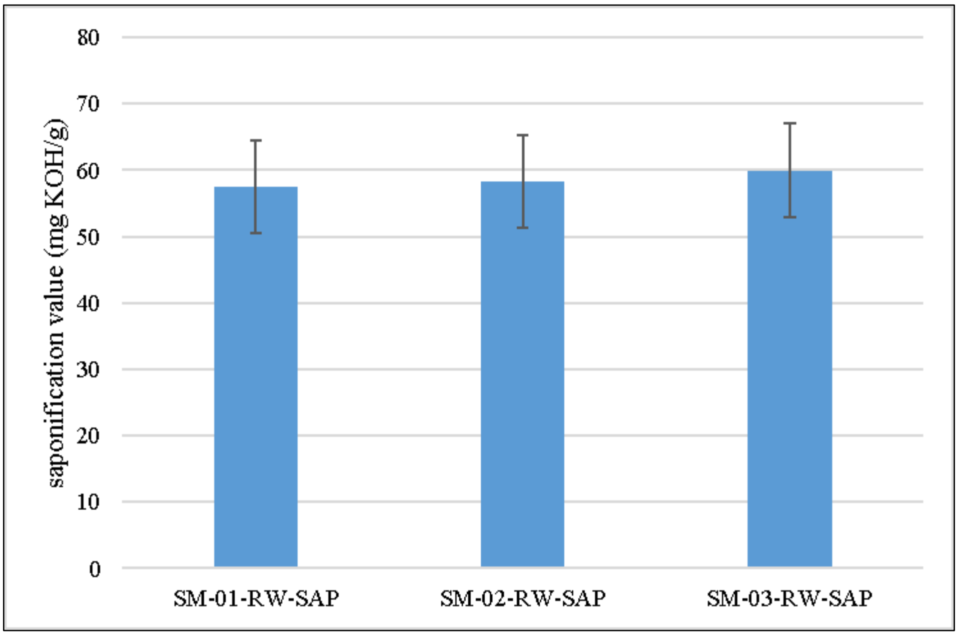


Figure 4- 14: Saponification values for three different batches of refined wax from DAF mud.

Values are given as average of 3 measurements per batch. The standard deviation shown is the maximum deviation of ±7 mg KOH/g between three titrations of the same sample.

The average saponification value for crude wax obtained by the melting method, from 3 different batches of DAF mud, is 58.6 mg KOH/g, with a standard deviation of 7 mg KOH/g, i.e. the difference between the batches is statistically insignificant. The experimental values obtained are comparable to literature values (65 - 77 mg KOH/g refined wax) reported by (Ray, 2003), which refer to refined wax derived from crude wax obtained from press mud.

4.5.3 Ester value

The average obtained ester value, i.e. the amount KOH consumed in the saponification of the esters, was 35 mg KOH/ g refined wax. This value was obtained by subtracting average refined wax acid values from average saponification values.

Table 4- 6: Refined wax ester value

Saponification value*	**Acid value***	**Average Ester value***
59 ± 7	24 ± 3	35 ± **7**

*mg KOH/ g refined wax

4.5.4 Iodine number

Characterization of three batches of refined wax included the iodine number to determine wax stability to oxidation and the degree of unsaturation.

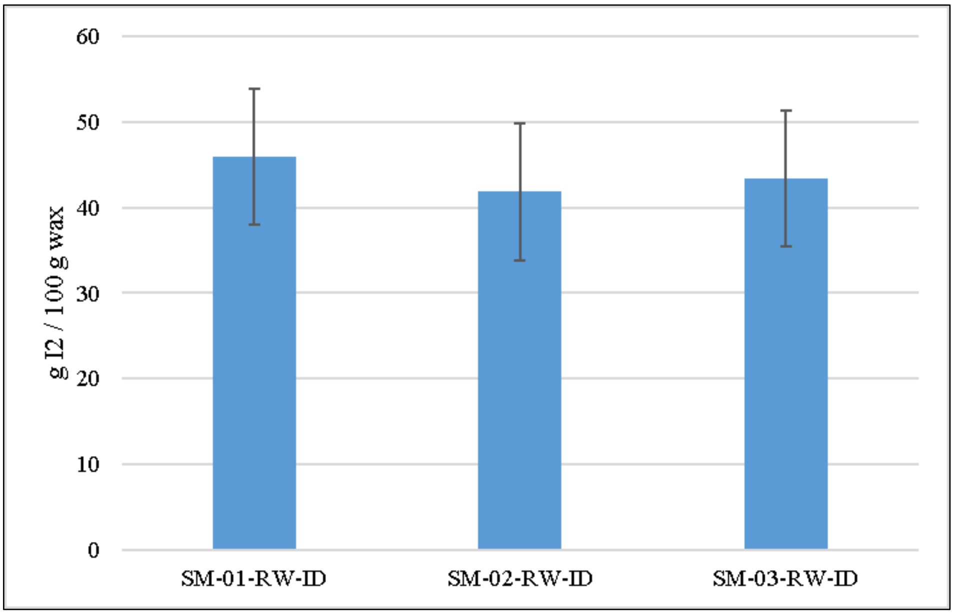


Figure 4- 15: Iodine numbers for refined wax. Error bars (± 8 g I_2/100 g wax) represent the maximum standard deviation of triplicate measurements of the same batch.

*SM=Sandile Mtolo, 01=Sample 1, RW = Refined wax, ID= Iodine number

The experimental iodine numbers obtained range from 42 – 46 g I_2/ 100 g of refined wax. The differences of the values obtained for the three batches* are statistically insignificant, with an average value of 44 ± 8 g I_2/ 100 refined wax. One way ANOVA at a confidence level of 0.05 resulted in a F-value of 5.0, indicating that the differences are statistically insignificant overall. More precisely, the ANOVA between two batches gave that while the difference in iodine value of batch 1 and 3 as well as 2 and 3 are statistically significant, for batch 1 and 2 it is insignificant.

Comparison to the average iodine number obtained for crude wax (53 ± 5 g I_2/ 100 g) suggests that the refining of the wax leads to a reduction of unsaturated components in the refined wax. However, taking the error of the measurements into consideration, one should be careful not to over-interpret the results. If the unsaturation is predominantly found in the carboxylic acid moieties (rather than the unsaponifiable matter), and the acid value is reduced by the refining step, then a reduction of the iodine number would also result.

The experimental iodine number range is relatively high compared to iodine numbers reported (Ray, 2003) which ranges from 13-29 g/100 refined wax. The high experimental iodine number indicates the presence of double bonds in the refined wax sample and, hence a high amount of unsaturated fats. Variations in the literature values and experimental values can be attributed to the uniqueness of the biomass as discussed in section 2.3.4.

4.5.5 Melting point

For refined wax, the melting points of the three batches SM-01-RW-MP, SM-02-RW-MP, and SM-03- RW-MP were determined in triplicate, and had ranges of 73 °°C to 76 °°C, with an average of 75 °°C, and a standard deviation of 2.0 °C. It is noteworthy that the difference in the average melting points of crude wax and refined wax are statistically insignificant. The treatment with activated charcoal did hence not affect the melting point.

Table 4- 7: Melting point measurement of sugarcane wax

Melting point °C	Refined wax
Batch 1	75 °C
Batch 2	73 °C
Batch 3	76 °C
Average	75 °C
Standard deviation	2.0

4.5.6 Density

Density measurements for refined wax was conducted using the method in section 3.7.7. Pycnometers or density cups were used to measure the density of the wax at various temperatures.

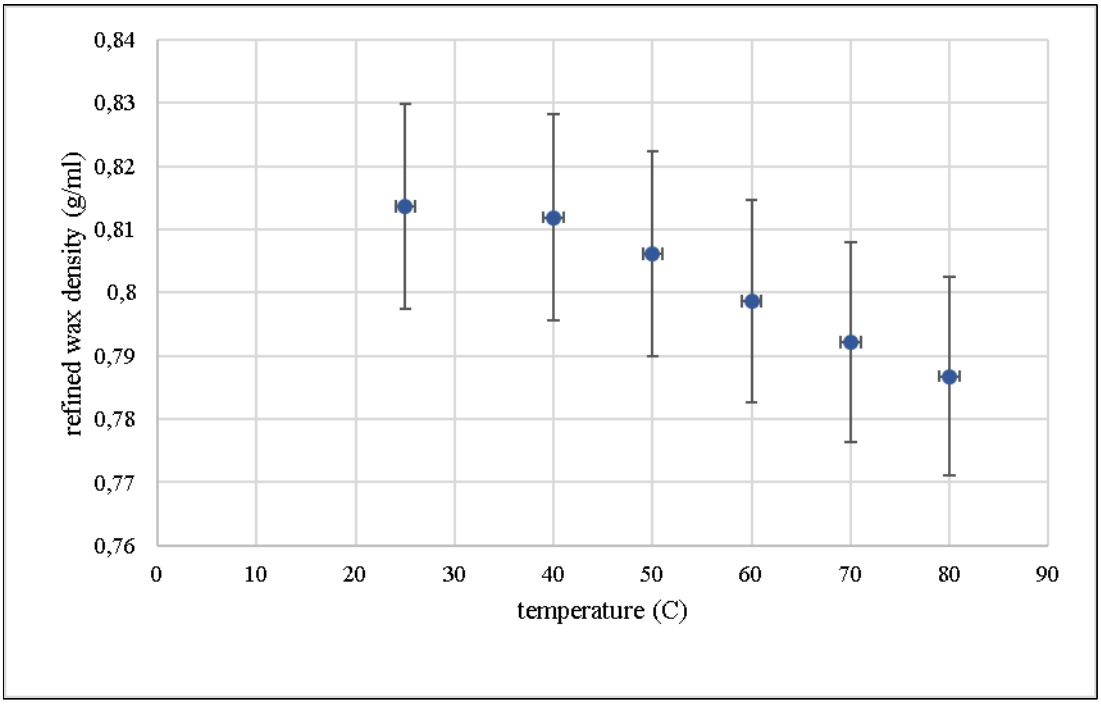


Figure 4- 16: Density of refined sugarcane wax at various temperatures

As mentioned in section 4.4.7, the density measurements were limited to within the temperature range of 25 - 80 °C due to apparatus used and temperature boundary limit, the melting point of sugarcane wax. Figure 4- 16 depicts the density of refined wax as a function of temperature. The standard deviation in the data is indicated as error bar, showing the highest standard deviation obtained between two measurements at the same temperature. The one way ANOVA analysis indicated that at a confidence level of 0.05, the difference in density values over the temperature range were significant, with the F value being 3.5. It is evident from the figure that an increase in temperature results in the decrease in density of refined wax. The density of refined wax ranges from 0.787 – 0.814 g/ cm^3, at temperatures between 20 and 80 °C. (DEUREX, 2021) reports micronized natural sugar cane wax density ranges of 0.80-0.85 g/ cm^3, which are comparable to refined wax density range obtained in this study.

4.5.7 Refractive index

The refractive index measurement was conducted as described in section in section 3.16. The refractive index for refined wax was 1.4867 and it was slightly lower than that of crude wax. However, this is comparable to literature value published by CAMEO (2020) of 1.510. The high refractive index reflects the high purity wax. This is would be beneficial to the cosmetic industry especially in lip-gloss, polish, nail polish manufacture as higher refractive index results in shinier the material.

4.5.8 Qualitative composition (GC-MS Analysis)

Refined wax was also subjected to the GC-MS analysis for characterization. Figure 4- 17 shows the chromatograph and peak report for the compounds present along with their retention time and percent composition. Similar to crude wax, refined wax was found to predominately consist of five main classes of compounds namely, fatty acids, alkanes, alcohols, aldehydes, and esters.

The n-hexadenoic acid and its butyl ester (39.45 and 14.8 %, respectively), 9,12-octadecadienoic acid and its butyl ester (5.43 and 7.44%, respectively) and 9-octadecenoic acid (4.35%) were the major identified fatty acids in the wax samples. Carboxylic acids and their derivatives (esters) contribute to 78% of the total composition, while compounds with retention times > 27 min., which would constitute to unsaponificable matter, amount to 20%. Compared to the results of the GC-MS analysis of the raw wax discussed above, which showed a carboxylic acid and ester content of 61%, this fraction has increased to 78%. Considering that the acid content is decreased in the refined wax, as shown above, one can conclude that the treatment with activated charcoal has removed free carboxylic acids mostly.

The main goal of the GC-MS analysis for SW samples was to verify the presence of policosanol. Policosanol compounds are applicable in the pharmaceuticals as they are known to have effective cardio protective properties (Inarkar & Lele, 2012). Policosanol compounds were found (as their alkane or aldehyde homologues) to be present in refined wax (retention times > 27 min.) (see Figure 4- 17).

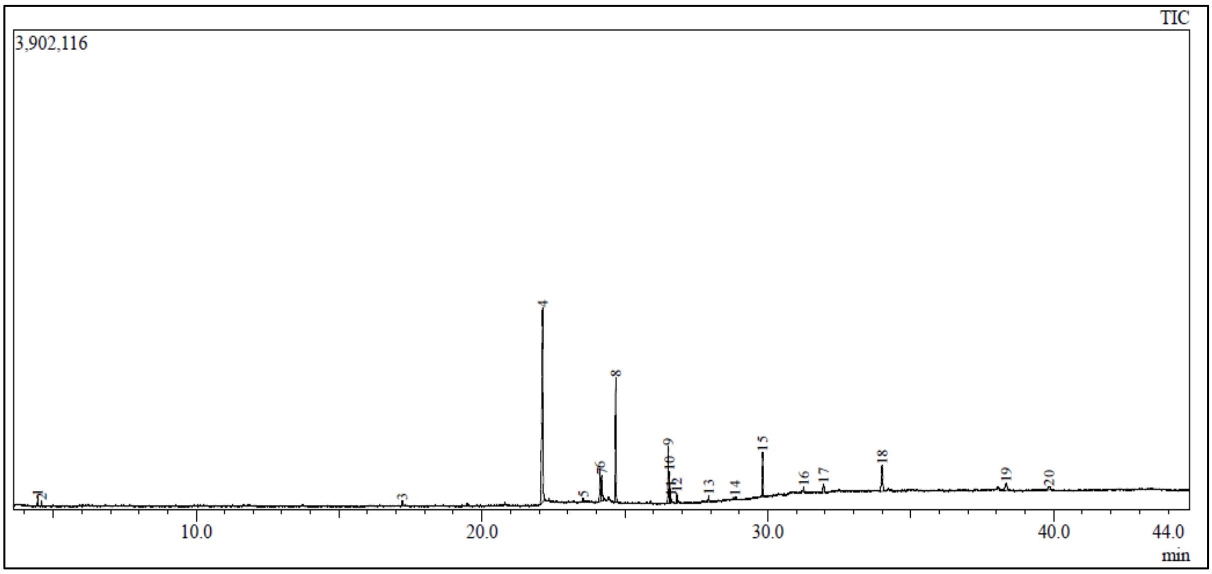
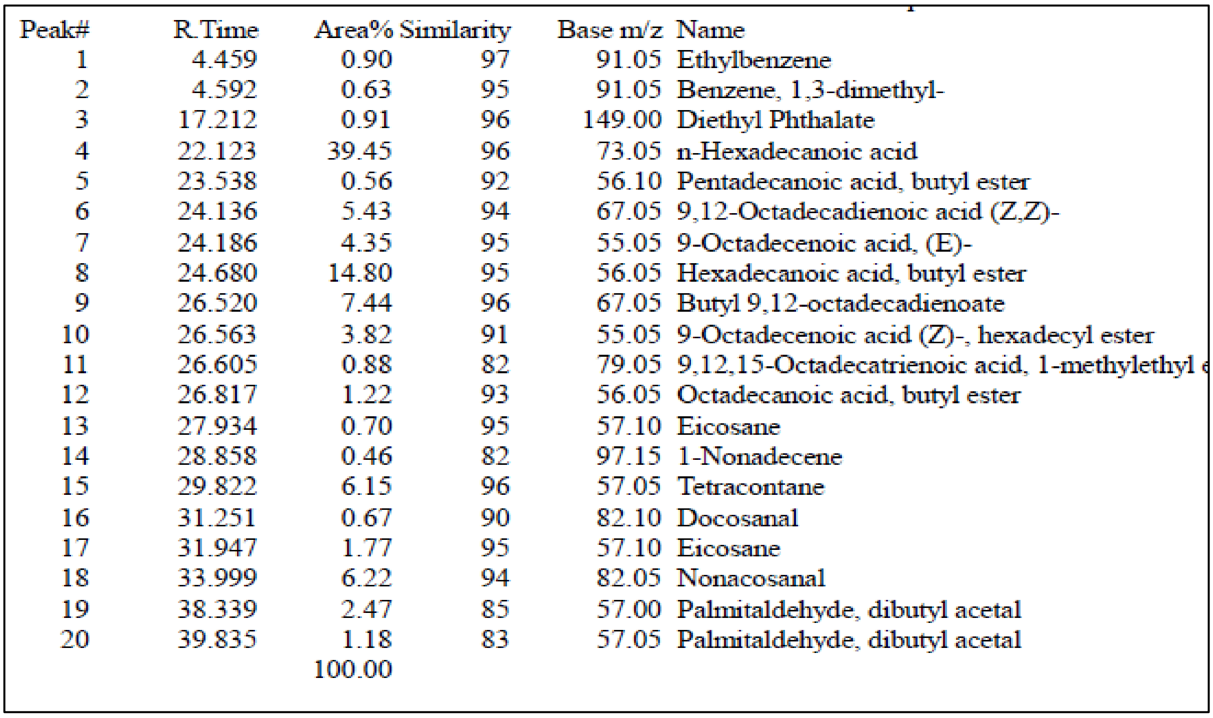


Figure 4- 17: GC-MS chromatogram of refined sugarcane wax (using ethanol)



Peak#	R.Time	Area%	Similarity	Base m/z	Name
1	4.459	0.90	97	91.05	Ethylbenzene
2	4.592	0.63	95	91.05	Benzene, 1,3-dimethyl-
3	17.212	0.91	96	149.00	Diethyl Phthalate
4	22.123	39.45	96	73.05	n-Hexadecanoic acid
5	23.538	0.56	92	56.10	Pentadecanoic acid, butyl ester
6	24.136	5.43	94	67.05	9,12-Octadecadienoic acid (Z,Z)-
7	24.186	4.35	95	55.05	9-Octadecenoic acid, (E)-
8	24.680	14.80	95	56.05	Hexadecanoic acid, butyl ester
9	26.520	7.44	96	67.05	Butyl 9,12-octadecadienoate
10	26.563	3.82	91	55.05	9-Octadecenoic acid (Z)-, hexadecyl ester
11	26.605	0.88	82	79.05	9,12,15-Octadecatrienoic acid, 1-methylethyl
12	26.817	1.22	93	56.05	Octadecanoic acid, butyl ester
13	27.934	0.70	95	57.10	Eicosane
14	28.858	0.46	82	97.15	1-Nonadecene
15	29.822	6.15	96	57.05	Tetracontane
16	31.251	0.67	90	82.10	Docosanal
17	31.947	1.77	95	57.10	Eicosane
18	33.999	6.22	94	82.05	Nonacosanal
19	38.339	2.47	85	57.00	Palmitaldehyde, dibutyl acetal
20	39.835	1.18	83	57.05	Palmitaldehyde, dibutyl acetal
		100.00			

Figure 4- 18: GC-MS peak report on the composition of refined sugarcane wax (using ethanol)

4.5.9 Summary

Table 4-8 summarizes the chemical properties of the refined wax obtained through the treatment with activated charcoal.

Table 4- 8: Chemical properties of refined wax.

	Refined wax
Acid value (mg KOH/g wax)	23 ± 3
Saponification value (mg KOH/g wax)	59 ± 7
% FFA	12 ± 1
Ester value (mg KOH/g wax)	35 ± 7
Iodine number (g I_2/100 g)	44 ± 8
Unsaponifiable matter (%)	ND*
Melting point (°C)	75 ± 2
Density (g/cm^3) between 20-80°C	0.787 – 0.814
Refractive index (26°C)	1.4867

* ND = not determined

4.6 Summary of sugarcane wax properties obtained from DAF mud, and comparison to carnauba wax

In summary, it can be stated that the crude sugarcane wax obtained from DAF mud is quite different than that obtained from filter mud. This is demonstrated in table 4- 9. As discussed above, fats and oils undergo hydrolysis in the furfural process, leading to relatively high acid and saponification numbers. The ester number is in the range given in the literature for filter mud-derived sugarcane wax. Interestingly, the iodine number of the DAF mud-derived raw wax is much higher than that of the conventional filter mud-derived wax, and the reason for this is presently not known. The unsaponifiable matter is lower. The melting point is in the range reported for filter mud-based crude wax.

The DAF mud-derived refined wax of this study is compared to different wax fractions derived from conventional filter mud-based waxes. It can be stated that the treatment with activated charcoal, as described in this work, reduces the acid value such that it lies in the ranges of “hard wax”, “soft wax” and “refined wax”. The saponification value lies within the ranges of “hard wax” and “refined wax”. The iodine number and the melting point of the refined wax from DAF mud lie within the ranges of “soft wax” and “hard wax”, respectively.

Density measurements for sugarcane wax were conducted over a temperature range of 25 - 80 °C. Figure 4 – 10 and figure 4 – 16 depicts the density of crude wax and refined wax as a function of temperature. As shown, both the crude and refined wax densities decreases with an increasing oven temperature. The density of crude wax ranges from 0.850 – 0.882 g/ cm^3 and refined wax has a density of 0.787 – 0.814 g/cm^3. The obtained densities are comparable to crude wax densities of 0.80-0.85 g/ cm^3 reported by (DEUREX ,2021).

As pointed out in the introduction, it was thought that DAF mud-derived refined wax could serve as a replacement for carnauba wax. Table 4- 9 gives comparative characterisation values. Carnauba wax is described as being soluble in diethyl ether, alkali and chloroform, and boiling ethanol, ethyl acetate and xylene. It is insoluble in water (CAMEO, 2020; Chemicalbook, 2017; Chemicals, 2021; ChemSrc., 2018; AEFS, 2012; CTS, 2020).

It can be stated that the acid value and iodine number are higher than that of carnauba wax, while the melting point and the saponification values are lower. The "total percentage of alcohols and hydrocarbons" is given as 55% (CAMEO, 2020). It is not clear how this percentage is defined, but it may be similar to the compounds eluding at retention times > 27 min. (GC/MS results). In this instance, the DAF mud-derived refined wax has a lower value of about 20%. Without additional refining, it can hence be concluded that the refined DAF mud-based wax may not fulfil the requirements to substitute for carnauba wax.

However, the DAF mud-derived refined wax' properties resemble those of candelilla wax, with the acid and saponification values as well as iodine number being in the same ranges. The melting point is 2-4°C higher than that specified for candelilla wax. Future studies should therefore focus on the market developments and application areas of candelilla wax, and additional refining steps be included, if the carnauba wax market is to be targeted.

Table 4- 9: Properties of sugarcane wax derived from DAF mud and filter mud

	Crude wax		**Refined wax**				**Carn-auba**	**Cande-lilla**
Source	**DAF mud**	**Filtermud**	**DAF mud**	**Filter mud**				
				"hard wax"	**"soft wax"**	**"refined wax"**		
Acid value (mg KOH/g wax)	155 ± 2.2	15-28	23 ± 3	10-30	24-32	23-28	0.4- 9.7	12-20
Saponification value (mg KOH/g wax)	227 ± 10	60-103	59 ± 7	27-77	144-189	56-77	75-95	35-86
% FFA	78 ± 1	-	12 ± 1					
Ester vale (mg KOH/g wax)	72 ± 10	37-120	35 ± 7					
Iodine number (g I_2/100 g)	53 ± 5	6-32	44 ± 8	13-35	49-85	13-29	7-14	14-37
Unsaponifiable matter (%)	21.5 ± 2	44	ND*		23-59			
Melting point (°C)	76 ± 2	66-79	75 ± 2	75-79		79	80-86	67-71
Density	0.850 –		0.787 –			0.80-	0.99-	0.95-

(g/cm^3)	0.882		0.814			0.98	1.00	0.99
Refractive index (26°C)	1.4923	1.50-1.51	1.4867				1.45-1.47	1.46

* ND = not determined. Literature values taken from: Ray 2003; Saleh-e-In et al., 2012; CAMEO, 2020; DEUREX, 2021; Paturau, 1982, 1982; Mitchell, 1979 ,Tinto et al., 2017.

Figure 4- 19 depicts an image for refined carnauba wax (left) (ChemSrc, 2018), and for refined sugarcane wax obtained from the experiments conducted in this study (right).

Figure 4- 19: Refined carnauba wax: literature (left) (ChemSrc, 2018) and of this study (right).

4.7 Process flow sheet and mass balance

In preparation for the estimation of process costing, a flow sheet was prepared (see figure 4-20) followed by the undertaking of mass balances around the whole process.

After a successful laboratory scale production of SW, the conditions were scaled up to an industrial scale to formulate mass balances that are fundamental for future estimation of the costs associated with the project and to assess the economic viability of the process. This was done by preparing a process flow diagram for the proposed process followed by calculation of mass balances. Sizing of major equipment, estimation of the capital cost, production cost and return on investment are to be implemented in a future project.

4.7.1 Preparation of a process flow diagram

The sugarcane wax plant process flow diagram (see figure 4-20) was developed in Aspen® simulation software. The main purpose of the process flow diagram is to depict the basic major units required for the process. It is important to note that the process flow diagram was developed as a preliminary step essential for future economic analyses of present. The sugarcane wax process developed in this study can be optimized by performing sensitivity analysis on the variable costs i.e. utilities to optimize for the TAC (Total Annual Cost) on Aspen ®. However, the simulation and optimization of the developed sugarcane wax process plant are beyond the scope of this dissertation.

The process layout shown in figure 4-20 was developed based on experimental data obtained from a laboratory scale of the process. According to laboratory scale experiments, it was concluded that heating and melting method is preferred over solvent extraction for the following reasons; eco-friendliness, cost effective, uses one solvent (green solvent) for refining crude wax, and faster. Therefore, the process flow diagram for the mass balance was developed using a laboratory scale data, which is based on the heating and melting method. The process flow diagram represents an industrial scale of the developed sugarcane wax process. In a laboratory scale, DAF mud was dried in the oven at 50 ^{o}C to remove water (see section 3.2), followed by the heating of DAF mud and melting of crude wax at 70 ^{o}C. The resulting crude wax was decanted off and separated from the solid residue (see section 3.3.2).

Purification of crude wax was accomplished by mixing crude wax, ethanol and activated charcoal in a heated vessel for about 60 minutes in ratios of 1:4:2 respectively. The separation of refined wax from crude wax achieved by filtration of the slurry cake in the press filter. The resulting wax was collected at the bottom of the filter and the compressed cake was removed and discarded after a complete filtration cycle. Drying of the refined wax was accomplished in the rotary evaporator to remove and recycle the solvent.

The experimental data has shown that crude DAF mud consist of 57.1% water, with 42.9% being the mixture of crude wax and fibrous material. Therefore, for a basis of 100 kg crude DAF mud, one would obtain 57.1 kg water/ 100 kg crude DAF mud and 42.9 kg of crude wax and fibre per 100 kg of crude DAF mud. However, laboratory experiments discussed in section 3.3.1 enabled the determination of dried DAF mud composition. From these experiments, maximum obtainable crude wax yield from dried DAF mud was 87.3% with the remainder being fibrous material. Now, the 87.3% yield of crude wax gives 37.45kg crude wax /42.9 kg dried DAF mud and the remainder is 5.45 kg fibre/42.9 kg dried DAF mud. Assumptions made in mass balance the calculations were based on these experimental results and they were treated as preliminary estimates.

In figure 3- 8, assuming DAF mud (F1) contains 58% water, 5% fibre and 37% wax (based on laboratory experiments), is fed in the drier (D-101) operated at 50 ºC. The DAF mud is assumed to be quantitatively air-dried counter-currently in a rotary drum dryer. Rotary drum dryers are normally used for dilute slurry feeds (Sinnott, 2005). The dried DAF mud stream (F3) is sent to a heater (H-101) operating at 80 ºC to heat the DAF mud and melt the crude wax. The resulting stream (F4) is sent to a decanter unit (V-101) where approximately 55% crude wax together with 10% of the fibre are separated. The remainder F6 is forwarded to extractor X-101.

The crude wax stream (F5) is sent to an agitated vessel (C-101) to mix with a stream of fresh ethanol (F8), activated charcoal stream (F7) and ethanol-wax stream (F14) from the extractor (X-101).

In the extraction unit (X-101) the remaining crude wax is separated from fibre via a solvent extraction method. The extraction is carried out by using the recycled ethanol stream (F13). The resulting two streams from the extraction unit are the ethanol- wax stream (F14) and the residue stream (F12). The residue stream F12 comprises of all residual fibre, as well as 7% and 2% of ethanol and wax, relative to the solids (fibre + wax) contained in F6. The remainder of ethanol and wax (F14) is carried forward to agitated vessel C-101. The residue stream (F12) is sent to a residue mixer (M-101). The ethanol-crude wax stream (F14) is fed to the agitated vessel (C- 101) to mix with the melted crude wax (F5). Activated charcoal and fresh ethanol F8 are added to yield in a ratio of 1:4:1 (crude wax : ethanol : activated charcoal). Both agitated vessels (C-101 and C-102) are assumed to operate isothermally at 75 ºC and isobarically at atmospheric pressure. The contact time in the vessels is kept around 0.5 hrs with perfect mixing assumed. The physical properties of the contents in the vessels are assumed constant throughout. The resulting stream (F10) from the first agitated vessel (C-101) is sent to a press filter (F-101) for about 1 hour to separate refined wax stream (F18) from the activated charcoal residue stream (F17). The refined wax yield obtained from crude wax after filtration is approximately 66.7%. The residue stream

(F17), consisting of the remainder of the wax, all fibre contained in F5, as well as 10% of alcohol, and all activated charcoal, is sent to a residue mixer (M-101), then to effluent treatment stream (F28).

The refined wax stream (F18) is sent to a second agitated vessel (C-102). The main objective of the second agitated vessel is to upgrade the colour purity of the refined wax, by contacting the refined wax-solvent stream (F18) with the split stream of activated charcoal (F19). Charcoal F 19 is added to give a ratio of wax : activated charcoal of 1:1. Note that the ratio wax: ethanol: charcoal is 1:5.4 :1 in C-102. The resulting slurry residue stream (F20) containing refined wax of high colour purity is sent to a second press filter (F-102) to produce refined wax of high colour purity (F22). The residue F19 comprises of all charcoal, 10% of the ethanol as well as 33% of the wax.

The refined wax stream (F22) from the second press filter (F-102) is sent to a steam-heated evaporator (E-102) which operates at a temperature of 80 ºC to boil off all the ethanol.. The steam-heated evaporator E-101 is assumed to have negligible refined wax losses. A 99.9% ethanol recovery in stream (F24) is assumed in E-102. This ethanol stream (F24) is sent to a cooler (B-102), and then to a compression unit (K-101). The compressed ethanol stream (F13) is recycled to the 4-stage extraction unit (X-101). The remainder of the evaporator E-102 is cooled in cooler unit (B-101). The cooled refined wax stream (F26) is collected as the final product.

Table 4- 10: Stream table for sugarcane wax production from DAF mud process

Equipment	**Unit name**	**Associated streams**	**Stream description**
Dryer	D-101	F1, F2, F3	-F1: DAF mud -F2: steam -F3: dried DAF mud
Heater	H-101	F3, F4	-F3: dried DAF mud -F4: molten crude wax
Decanter	V-101	F4, F5, F6	-F4: molten crude wax -F5: crude wax -F6: residue contain some amount of crude wax
Extractor	X-101	F6, F12, F13, F14	-F6: residue contain some amount of crude wax -F12: exhausted residue to M-101, then effluent treatment -F13: recycled ethanol -F14: ethanol wax extract stream

Agitated vessel-1	C-101	F7, F8, F14, F10, F5	-F7: activated charcoal stream -F8: fresh ethanol feed stream - F14: ethanol wax extract stream -F10: slurry stream -F5: crude wax
Filter-1	F-101	F10, F17, F18	-F10: intermediate slurry stream -F17: residue to effluent treatment -F18: refined wax of low colour purity
Agitated vessel-2	C-102	F18, F19, F20	-F18: refined wax of low colour purity -F19: activated charcoal split stream -F20: slurry stream containing refined wax
Filter-2	F-102	F20, F21, F22	-F20: slurry stream containing refined wax -F21: residue stream to M-101 -F22: refined wax of high colour purity in ethanol
Evaporator	E-102	F22, F24, F25	-F22 :refined wax of high colour purity in ethanol -F24: recyle ethanol containing traces of refined wax -F25: refined wax to cooler (B-101)
Cooler-1	B-101	F25, F26	-F25: refined wax to cooler -F26: final product of high colour purity refined wax
Cooler-2	B-102	F23, F24	-F23: cooled ethanol recycle stream -F24: hot ethanol recycle stream
Compressor	K-101	F23, F13	-F23: cooled ethanol recycle stream-F13:compressed ethanol recycle stream
Splitter	S-101	F7, F19, F27	-F7: fresh activated charcoal inlet stream -F19: fresh activated charcoal split stream to C-102 -F27: fresh activated charcoal split stream to C-101
Mixer	M-101	F12, F17, F21, F28	-F12: residue from X-101 -F17: residue from F-101 -F21: residue from F-102 -F28: residue to effluent treatment

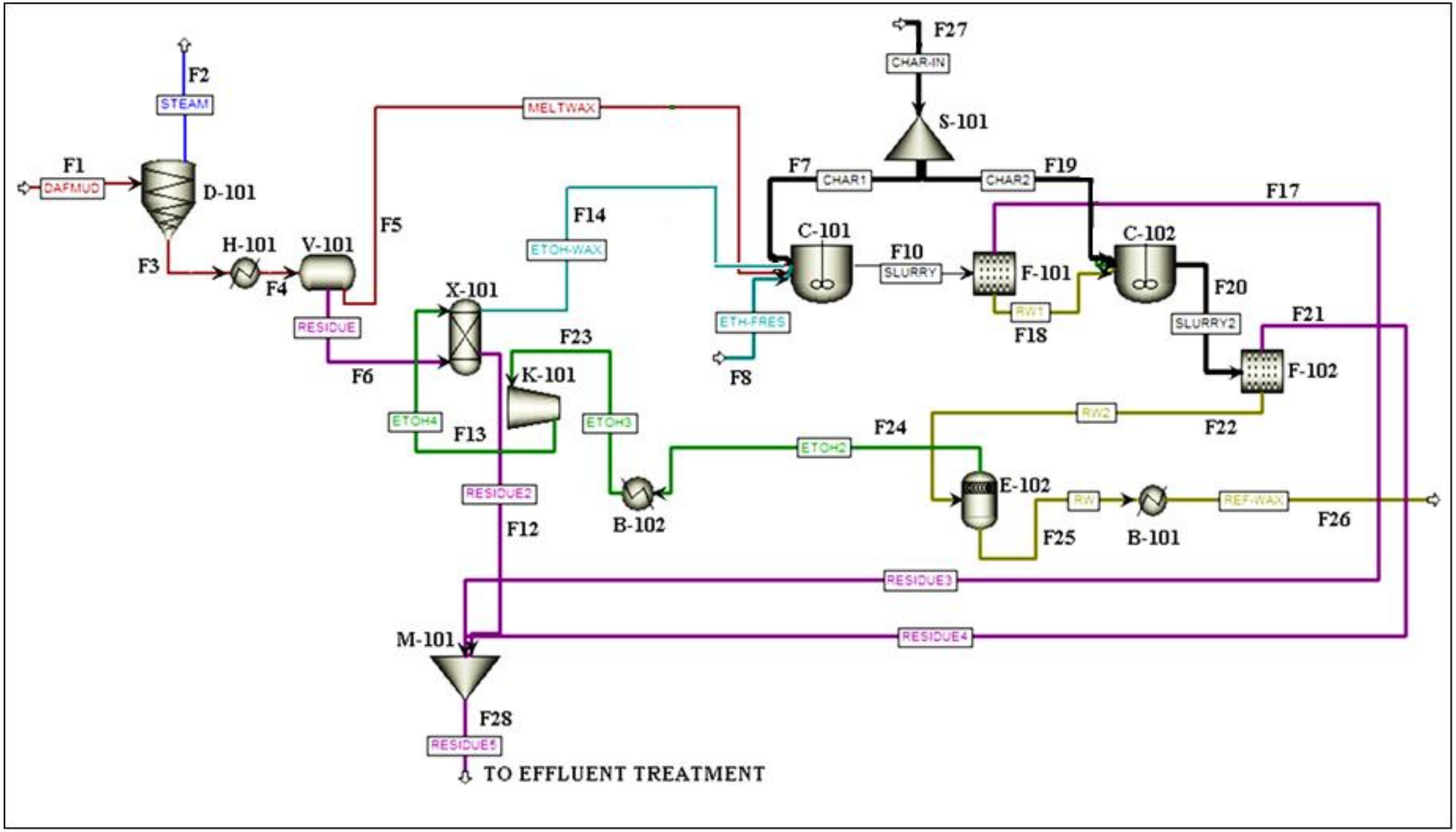


Figure 4- 20: The proposed sugarcane wax plant process flow diagram

4.7.2 Calculation of material balances

The material balances were accomplished using equation **Error! Reference source not found.** assuming that the relevant system properties do not change over time. Under these conditions, the material balance equation simplifies to

$$\text{Input} = \text{output}. \tag{4.1}$$

The following equations were developed from material balances around each unit shown in the process flow diagram (see figure 4-20 **Error! Reference source not found.**).

Mass balances around the dryer (D-101)

Specifications: laboratory experiments have shown that crude DAF mud contains 57.1% water content.

- **Basis**: DAF mud 614.385 kg to get output of 100 kg refined wax/day
- **Assumptions**: 58% water content, 5 % fibre, 37% wax (as discussed in section 4.7.1)

- F1: DAF mud (58% water, 5% fibre, 37% wax)

$$\text{Water}: F1_w = x1_w * F1 \tag{4.2}$$

$$\text{Fibre}: F1_f = x1_f * F1 \tag{4.3}$$

$$\text{Wax}: F1_{wax} = x1_{wax} * F1 \tag{4.4}$$

- F2: water out
- Assumption: complete removal of water in DAF mud

$$\text{Water out}: F2_w = F2 = x2_w * F1_w \tag{4.5}$$

- F3 =F4 crude wax

$$\text{Fibre}: F4_f = F1_f \tag{4.6}$$

$$\text{Wax}: F4_{wax} = F1_{wax} \tag{4.7}$$

$$F3 = F4\ (\text{Total}): F4_{wax} + F4_f \tag{4.8}$$

Crude wax percentage composition in F4

$$\text{fibre}: x3_f = \left(\frac{F1_f}{F1_f + F1_{wax}}\right) * 100 \tag{4.9}$$

$$\text{wax}: x3_{wax} = \left(\frac{F1_{wax}}{F1_f + F1_{wax}}\right) * 100 \tag{4.10}$$

V-101

- F5: crude wax of F4
- assumption that 55% of F4 is contained in F5

- assumption that 10% of the fibre in F4 is contained in F5

crude wax of F4: $F5 = 0.55 * F4$ (4.11)
fiber in crude wax : $F5_f = 0.10 * F4f$ (4.12)
wax in crude wax: $F5_{wax} = F5 - F5_f$ (4.13)

- ➢ F6: residue to X-101
- assumption F6 is 45% of F4

$F6 = 0.45 * F4$ (4.14)

fibre in residue: $F6_f = F4_f - F5_f$ (4.15)
wax in residue: $F6_{wax} = F4_{wax} - F5_{wax}$ (4.16)

<u>X-101</u>

- ➢ Incoming streams: F6 (residue)
  : F13 (ethanol)

- ➢ $F6 = 0.45 * F4$ (4.17)

fibre in residue: $F6_f$ (4.18)
wax in residue: $F6_{wax}$ (4.19)
all ethanol in F24: F13 (4.20)

Outgoing streams: F12 (residue)
: F14 (ethanol wax)

- ➢ F12 (residue):

Assumptions:

- 7% ethanol relative to solids (wax + fibre) in residue F6
- 2% wax lost relative to residue F6

ethanol out: $F12_{ethanol} = 0.07 * (F6_f + F6_{wax})$ (4.21)
wax out: $F12_{wax} = 0.02 * (F6_f + F6_{wax})$ (4.22)
fibre: $F12_f = F6_f$ (4.23)

- ➢ F14 (Ethanol-wax):

wax: $F14_{wax} = F6_{wax} - F12_{wax}$ (4.24)
ethanol: $F14_{ethanol} = F13_{ethanol} - F12_{ethanol}$ (4.25)

$$x13_{ethanol} = \left(\frac{F14_{ethanol}}{F14_{wax} + F14_{ethanol}}\right) * 100 \quad (4.26)$$

<u>C-101</u>

Specifications:

- Laboratory experiments has shown that a crude wax yield of 55% is obtainable from dried DAF mud. It is assumed that over the two activated charcoal treatments, this yield is obtained. Hence, the loss of wax was allocated to the two treatment steps to result in this overall yield.

Assumptions:

- Solids residue retain approximately 10% of crude wax in stream F5

- F5: crude wax of F4

$$\text{crude wax of F4: } F5 = 0.55 * F4 \tag{4.27}$$
$$\text{fiber in crude wax : } F5_f = 0.10 * F4f \tag{4.28}$$
$$\text{wax in crude wax: } F5_{wax} = F5 - F5_f \tag{4.29}$$

- F14: (Ethanol-wax)

$$\text{wax: } F14_{wax} = F6_{wax} - F12_{wax} \tag{4.30}$$
$$\text{ethanol: } F14_{ethanol} = F13_{ethanol} - F12_{ethanol} \tag{4.31}$$

- F8: fresh ethanol required to give a total of 4x of crude wax

$$\text{Fresh ethanol: } F8 = (F5_{wax} + F14_{wax}) * 4 - F14_{ethanol} \tag{4.32}$$

- F7: activated charcoal required to give 1:1 ratio to inlet crude wax

$$\text{activated charcoal: } F7 = F5_{wax} + F14_{wax} \tag{4.33}$$

F10: slurry out

Total slurry out : ratio wax: ethanol: charcoal is 1:4:1

$$\text{Total slurry out: } F10 = F5_{wax} + F8 + F7 + F14_{wax} + F14_{ethanol} \tag{4.34}$$

$$\text{wax: } F10_{wax} = F5_{wax} + F14_{wax} \tag{4.35}$$
$$\text{fibre: } F10_f = 0.10 * F4f \tag{4.36}$$
$$\text{ethanol: } F10_{ethanol} = F14_{ethanol} + F8 \tag{4.37}$$
$$\text{activated charcoal: } F10_{charcoal} = F7 = F5_{wax} + F14_{wax} \tag{4.38}$$

$$\text{The ratio is } = \frac{F10_{wax}}{F10_{wax}} : \frac{F10_{ethanol}}{F10_{wax}} : \frac{F10_{charcoal}}{F10_{wax}} \tag{4.39}$$

$$x10_{wax} = \left(\frac{F10_{wax}}{F10_{total}}\right) * 100 \tag{4.40}$$

$$x10_{fibre} = \left(\frac{F10_{fibre}}{F10_{total}}\right) * 100 \tag{4.41}$$

$$x10_{\text{ethanol}} = \left(\frac{F10_{\text{ethanol}}}{F10_{\text{total}}}\right) * 100 \tag{4.42}$$

$$x10_{\text{charcoal}} = \left(\frac{F10_{\text{charcoal}}}{F10_{\text{total}}}\right) * 100 \tag{4.43}$$

<u>F-101</u>

- F17: Residue

Assumptions:

- contains 10% of the ethanol of F10
- 33.3% of wax loss relative to charcoal.

ethanol: $F17_{\text{ethanol}} = 0.10 * F10_{\text{ethanol}}$ (4.44)
fibre: $F17_{\text{f}} = F10_{\text{f}}$ (4.45)
activated charcoal: $F17_{\text{charcoal}} = F10_{\text{charcoal}}$ (4.46)
wax: $F17_{\text{wax}} = 0.33 * F17_{\text{charcoal}} =$ (4.47)

- F18: refined wax

refined wax: $F18_{\text{wax}} = F10_{\text{wax}} - F17_{\text{wax}}$ (4.48)
ethanol: $F18_{\text{ethanol}} = 0.90 * F10_{\text{ethanol}}$ (4.49)

<u>C-102</u>

- F19: activated charcoal

activated charcoal: $F19_{\text{charcoal}} = F18_{\text{wax}}$ (4.50)

ethanol: $F19_{\text{ethanol}} = 0.90 * F10_{\text{ethanol}}$ (4.51)

- F20: Slurry out

activated charcoal: $F20_{\text{charcoal}} = F19_{\text{charcoal}}$ (4.52)

ethanol: $F20_{\text{ethanol}} = 0.90 * F10_{\text{ethanol}}$ (4.53)

refined wax: $F20_{\text{wax}} = F18_{\text{wax}}$ (4.54)

Total $F20 = F20_{\text{wax}} + F20_{\text{ethanol}} + F20_{\text{charcoal}}$ (4.55)

$$\text{The ratio is } = \frac{F20_{\text{wax}}}{F20_{\text{wax}}} : \frac{F20_{\text{ethanol}}}{F20_{\text{wax}}} : \frac{F20_{\text{charcoal}}}{F20_{\text{wax}}} \tag{4.56}$$

<u>F-102</u>

- F21 (residue)

Assumption:

- contains 10% of the ethanol of F10
- 33.3% of wax loss relative to charcoal.
-

$$\text{activated charcoal: } \mathrm{F21_{charcoal}} = \mathrm{F20_{charcoal}} \tag{4.57}$$

$$\text{wax: } \mathrm{F21_{wax}} = 0.33 * \mathrm{F21_{charcoal}} \tag{4.58}$$

$$\text{ethanol: } \mathrm{F21_{ethanol}} = 0.10 * \mathrm{F20_{ethanol}} \tag{4.59}$$

- F22: filtrate

$$\text{wax: } \mathrm{F22_{wax}} = \mathrm{F20_{wax}} - \mathrm{F21_{wax}} \tag{4.60}$$

$$\text{ethanol: } \mathrm{F22_{ethanol}} = 0.90 * \mathrm{F20_{ethanol}} \tag{4.61}$$

$$\text{Total } \mathrm{F22} = \mathrm{F22_{wax}} + \mathrm{F22_{ethanol}} \tag{4.62}$$

E-102

Assumption:

- 99.99% ethanol recovery on the evaporator

$$\text{ethanol: } \mathrm{F24_{ethanol}} = \mathrm{F22_{ethanol}} = F13 \tag{4.63}$$

$$\text{refined wax: } \mathrm{F25_{wax}} = \mathrm{F22_{wax}} \tag{4.64}$$

The mass balance stream table is displayed in table 4 -11. From the table, it is evident that mass input equals the mass output as per law of conservation. Mass balances calculations displayed in Appendix B and in table 4-11 showed that to produce 100 kg of refined wax one would need 614.4 kg of DAF mud. Mass balance information is essential in subsequent economic evaluation calculations that involves, equipment sizing and overall project costing.

Table 4- 11: Properties of sugarcane wax derived from DAF mud and filter mud

Stream no.	**IN**			**Stream no.**	**OUT**		
F1	DAF mud	614.385	kg	**F2**	water	356.34	kg
	consisting of	356.34	kg water	**F12**	ethanol	8.13	kg
		30.72	kg fibre		wax	2.32	kg
		227.32	kg wax		fibre	27.64	kg
F7	activated charcoal	225.00	kg	**F17**	ethanol	90.00	kg
F19	activated charcoal	150.00	kg		charcoal	225.00	kg
F8	ethanol	79.12	kg		fibre	3.07	kg
					wax	75.00	kg
				F21	wax	50.00	kg
					activated charcoal	150.00	kg
					ethanol	81.00	kg
				F25	product	100.00	kg

				F28	residue	514.39	kg
Total		**1682.90**	**kg**			**1682.90**	**kg**

5 Conclusions and future work

The primary goal of the present study was to valorise a low-cost biomass (DAF mud) through the development of a unique process to produce high value product (refined wax) that could serve as a replacement for carnauba wax. This study has successfully developed a new method for producing sugarcane wax from DAF mud of Illovo's Sezela furfural plant. The newly developed sustainable method has demonstrated success in obtaining 'the DAF mud-derived refined wax' with properties that resemble those of candelilla wax. While most studies in literature have focused on the traditional methods of producing sugarcane wax from press mud using two or more solvents, this study has proven that crude sugarcane wax can be produced using a solvent-free method i.e. heating and melting method. Also, 'the DAF mud-derived refined wax' is produced using ethanol (green solvent), thus making the newly developed process eco-friendly and cost effective (uses less solvent) compared to conventional methods.

Physico-chemical properties (acid value, saponification value, iodine number, unsaponifiables, percentage yield, melting point, density, refractive index and GC-MS) of sugarcane wax were assayed and compared with published literature values and existing commercial waxes. At present, there are no published literature values for 'the DAF mud-derived refined wax' as this is a unique product. However, the results obtained in this study showed that 'the DAF mud-derived refined wax' has properties that resemble those of candelilla wax, with the acid and saponification values as well as iodine number being in the same ranges. However, without additional refining, it can hence be concluded that the refined DAF mud-based wax may not fulfil the requirements to substitute for carnauba wax. Future studies should therefore focus on the market developments and application areas of candelilla wax to assess whether the sugarcane wax could be considered an alternative..

Following successful laboratory scale, the process was scaled up to a larger scale. Up to 65.12 % yield of "the DAF mud derived refined wax" was obtained in a larger scaler using ethanol solvent at ratios 1:4:2. The experimental values (DAF mud composition, yields etc. formed the basis for the mass balance.

A qualitative analysis carried out on sugarcane wax using GC-MS revealed the presence of compound of interest i.e. policosanol. The presence of this compound supports the evidence that sugarcane wax obtained from this study can be applicable to pharmaceutical industries.

Mass balance undertaken as a preliminary project cost estimation showed that a production target of 100 kg refined wax could be achieved requiring 614.4 kg of DAF mud.

Future work should include the investigation of the size and cost of equipment required to produce a completely eco-friendly sugarcane wax, using the developed mass balance equations, as well as performing economic analysis of the process by calculation of the overall project cost and return on investments (ROI) to determine the feasibility of the process.

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Appendices

Appendix A1: Raw data for preparation of standard solutions

i. Standardisation of 0.1M KOH with 0.1 M KHP

Table A1 - 1: Standardisation of 0.1M KOH with 0.1010 M KHP

Run	Start volume (mL)	End volume (mL)	Titre (mL)
Rough	0.0	9.4	9.4
1	9.4	19.4	10.0
2	19.4	28.6	9.2
3	28.6	36.5	7.9
4	0.0	9.2	9.2
5	9.2	17.5	8.3
Average			8.92

Sample calculation for the preparation of 250 mL of a 0.1M KHP, using 99.5% pure KHP

$$\mathrm{C_{KHP}} = \frac{\mathrm{m_{KHP}}}{\mathrm{MM_{KHP} * V_{KHP}}} = \frac{5.1850\mathrm{g} * 0.995}{204.22\frac{\mathrm{g}}{\mathrm{mol}} * 0.25\ \mathrm{L}} = 0.1010\ \mathrm{M}$$

Sample calculation for the preparation of 1L of a 0.1 M KOH solution, using 85% pure KOH, and its standardization with 0.101 M KHP

The theoretical concentration of the KOH solution was calculated by using the actual mass of the KOH weighed out.

$$C_{\mathrm{KOH}} = \frac{\mathrm{m_{KOH}}}{\mathrm{MM_{KOH} * V_{KOH}}} = \frac{6.601\ * 0.85\mathrm{g}}{56.11\frac{\mathrm{g}}{\mathrm{mol}} * 1\mathrm{L}} = 0.1000\ \mathrm{mol\ (theoretically)}$$

The concentration of the KOH solution prepared is not accurate because KOH is hygroscopic. Thus, the corrected concentration was calculated using the average titre volume. 10mL aliquots of the 0.1010 MKHP were pipetted into conical flask and titrated against KOH. See table A1-1

$$\mathrm{C_{KHP}V_{KHP}} = \mathrm{C_{KOH}V_{avg\ KOH\ delivered}}$$

$$(0.10105\mathrm{M})(10\mathrm{ml}) = \mathrm{C_{KOH}}(8.92\mathrm{ml})$$

$$\mathrm{C_{KOH}} = \mathbf{0.1133\ M}$$

ii. Standardisation of 0.1 M HCl with 0.1M KOH

Table A1 - 2: Raw data used for standardisation of 0.1M HCl with 0.1133 M KOH

Run	Start (ml) KOH	End (ml) KOH	Titre (ml) KOH
Rough	0.0	9.5	9.5
1	9.5	18.8	9.3
2	18.8	29.0	10.2
3	29.0	38.8	9.8
4	38.8	47.9	9.1
Average			9.58

Sample calculation for the preparation of 1L of a 0.1 M HCl and standardization with 0.1133 M KOH

The density of a 37% concentrated HCl is 1.19 g/ml, the atomic mass of HCl 36.46 g/mol

$$\text{Molarity} = \frac{(37\%)(1000)(1{,}19)}{(100)(36{,}46)} = 12{,}07\frac{\text{mol}}{\text{mL}} = 12{,}07\ \text{M}$$

If 37% dilute HCl has a molarity of 12.07 M, then to make a 1L solution of 0,1 M HCl

$$\text{Molarity}_{\text{HCL}(37\%)} * \text{Vol}_{\text{HCL to dilute}} = \text{Molarity}_{\text{HCL}(100\%)} * \text{Vol}_{\text{HCL (in 1L)}}$$

$$\text{Vol}_{\text{HCL to dilute}} = \frac{\text{Molarity}_{\text{HCL}(100\%)} * \text{Vol}_{\text{HCL (in 1L)}}}{\text{Molarity}_{\text{HCL}(37\%)}} = \frac{(0.1\ \text{M}) * (1\text{L})}{12.07\text{M}}$$

$$= 0.0083 * 1000 = \mathbf{8.283\ ml\ \frac{HCl}{L}}$$

8.3 mL HCl were used and diluted to 1L with water. Table A1-3 depicts the raw data for standardization of HCl with KOH. The obtained average titre volume is 9.58 ml.

$$0.1133\text{M} * 9.58\text{ml} = \text{C}_{\text{HCl}} * 10\ \text{ml} => \ \text{C}_{\text{HCl}} = \frac{0.1123\text{M} * 9.58\text{ml}}{10\ \text{ml}} = 0.1085\ \text{M HCl}$$

iii. **Standardisation of 0.1 M ethanoic KOH with 0.1 M HCl**

Table A1 - 3: Standardisation of 0.1 M ethanoic KOH with 0.1085 M HCl

Run	**Start (ml) tOH KOH**	**End(ml) etOH KOH**	**Titre(ml) etOH KOH**
rough	0.0	9.9	9.9
1	9.9	19.2	9.3
2	19.2	28.6	9.4
3	28.6	38.0	9.4
4	38.0	47.5	9.5
5	0.0	9.3	9.3
Average			9.38

Sample calculation for the standardisation of 100 mL of a 0.1 M ethanolic KOH solution with 0.1010 M KHP

10mL aliquots of the 0.1010 MKHP were pipetted into conical flask and titrated against KOH. See table A1-1

$$\text{C}_{\text{KHP}}\text{V}_{\text{KHP}} = \text{C}_{\text{KOH}}\text{V}_{\text{avg KOH delivered}}$$

$$(0.1010\text{M})(10.00\ \text{ml}) = \text{C}_{\text{KOH}}(9.38\text{ml})$$

$$\text{C}_{\text{KOH}} = \mathbf{0.1077133\ M}$$

iv. Standardisation of 0.1 M sodium thiosulfate

Table A1 - 4: Raw data for standardization of 0.1 M sodium thiosulfate

Volume chloroform (mL)	10			
Volume Hanus (IBr) (mL)	25			
Runs	**Mass of $K_2Cr_2O_7$(g)**	**Start (mL) $H_{10}Na_2O_8S_2$**	**End (mL) $H_{10}Na_2O_8S_2$**	**Titre (mL) $H_{10}Na_2O_8S_2$**
Rough	0.211	0.0	46.0	46.0
1	0.246	0.0	44.0	44.0
2	0.208	0.0	43.0	43.0
3	0.216	0.0	46.0	46.0
4	0.244	0.2	43.0	43.0
5	0.201	0.3	44.0	44.0
6	0.239	0.0	46.0	46.0
Average	**0.226**			**44.3**

Sample calculation for the preparation of 1 L of 0.1M sodium thiosulfate solution and its standardization with 0.1010 M KHP

From equation 3-1, and the raw data provided in Appendix A1, table A1-4, the normality of sodium thiosulfate was calculated as below;

$$\mathrm{N} = 20.394 * \left(\frac{\mathrm{W}}{\mathrm{V}}\right)$$

Where W (average $Cr_2K_2O_7$ weight (g) = 0.226

V (Average titre volume) (ml) = 43.67, thus;

$$\mathrm{N} = 20.394 * \left(\frac{\mathrm{W}}{\mathrm{V}}\right) = 20.394 * \left(\frac{0.226}{44.3}\right) = 0.1040\ \mathrm{N}$$

Appendix A2: Acid values of solvents

Table A2 - 1:Summary of raw data used for the calculations of the acid values of neutral solvents. Each titration is based on the average volume of KOH used in 4 titrations.

solvent	**Sample name**	**Volume solvent (ml)**	**Mass solvent (g)**	**volume KOH (ml)**	**Acid value (mg KOH/g)**
butanol	SM-01-BUT-AV	10.00	7.778	0.063	**0.0506**
toluene	SM-01-TOL-AV	10.00	8.613	0.063	**0.0457**
turpentine	SM-03-TUP-AV	10.00	8.398	0.050	**0.0375**
2-butanone	SM-01-BTN-AV	10.00	8.048	0.063	**0.0489**
ethanol	SM-03-BTN-AV	10.00	7.888	0.063	**0.0499**

Sample calculation for the solvent acid value

The sample calculation below is based on toluene solvent (SM-TOL-AV) for values.

$$\text{Acid value} = \frac{\text{Molecular Weight KOH}\left(\frac{\text{g}}{\text{mol}}\right) * \text{Molarity KOH}\left(\frac{\text{mol}}{\text{L}}\right) * \text{titre vol. (ml)}}{\text{mass of solvent sample (g)}}$$

The density and the purity of toluene at room temperature as provided by the supplier are 0.870 g/ml and 99.00% respectively, thus mass of toluene in a 10 ml aliquot sample is given by:

$$\text{mass of solvent sample (g)} = \text{density} * \text{vol of sample} * \text{purity of solvent}$$

$$\text{mass of sample (g)} = 0.870\,\frac{\text{g}}{\text{ml}} * 10\text{ml} * 0.99 = 8.613\text{ g}$$

$$\text{Acid value} = \frac{56.11\left(\frac{\text{g}}{\text{mol}}\right) * 0.1123\left(\frac{\text{mol}}{\text{L}}\right) * 0.0625(\text{ml})}{8.613\text{ (g)}} = 0.0457\,\frac{\text{mg KOH}}{\text{g sample}}$$

Appendix A3: Raw data (moisture content, heating time, and crude wax yield)

i. Moisture content: DAF mud

Table A3 - 1:Raw data for determination of moisture content of DAF mud

Batch no.	Sample no.	Mass loss (g)	Mass loss (%)
SM-01-T-t-WC	1	108.40	56.94
SM-01-T-t-WC	2	110.02	57.97
SM-01-T-t-WC	3	105.91	57.79
Average		**108.11**	**57.57**
SM-02-T-t-WC	1	106.60	55.82
SM-02-T-t-WC	2	114.70	60.34
SM-02-T-t-WC	3	104.60	57.28
Average		**108.63**	**57.81**
SM-03-T-t-WC	1	109.00	56.21
SM-03-T-t-WC	2	99.10	52.79
SM-03-T-t-WC	3	107.20	59.09
Average		**105.10**	**56.03**

Sample calculation for moisture content of crude DAF mud

$$\text{Water content }(\%) = \frac{(\text{Mass of original sample} - \text{Mass of the dried sample})}{\text{Mass of original sample}} \text{ x } 100$$

$$\text{Water content }(\%) = \frac{(190.4 - 82.0)}{190.4} \text{ x } 100 = 56.9\%$$

The average water content from table A3-1 is given by:

$$\text{Water content}(\%) = \frac{57.57\% + 57.81\% + 56.03\%}{3} = 57.1\ \%$$

ii. Crude wax yield

Table A3 - 2: Raw data for determination of crude wax yield from dried DAF mud-extraction method

solvent	Sample name	DAF mud (g)	solids (g)	% solids	mass wax (g)	total volume (ml)	% yield
butanol	SM-01-BUT-AV	10.305	1.358	13.2	8.947	100	86.8
butanol	SM-02-BUT-AV	10.129	1.256	12.4	8.873	100	87.6
butanol	SM-03-BUT-AV	10.338	1.287	12.4	9.051	100	87.6
toluene	SM-01-TOL-AV	10.011	1.385	13.8	8.626	100	86.2
toluene	SM-02-TOL-AV	10.11	1.501	14.8	8.609	100	85.2
toluene	SM-03-TOL-AV	10.025	1.441	14.4	8.584	100	85.6
turpentine	SM-01-TUP-AV	10.019	2.021	20.2	7.998	100	79.8
turpentine	SM-02-TUP-AV	10.018	1.868	18.6	8.15	100	81.4
turpentine	SM-03-TUP-AV	10.124	1.832	18.1	8.292	100	81.9
2-butanone	SM-01-BTN-AV	10.113	1.311	13.0	8.802	100	87.0
2-butanone	SM-02-BTN-AV	10.238	1.621	15.8	8.617	100	84.2
2-butanone	SM-03-BTN-AV	10.148	1.624	16.0	8.524	100	84.0

$$\%\text{ yield crude wax (dry basis)} = \frac{\text{Mass of dried Daf mud (g)} - \text{Mass of solids(g)}}{\text{Mass of dried DAF mud (g)}} \text{ x } 100 = \frac{10.305\text{ g} - 1.358\text{ g}}{10.305\text{ g}} = 86.82\ \%$$

Table A3 - 3: Raw data for determination of crude wax yield from dried DAF mud- heating and melting method

	SM-01-T-CWY			SM-02-T-CWY			SM-03-T-CWY		
Temperature (°C)	Initial mass DAF mud (g)	Final mass after decanting (g)	Crude wax yield (%)	Initial mass DAF mud (g)	Final mass after decanting (g)	Crude wax yield (%)	Initial mass DAF mud (g)	Final mass after decanting (g)	Crude wax yield (%)
65	112.68	46.18	40.98	100.2	41.2	41.11	199.5	85.4	42.80
70	109.87	49.50	45.05	99.5	46.8	47.03	200.1	98.2	49.07
75	100.75	52.95	52.56	97.6	50.1	51.33	198.5	102.2	51.48
80	111.55	61.75	55.35	98.6	52.6	53.34	197.2	103.0	52.23
85	94.16	50.93	54.08	101.3	54.2	53.50	201.5	102.5	50.86

Sample calculation for crude wax yield

The following percentage yield calculation is based on the crude wax SM-01-T-CWY sample corresponding to 80 ˚C temperature interval.

$$\%\ \text{crude wax yield (dry basis)} = \frac{\text{Mass of crude wax received}}{\text{mass of DAF mud before melting}}\ \text{x}\ 100 = \frac{61.75\text{g}}{111.55\ \text{g}} = 55.35\ \%$$

iii. Refined wax yield

Table A3 - 4: Raw data for determination of refined wax yield from crude wax (mud- heating and melting method

Entry	**Solvent**	**Ratios(CW/ Solvent/ Charcoal)**	**Yield (%)Refined wax**
1	Butan-1-ol	1:05:01	62.6
2	Butan-1-ol	1:05:02	63.2
3	Butan-1-ol	1:08:02	65.4
4	Butan-1-ol	1:10:04	67.1
5	2-Butanone	1:05:01	33.9
6	2-Butanone	1:08:02	42.1
7	Toluene	1:05:02	44.0
8	Toluene	1:08:02	46.6
9	Toluene	1:08:02	44.5
10	Ethanol	1:04:02	65.1
11	Ethanol	1:08:02	56.2
12	Ethanol	1:10:04	55.3

Sample calculation for refined wax yield

The following percentage yield calculation is based on the refined wax sample (entry 10) using ethanol (Ratios(CW/ Solvent/ Charcoal, 1:04:02)) as shown in table A3- 4.

$$\%\ \text{refined wax} = \frac{\text{Mass of refined wax obtained}}{\text{initial mass of crude wax}}\ \text{x}\ 100 = \frac{13.116\ \text{g}}{20.141\ \text{g}} = 65.12\ \%$$

Appendix A4: Raw data for characterization of crude wax (solvent extraction method)

i. Acid values and percentage free fatty acids

Table A4 - 1:Summary of raw data used for the calculations of crude wax acid values extracted from dried DAF mud. Each titration is based on the average volume of KOH used in 4 titrations.

solvent	Sample name	mass wax (g)	total volume (ml)	volume of sample (ml)	mass in sample (g)	volume KOH (ml)	Acid value (mg KOH/g)	%FFA
butanol	SM-01-BUT-AV	8.947	100	10.00	0.895	16.28	115.6	58.2
butanol	SM-02-BUT-AV	8.873	100	10.00	0.887	16.16	115.8	58.3
butanol	SM-03-BUT-AV	9.051	100	10.00	0.905	16.42	115.3	58.1
toluene	SM-01-TOL-AV	8.626	100	10.00	0.863	15.58	114.8	57.8
toluene	SM-02-TOL-AV	8.609	100	10.00	0.861	15.56	114.9	57.8
toluene	SM-03-TOL-AV	8.584	100	10.00	0.858	15.48	114.7	57.7
turpentine	SM-01-TUP-AV	7.998	100	10.00	0.800	14.40	114.4	57.6
turpentine	SM-02-TUP-AV	8.150	100	10.00	0.815	14.72	114.8	57.8
turpentine	SM-03-TUP-AV	8.292	100	10.00	0.829	14.96	114.7	57.8
2-butanone	SM-01-BTN-AV	8.802	100	10.00	0.880	15.92	115.0	57.9
2-butanone	SM-02-BTN-AV	8.617	100	10.00	0.862	15.58	114.9	57.8
2-butanone	SM-03-BTN-AV	8.524	100	10.00	0.852	15.40	114.9	57.8

ii. Saponification and ester values

Table A4 - 2: Summary of raw data used in the calculations of crude wax saponification values and ester values extracted from dried DAF mud. Each titration is based on the average volume of KOH used in 3 titrations.

Sample name	Solvent	mass wax (g)	total volume (ml)	volume of sample (ml)	mass in sample (g)	Volume HCl (mL)	Volume HCl blank (mL)	Saponification value (mg KOH/g)	Ester value (mg KOH/g)
SM-01-DAF-BUT-SAP	butanol	8.477	100	10	0.141	3.38	5.95	110.7	-4.9
SM-02-DAF-BUT-SAP	butanol	7.180	100	10	0.120	3.25	5.38	108.1	-7.7
SM-03-DAF-BUT-SAP	butanol	6.00	100	10	0.100	3.50	5.65	130.9	15.5
SM-01-DAF-TOL-SAP	toluene	8.163	100	10	0.136	3.48	5.70	99.6	-15.2
SM-02-DAF-TOL-SAP	toluene	7.638	100	10	0.127	3.30	5.18	89.7	-25.2
SM-03-DAF-TOL-SAP	toluene	6.465	100	10	0.108	3.25	5.58	131.4	16.7
SM-01-DAF-TUP-SAP	turpentine	6.756	100	10	0.113	3.38	5.63	121.7	7.2
SM-02-DAF-TUP-SAP	turpentine	6.492	100	10	0.108	3.28	5.23	109.7	-5.1
SM-03-DAF-TUP-SAP	turpentine	7.973	100	10	0.133	3.33	5.50	99.6	-15.1
SM-01-DAF-BTN-SAP	2-butanone	6.609	100	10	0.110	3.52	5.43	105.3	-9.7
SM-02-DAF-BTN-SAP	2-butanone	4.955	100	10	0.083	3.36	5.33	144.9	30.0
SM-03-DAF-BTN-SAP	2-butanone	7.436	100	10	0.124	3.56	5.70	105.1	-9.8

Appendix A5: Raw data for characterization of crude wax (heating and melting method) acid values and percentage free fatty acids

Table A5 - 1: Summary of the raw data used for the calculations of crude wax acid values obtained from the heating and melting method from dried DAF mud. Each titration is based on the average volume of KOH used in 4 titrations

solvent	Sample name	mass wax (g)	volume KOH (ml)	Acid value (mg KOH/g sample)	FFA%
butanol	SM-01-CW-BUT-AV	0.254	6.30	157.7	79.4
butanol	SM-02-CW-BUT-AV	0.255	6.04	150.6	75.8
butanol	SM-03-CW-BUT-AV	0.254	6.30	157.7	79.4
toluene	SM-01-CW-TOL-AV	0.256	6.15	152.7	76.9
toluene	SM-02-CW-TOL-AV	0.258	6.26	154.2	77.7
toluene	SM-03-CW-TOL-AV	0.254	6.30	157.7	79.4
turpentine	SM-01-CW-TUP-AV	0.256	6.20	154.0	77.5
turpentine	SM-02-CW-TUP-AV	0.255	6.28	156.6	78.8
turpentine	SM-03-CW-TUP-AV	0.258	6.30	155.2	78.1
2-butanone	SM-01-CW-BTN-AV	0.250	6.10	155.1	78.1
2-butanone	SM-02-CW-BTN-AV	0.251	6.20	157.0	79.1
2-butanone	SM-03-CW-BTN-AV	0.252	6.15	155.1	78.1

i. Saponification

Summary of raw data used in the calculations of crude wax saponification values and ester values extracted from dried DAF mud. Each titration is based on the average volume of KOH used in 3 titrations.

Sample name	**Solvent**	**mass wax (g)**	**total volume (ml)**	**volume of sample (ml)**	**mass in sample (g)**	**Volume HCl (mL)**	**Volume HCl blank (mL)**	**Saponification value (mg KOH/g)**
S-01-CW-SAP-01	ethanol	0.252	30	5	0.042	1.65	4.15	239.2
S-01-CW-SAP-02*	ethanol	0.275	30	5	0.045833	1.95	4.33	259.0
S-01-CW-SAP-03*	ethanol	0.256	30	5	0.042667	2.01	4.33	286.8
S-02-CW-SAP-01	ethanol	0.251	30	5	0.041833	1.46	4.08	212.5
S-02-CW-SAP-02	ethanol	0.251	30	5	0.041833	1.52	4.08	221.2
S-02-CW-SAP-03	ethanol	0.256	30	5	0.042667	1.54	4.22	219.7
S-03-CW-SAP-01	ethanol	0.254	30	5	0.042333	1.58	4.18	227.2
S-03-CW-SAP-02	ethanol	0.254	30	5	0.042333	1.59	4.17	228.7
S-03-CW-SAP-03	ethanol	0.254	30	5	0.042333	1.68	4.18	241.6

*outlier

ii. Iodine number

Table A5 - 2: Summary of raw data used in the calculations of iodine number for samples extracted from dried DAF mud. Each titration is based on the average of 3 titrations.

Sample name	mass wax (g)	Volume thiosulfate (mL)	Volume thiosulfate blank (mL)	Iodine number (gI_2/100g)
SM-01-CW-ID-01	0.255	41.0	51.5	55.1
SM-01-CW- ID -02	0.254	44.5	55.7	59.0
SM-01-CW- ID -03	0.254	43.2	54.8	61.1
SM-02-CW- ID -01	0.254	42.8	52.1	49.0
SM-02-CW- ID -02	0.256	43.5	51.3	40.8
SM-02-CW- ID -03	0.254	42.1	50.8	45.9
SM-03-CW- ID -01	0.251	41.8	51.4	51.2
SM-03-CW- ID -02	0.258	43.2	54.1	56.6
SM-03-CW- ID -03	0.253	40.5	52.1	61.4

iii. Raw data for determination of unsaponifiable matter of crude wax

Table A5 - 3: Summary of raw data used in the calculations of the unsaponifiable matter for samples extracted from dried DAF mud.

Sample name	mass wax (g)	Mass unsaponifiable matter (g)	% unsaponifiable matter
SM-01-UNSP-A	5.338	1.116	20.91
SM-01- UNSP-B	5.373	1.026	19.10
SM-02- UNSP-C*	5.076	0.536	10.56
SM-02- UNSP-D	5.114	1.166	22.80
SM-03- UNSP-E	5.331	1.088	20.41
SM-03- UNSP-F	5.331	1.296	24.31

* outlier

Appendix A6: Raw data for characterization of refined wax

i. Acid values and percentage free fatty acid

Table A6 - 1: Summary of raw data used for the calculations of refined wax acid values. Each titration is based on the average volume of KOH (0.1044 M) used in 3 titrations.

solvent	**Sample name**	**mass wax (g)**	**total volume (ml)**	**volume KOH (ml)**	**Acid value (mg KOH/g)**	**%FFA**
butanol	SM-01-RW-BUT-AV	0.257	25	1.000	22.8	11.5
butanol	SM-02-RW-BUT-AV	0.255	25	0.900	20.7	10.4
butanol	SM-03-RW-BUT-AV	0.253	25	1.075	24.9	12.5
toluene	SM-01-RW-TOL-AV	0.251	25	0.600	14.0	7.0
toluene	SM-02-RW-TOL-AV	0.253	25	0.825	19.1	9.6
toluene	SM-03-RW-TOL-AV	0.253	25	1.100	25.5	12.8
turpentine	SM-01-RW-TUP-AV	0.255	25	0.925	21.2	10.7
turpentine	SM-02-RW-TUP-AV	0.252	25	0.925	21.5	10.8
turpentine	SM-03-RW-TUP-AV	0.249	25	0.975	22.9	11.5
2-butanone	SM-01-RW-BTN-AV	0.254	25	1.000	23.1	11.6
2-butanone	SM-02-RW-BTN-AV	0.250	25	0.975	22.8	11.5
2-butanone	SM-03-RW-BTN-AV	0.249	25	0.950	22.3	11.3

ii. Saponification values and ester values

Table A6 - 2: Summary of raw data used in the calculations of refined wax saponification values and ester values. Each titration is based on the average volume of KOH used in 4 titrations.

Sample name	**Solvent**	**mass wax (g)**	**total volume (ml)**	**volume of sample (ml)**	**mass in sample (g)**	**Volume HCl (mL)**	**Volume HCl blank (mL)**	**Saponification value (mg KOH/g)**
S-01-RW-SAP-01	ethanol		30	5	0.254	3.18	5.72	60.8
S-01-RW-SAP-02	ethanol		30	5	0.230	3.44	5.60	57.1
S-01-RW-SAP-03	ethanol		30	5	0.244	3.50	5.70	54.8
S-02-RW-SAP-01	ethanol		30	5	0.206	3.60	5.92	68.5
S-02-RW-SAP-02	ethanol		30	5	0.244	3.44	5.74	57.3
S-02-RW-SAP-03	ethanol		30	5	0.223	3.60	5.40	49.2
S-03-RW-SAP-01	ethanol		30	5	0.206	3.40	5.68	67.3
S-03-RW-SAP-02	ethanol		30	5	0.200	3.42	5.54	64.5
S-03-RW-SAP-03	ethanol		30	5	0.243	3.48	5.40	48.2

iii. Iodine number

Table A6 - 3: Summary of raw data used in the calculations of iodine number for refined wax samples. Each titration is based on the average of 3 titrations.

Sample name	**mass wax (g)**	**Volume thiosulfate (mL)**	**Volume thiosulfate blank (mL)**	**Iodine number (gI_2/100g)**
SM-01-CW-ID-01	0.253	37.0	46.0	47.6
SM-01-CW- ID -02	0.258	36.8	45.0	42.6
SM-01-CW- ID -03	0.251	37.5	46.8	49.6
SM-02-CW- ID -01	0.251	35.0	44.5	50.7
SM-02-CW- ID -02	0.255	36.7	45.0	43.6
SM-02-CW- ID -03	0.259	37.2	43.6	33.1
SM-03-CW- ID -01	0.247	35.8	44.5	47.2
SM-03-CW- ID -02	0.251	34.7	43.0	44.3
SM-03-CW- ID -03	0.257	36.5	44.3	40.6

Appendix A 7: Density of crude and refined wax

Table A7 - 1: Density of crude wax at various temperatures

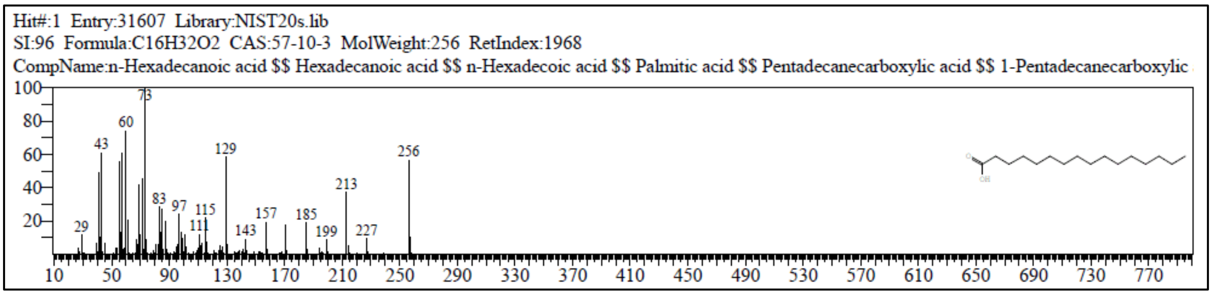
Temperature	Vessel no.	Vessel + Lid (g)	Density water (g/ml)	(vessel +lid + water)(g)	Mass of water (g)	Vessel volume (ml)	Wax. vessel+lid (g)	mass of wax (g)	density of wax(g/ml)	Average density (g/ml)	SD %
25	**13**	58.519	0.997	66.905	8.386	8.411	65.967	7.451	0.886		
	14	57.491	0.997	65.822	8.331	8.356	64.855	7.369	0.882	0.884	0.317
	17	56.916	0.997	65.304	8.388	8.413	64.290	7.374	0.876		
	18	60.217	0.997	68.430	8.213	8.238	67.330	7.113	0.863	0.870	1.057
	4	57.379	0.997	66.260	8.881	8.908	65.487	8.111	0.911		
	1	57.888	0.997	65.749	7.861	7.885	64.769	6.882	0.873	0.892	2.991
										0.882	
40	**13**				8.313	8.411	65.966	7.451	0.886		
	14				8.248	8.356	64.854	7.359	0.881	0.883	0.413
	17				8.302	8.413	64.290	7.374	0.876		
	18				8.110	8.238	67.329	7.113	0.863	0.870	1.057
	4				8.816	8.908	65.488	8.111	0.911		
	1				7.780	7.885	64.764	6.872	0.872	0.891	3.094
										0.881	
50	**13**				8.236	8.411	65.965	7.451	0.886		
	14				8.14	8.356	64.854	7.359	0.881	0.883	0.413
	17				8.197	8.413	64.288	7.374	0.876		
	18				8.024	8.238	67.329	7.113	0.863	0.870	1.057
	4				8.751	8.908	65.486	8.111	0.911		
	1				7.706	7.885	64.763	6.872	0.872	0.891	3.094
										0.881	
60	**13**				7.862	8.411	65.724	7.201	0.856		
	14				7.689	8.356	64.811	7.319	0.876	0.866	1.615
	17				7.736	8.413	64.051	7.134	0.848		
	18				7.639	8.238	67.087	6.873	0.834	0.841	1.145
	4				8.427	8.908	65.121	7.741	0.869		
	1				7.374	7.885	64.487	6.602	0.837	0.853	2.627
										0.853	
70	**13**				7.474	8.411	65.720	7.201	0.856		
	14				7.340	8.356	64.716	7.229	0.865	0.861	0.740
	17				7.339	8.413	64.049	7.134	0.848		
	18				7.372	8.238	67.085	6.873	0.834	0.841	1.145
	4				8.118	8.908	65.120	7.741	0.869		
	1				7.084	7.885	64.476	6.592	0.836	0.853	2.734
										0.851	
80	**13**				6.457	8.411	65.714	7.191	0.855		
	14				6.506	8.356	64.672	7.179	0.859	0.857	0.347
	17				6.641	8.413	64.048	7.134	0.848		
	18				6.588	8.238	67.082	6.863	0.833	0.841	1.248
	4				7.222	8.908	65.116	7.741	0.869		
	1				6.131	7.885	64.471	6.582	0.835	0.852	2.842
										0.850	

Table A7 - 2: Density of refined wax (using ethanol, ratio 1:4:2) at various temperatures

Temperature	**Vessel no.**	**Vessel + Lid (g)**	**Density (g/ml)**	**(vessel +lid + water)(g)**	**Mass of water (g)**	**Vessel volume (ml)**	**Wax. vessel+lid (g)**	**mass of wax (g)**	**density of wax(g/ml)**	**Average Density (g/ml)**	**SD %**
25	**13**	58.519	0.997	66.905	8.386	8.411	64.712	6.193	0.736		
	14	57.491	0.997	65.822	8.331	8.356	64.289	6.798	0.814	0.775	7.050
	17	56.916	0.997	65.304	8.388	8.413	63.926	7.010	0.833		
	18	60.217	0.997	68.430	8.213	8.238	66.905	6.688	0.812	0.823	1.834
	4	57.379	0.997	66.260	8.881	8.908	64.076	6.697	0.752		
	1	57.888	0.997	65.749	7.861	7.885	65.261	7.373	0.935	0.843	15.366
										0.814	
40	**13**	58.519				8.411	64.689	6.170	0.734		
	14	57.491				8.356	64.271	6.780	0.811	0.772	7.126
	17	56.916				8.413	63.914	6.998	0.832		
	18	60.217				8.238	66.885	6.668	0.809	0.821	1.925
	4	57.379				8.908	64.070	6.691	0.751		
	1	57.888				7.885	65.253	7.365	0.934	0.843	15.352
										0.812	
50	**13**	58.519				8.411	64.631	6.112	0.727		
	14	57.491				8.356	64.216	6.725	0.805	0.766	7.217
	17	56.916				8.413	63.858	6.942	0.825		
	18	60.217				8.238	66.830	6.613	0.803	0.814	1.942
	4	57.379				8.908	64.035	6.656	0.747		
	1	57.888				7.885	65.223	7.335	0.930	0.839	15.434
										0.806	
60	**13**	58.519				8.411	64.563	6.044	0.719		
	14	57.491				8.356	64.153	6.662	0.797	0.758	7.343
	17	56.916				8.413	63.792	6.876	0.817		
	18	60.217				8.238	66.771	6.554	0.796	0.806	1.900
	4	57.379				8.908	63.970	6.591	0.740		
	1	57.888				7.885	65.166	7.278	0.923	0.831	15.574
										0.799	
70	**13**	58.519				8.411	64.521	6.002	0.714		
	14	57.491				8.356	64.099	6.608	0.791	0.752	7.260
	17	56.916				8.413	63.735	6.819	0.811		
	18	60.217				8.238	66.708	6.491	0.788	0.799	1.995
	4	57.379				8.908	63.920	6.541	0.734		
	1	57.888				7.885	65.109	7.221	0.916	0.825	15.557
										0.792	
80	**13**	58.519				8.411	64.50	5.981	0.711		
	14	57.491				8.356	64.078	6.587	0.788	0.750	7.283
	17	56.916				8.413	64.723	7.807	0.928		
	18	60.217				8.238	66.101	5.884	0.714	0.821	18.400
	4	57.379				8.908	63.907	6.528	0.733		
	1	57.888				7.885	64.560	6.672	0.846	0.790	10.152
										0.787	

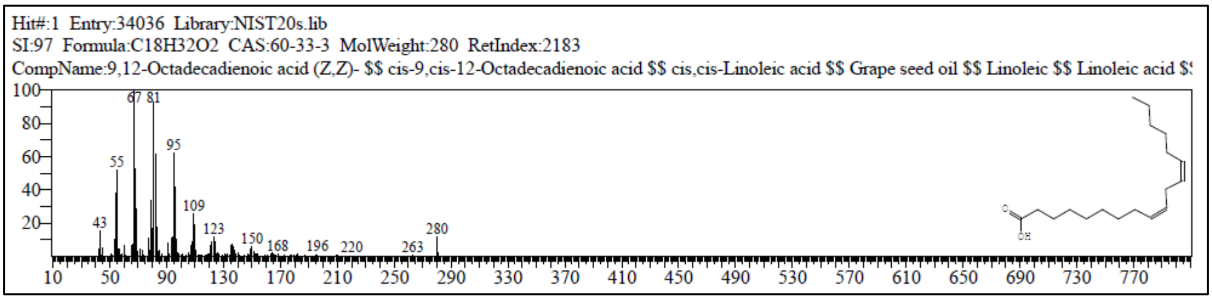
Appendix A 8: GC-MS NIST library molecular structures for major peaks

i. Crude wax



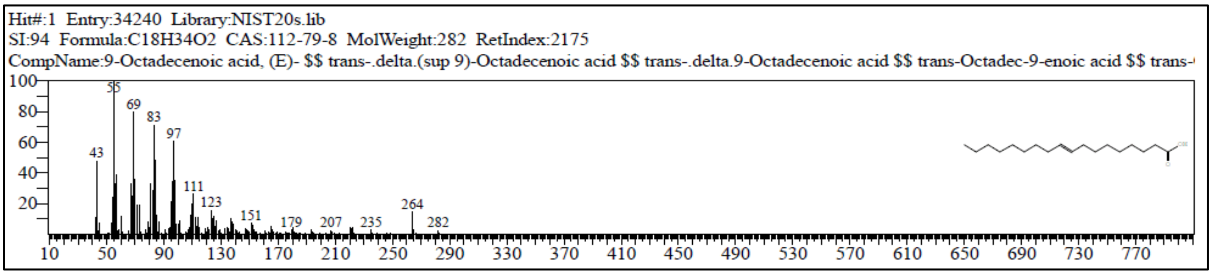
Hit#:1 Entry:31607 Library:NIST20s.lib
SI:96 Formula:C16H32O2 CAS:57-10-3 MolWeight:256 RetIndex:1968
CompName:n-Hexadecanoic acid $$ Hexadecanoic acid $$ n-Hexadecoic acid $$ Palmitic acid $$ Pentadecanecarboxylic acid $$ 1-Pentadecanecarboxylic

Figure A8 - 1:Hexadecanoic acid structure



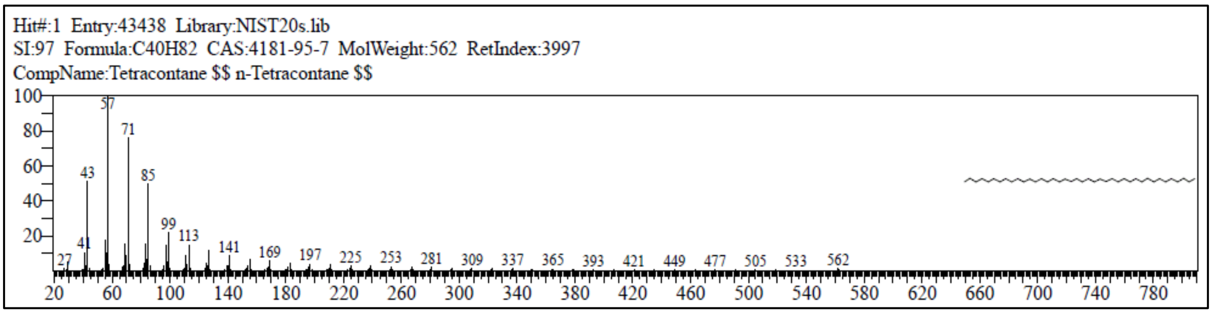
Hit#:1 Entry:34036 Library:NIST20s.lib
SI:97 Formula:C18H32O2 CAS:60-33-3 MolWeight:280 RetIndex:2183
CompName:9,12-Octadecadienoic acid (Z,Z)- $$ cis-9,cis-12-Octadecadienoic acid $$ cis,cis-Linoleic acid $$ Grape seed oil $$ Linoleic $$ Linoleic acid $$

Figure A8 - 2:9,12-Octadecadienoic acid (Z, Z) structure



Hit#:1 Entry:34240 Library:NIST20s.lib
SI:94 Formula:C18H34O2 CAS:112-79-8 MolWeight:282 RetIndex:2175
CompName:9-Octadecenoic acid, (E)- $$ trans-.delta.(sup 9)-Octadecenoic acid $$ trans-.delta.9-Octadecenoic acid $$ trans-Octadec-9-enoic acid $$ trans-

Figure A8 - 3:9-Octadecenoic acid structure



Hit#:1 Entry:43438 Library:NIST20s.lib
SI:97 Formula:C40H82 CAS:4181-95-7 MolWeight:562 RetIndex:3997
CompName:Tetracontane $$ n-Tetracontane $$

Figure A8 - 4:Tetracontane structure

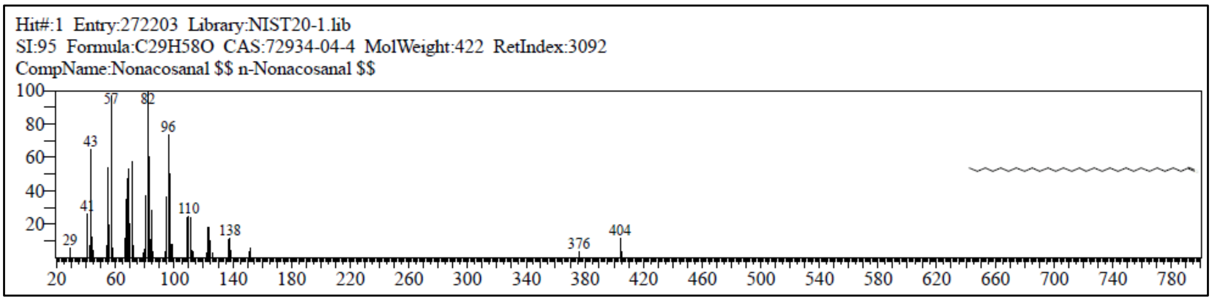

Hit#:1 Entry:272203 Library:NIST20-1.lib
SI:95 Formula:C29H58O CAS:72934-04-4 MolWeight:422 RetIndex:3092
CompName:Nonacosanal $$ n-Nonacosanal $$

Figure A8 - 5:Nonacosanal structure

ii. Refined wax

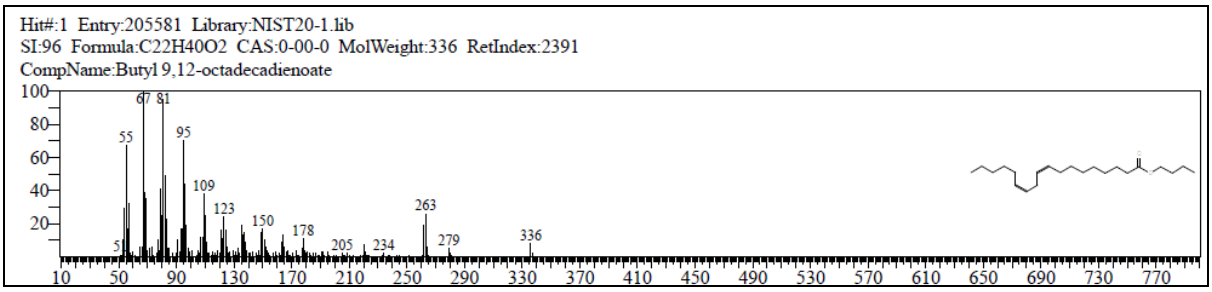

Hit#:1 Entry:205581 Library:NIST20-1.lib
SI:96 Formula:C22H40O2 CAS:0-00-0 MolWeight:336 RetIndex:2391
CompName:Butyl 9,12-octadecadienoate

Figure A8 - 6:Butyl 9, 12-octadecadienoate

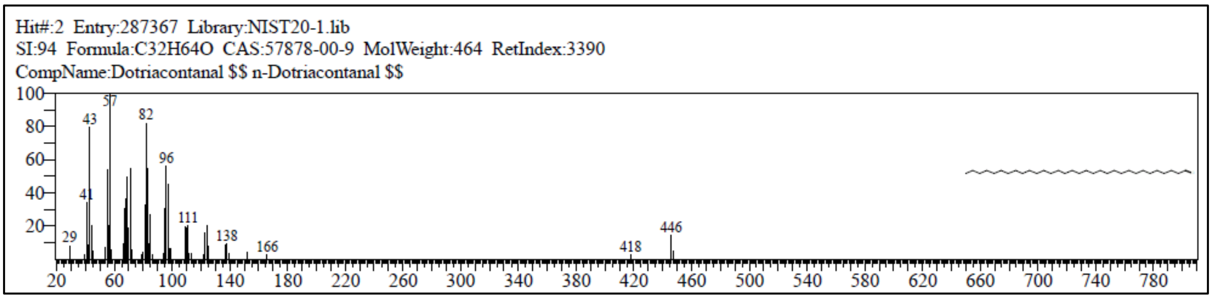

Hit#:2 Entry:287367 Library:NIST20-1.lib
SI:94 Formula:C32H64O CAS:57878-00-9 MolWeight:464 RetIndex:3390
CompName:Dotriacontanal $$ n-Dotriacontanal $$

Figure A8 - 7:Dotriacontanal structure

Appendix B – Sample Calculations

i. Characterization of crude wax (extraction method)

a) Acid value

Sample no: SM-01-BUT-AV

Solvent: 1-Butanol

Determination of mass of wax in the filtrate

Mass of dried DAF mud =10.305 g

Mass of solids = 1.358 g

$$\% \text{ of Solids} = \frac{1.358 \text{ g}}{10.305\text{g}} * \ 100\% = 13.178\ \%$$

Mass of wax = mass of mud – mass of solids = 10.305 g – 1.358 g = 8.947 g

Butan-1-ol volume lost during filtration was 40 ml. Thus, another 40 ml of fresh solvent (butan-1-ol) was added in the dried DAF mud butan-1-ol filtrate solution to make up to 100 ml initial volume of solvent. 10 ml aliquots of this solvent was pipetted to a conical flask for acid value analysis using titration technique.

Determination of mass of wax in the aliquot sample

Total volume = 100 ml

Volume of a sample = 10 ml

$$\text{mass of wax in sample} = \frac{\text{mass of wax (g)} * \text{volume of sample (ml)}}{\text{Total volume (ml)}}$$

$$\text{mass of wax in sample} = \frac{8.947\text{g} * 10 \text{ ml}}{100 \text{ ml}} = 0.8947 \text{ g}$$

Determination of the acid value

Titre Volume of KOH = 16.28 ml

Molarity = 0.1123 mol/L

$$\text{Mol of KOH in sample} = \ \text{Molarity} \left(\frac{\text{mol}}{\text{L}}\right) * \text{Titre volume of KOH (L)}$$

$$\text{Mol of KOH in sample} = \ 0.1123 \ \left(\frac{\text{mol}}{\text{L}}\right) * 16.28 * 10^{-3} \text{ (L)} = 0.001828 \text{ mol}$$

$$\text{Acid value} \left(\text{mg} \frac{\text{KOH}}{\text{g sample}}\right) = \frac{\text{(mol of KOH in sample)} * \text{(Mol. weight KOH)}}{\text{mass of wax in sample}}$$

$$\text{Acid value} \left(\text{mg} \frac{\text{KOH}}{\text{g sample}}\right) = \frac{0.001828 \text{ mol} * 56.11 \frac{\text{g KOH}}{\text{mol}} * 1000}{0.8947\text{g sample}} = 114.62 \frac{\text{mg KOH}}{\text{g sample}}$$

Determination of FFA% (oleic acid equivalent)

$$\text{FFA\%} = \frac{\text{mol of KOH in a sample} * \text{Mol.weight (oleic acid)}}{\text{mass of wax in sample (g)}} * 100 = \frac{0.001828 \text{ mol} * 282.47 \frac{\text{g}}{\text{mol}}}{0.8947 \text{ g}} * 100 = 57.7\%$$

b) Saponification value

Using data for sample name: SM-01-DAF-BUT-SAP (Table A4 - 2, Appendix A4)

Solvent: Butan-1-ol

Determination of mass of wax in the filtrate

Mass of dried DAF mud =10.478 g

Mass of solids = 2.001 g

$$\% \text{ of Solids} = \frac{2.001\text{ g}}{10.478\text{g}} * \ 100\% = 19.097\ \%$$

Mass of wax = mass of mud – mass of solids = 10.478 g – 2.001g = 8.477 g

Butan-1-ol volume lost during filtration was 4.0 ml. Thus, another 4.00 ml of fresh solvent (butan-1-ol) was added in the dried DAF mud butan-1-ol filtrate solution to make up to 100 ml initial. 10ml of this 100 ml solution, was mixed with 20ml alcoholic 0.1019 M KOH under reflux. After an hour was complete and the solution cool, 6 times 5 ml aliquots were pipetted to a conical flask and titrated against 0.1076 M HCl.

Determination of mass of wax in the aliquot sample

Total volume = 100 ml

Volume of a sample = 10 ml

Volume of aliquots for analysis = 5 ml

$$\text{mass of wax in sample} = \frac{\text{mass of wax (g)} * \text{volume of sample (ml)}}{\text{Total volume (ml)}}$$

$$\text{mass of wax in sample} = \frac{8.477\text{g}}{10*6} = 0.1412\text{ g in 5 ml sample}$$

$V_{\text{blank}}^{\text{Hcl}} = 5.95\text{ ml},$

$V_{\text{needed for KOH neutralization}}^{\text{Hcl}} = 3.38\ \text{ ml}$

$$\text{Saponification value} = \frac{(V_{\text{Blank}} - V_{\text{wax}})N_{\text{HCl}}MM_{\text{KOH}}}{W_{\text{wax}}}$$

$$\text{Saponification value} = \frac{(5{,}95-3{,}38)(0.1076)(56.11)}{0{,}1412} = 109.8\ \frac{\text{mg KOH}}{\text{g crude wax}}$$

ii. Characterization of crude wax (melting method)

a) Acid value

Using data for SM-01-CW-BUT-AV

- The mas of the sample = 0,2542g
- The average titre volume is = 6,3 ml
- KOH molecular weight = 56.11 g/mol
- KOH solution concentration prepared = 0.1123M

The acid value is given by the following equation:

$$\text{Acid value} = \frac{V_{\text{KOH x N x MM}_{\text{KOH}}}}{\text{W}} = \frac{(6.3)*(0.1123)*(56.1056)}{0.2542} = \mathbf{156.3\ mg}\frac{\text{KOH}}{\text{g crude wax}}$$

Crude wax precision calculation (decimal digits to be reported)

- The volume of the burette can be read to 0,05 ml KOH (since titrations are given with one decimal of KOH volume titrated)
- Tolerance of volume of the burette = 0.05 ml
- KOH conc. = 0.1123M
- Moles in 0.05 ml = C*V = 0.1123M * 0.05x 10^{-3} = 5.615 x 10^{-6} mol KOH in 0.05 mol
- mg KOH in 0.05 ml = 5.615 x 10^{-6} mol x 56.11 g/mol x 1000 mg/g = 0.315 mg KOH.
- mg KOH/g sample, with sample weighs being 0.25 g = 1,26 mg KOH / g.
- Hence, the acid values can be reported as 156 ± 1 mg KOH/g sample.

b) Saponification value

Saponification:

This calculation is based on the raw data depicted in Table A5 - 2 in Appendix A5

0, 252 g sample (wax)

56.11 g/mol (KOH)

25 ml volume (KOH)

N_{HCl}: 0,1076 mol/l

4.15 ml HCl blank

2.5 ml HCl required to neutralize the remaining KOH

0,252g of crude wax was dissolved in 5 ml ethanol and 25 ml KOH. Of this solution, 5 ml aliquots, were pipetted to a conical flask after the solution has boiled and cooled off, thus the sample mass is (0, 252 /6) g

$$\text{mols of HCl blank} = \frac{\text{Mols HCl blank(ml)}}{\text{approximate HCl conc.}\left(\frac{\text{mol}}{\text{l}}\right)*1000} = \frac{4.15\text{ml}}{\left(0.1\frac{\text{mol}}{\text{l}}\right)*1000} = 0.00041 \text{ mol}$$

$$\text{Exact M of HCl} = \frac{\left(\frac{\text{KOH added (ml)}}{6}\right)*\text{M of KOH}\left(\frac{\text{mol}}{\text{l}}\right)}{H\text{Cl blank (ml)}} = \frac{\left(\frac{25\text{ml}}{6}\right)*0.1019\text{mol/l}}{4.15 \text{ ml}} = 0.1023 \text{ M}$$

The average exact molarity of HCl is 0.1013 mol/l.

$$\text{Exact mol HCl blank} = \frac{\text{HCl blank(ml)}}{1000*\text{Average exact M HCl}\left(\frac{\text{mol}}{\text{l}}\right)} = \frac{4.15\text{ml}}{1000*0.1013\text{M}} = 0.000421 \text{ mol}$$

$$\text{Mol HCl needed} = \frac{\text{Average exact M HCl }\left(\frac{\text{mol}}{\text{l}}\right)}{1000*\text{HCl needed to neutralize KOH(ml)}} = \frac{0.1139\text{mol/l}}{1000*2.48 \text{ ml}} = 0.000253\text{mol}$$

Thus, base remaining after hydrolysis is 0.000253 mol

$$\text{Total mols} = \text{ Exact mol HCl blank} - \text{mol HCl needed} = 4.21 * 10^{-4} - 2.53 * 10^{-4} = 1.67 * 10^{-4} \text{ mols}$$

$$\text{Saponification value}\ \left(\text{mg}\frac{\text{KOH}}{\text{g crude wax}}\right)=\frac{\text{Total mols(mol)}*\text{MM KOH}\left(\frac{\text{g}}{\text{mol}}\right)*10^{3}}{\left(\frac{\text{mass of crude wax(g)}}{6}\right)}$$

$$\text{Saponification value}\ \left(\text{mg}\frac{\text{KOH}}{\text{g crude wax}}\right)=\frac{1.67*10^{-4}*56.11\left(\frac{\text{g}}{\text{mol}}\right)*10^{3}}{\left(\frac{0.252(\text{g})}{6}\right)}=223.4\frac{\text{mgKOH}}{\text{g crude wax}}$$

Alternatively, the saponification value can be calculated using equation 2-2

$$\text{Saponification value}=\frac{(V_{\text{Blank}}-V_{\text{wax}})N_{\text{HCl}}MM_{\text{KOH}}}{W_{\text{wax}}}$$

$$\text{Saponification value}=\frac{(4.15-2.50)(0.1076)(56.11)}{\frac{0.252}{6}}=237.2\ \frac{\text{mg KOH}}{\text{g crude wax}}$$

c) Ester value

Using the average values, the ester value is calculated as below:

Ester value = Average saponification value – Average acid value

= 251.9 – 154.87

= 97.033 mg KOH/ g crude wax

d) Iodine number

i. Preparation of sodium thiosulfate ($Na_2S_2O_3$)

$$\text{Molarity}=\frac{\text{moles of solute}}{\text{Liter of solution}}=\frac{\text{weight of solute}}{\text{molar weight of solute}}=\frac{1}{\text{volume (L)}}$$

$Na_2S_2O_3 . 5H_2O$ = 248.17 g/mol

$$C=\frac{m}{V*MM}\rightarrow m=\ C*MM*V=0.1*248.17*1L=24.817g$$

ii. Calculation of iodine number

The following iodine number calculation is based on the values depicted on Table A5-1, Appendix 5 for batch 1 (SM-01-CW-ID-01), sample one. From equation 3-1, and the raw data provided in Table A5 - 3, the normality of sodium thiosulfate was calculated as below;

$$N=20.394*\left(\frac{W}{V}\right)$$

Where W (average $Cr_2K_2O_7$ weight (g)) = 0.226

V (Average titre volume) (ml) = 43.67, thus;

$$N=20.394*\left(\frac{W}{V}\right)=20.394*\left(\frac{0.226}{43.67}\right)=0.1055\ N$$

$$\text{Iodine number}=\frac{\text{Nx(B}-\text{T) x 12.69}}{\text{w}}=\frac{0.1055*(51.50-41.00)*12.69}{0.255}$$

$$=55.13\ \frac{\text{g}}{\text{100 g crude wax}}$$

a) Percentage of unsaponifiable matter

The %unsaponifiable matter was determined using the equation below;

$$\%\text{Unsaponifable matter} = \left(\frac{\text{final constant mass (g)}}{\text{initial mass weighed (g)}}\right) * 100\%$$

Using batch 01, sample A, SM-01-UNSP-A;

$$\%\text{Unsaponifable matter} = \left(\frac{1.116\text{g}}{5.338\text{g}}\right) * 100\% = 20.91\%$$

The same procedure was followed to calculate the %unsaponifiable matter for the other samples, and the results are summarised in chapter 4, Section 4.8.

iii. Characterization of refined wax

a) Acid values

Using data for SM-01-RW-BUT-AV, in Appendix A6, Table A6 - 1

- The mas of the sample = 0,2573g
- The average titre volume is = 1.0 ml
- KOH molecular weight = 56.1056 g/mol
- KOH solution concentration prepared = 0.1144M

$$\text{Molesof KOH in a sample} = \frac{0.1044\ \text{mol/l}}{1\ \text{ml} * 1000} = \mathbf{0.0001}\ \boldsymbol{mol}$$

$$\text{Acid value }(\frac{\text{mgKOH}}{\text{g}}) = \frac{\text{mol of KOH in sample (mol)} * \text{Molar mass KOH}(\frac{\text{g}}{\text{mol}})}{\text{sample mass(g refined wax)} * 1\text{x}10^{-3}}$$

$$\text{Acid value } \left(\frac{\text{mgKOH}}{\text{g}}\right) = \frac{0.0001\ \text{(mol)} * 56.1056\ \left(\frac{\text{g}}{\text{mol}}\right)}{0.2573\text{(g refined wax)} * 1\text{x}10^{-3}} = 22.77\frac{mgKOH}{g\ refined\ wax}$$

Calculations of the acid values for other batches and samples followed a similar procedure as the one displayed above, and the results are summarised in section 4.5.1, Chapter 4 of this study

b) Saponification values

Using data for sample no: SM-01-RW-SAP-01
Raw data available from Appendix A6, Table A6 - 2
Normality of KOH = 0.1130 N
Refined wax sample weight = 1.271 g
Blank titre volume (ml) = 5.72
Sample titre volume (ml) = 3.18
KOH added (ml) = 30
Absolute ethanol added (ml) = 20
Aliquots taken 5 x 10 ml

$$\text{Saponification value}\left(\text{mg}\frac{\text{KOH}}{\text{g wax}}\right) = \frac{\text{MM KOH}\left(\frac{\text{g}}{\text{mol}}\right)*\text{N HCl}\left(\frac{\text{mol}}{\text{l}}\right)*\text{Vol(Blank−Test)(ml)}}{\text{sample weight (g)}}$$

$$\text{Saponification value}\left(\text{mg}\frac{\text{KOH}}{\text{g wax}}\right) = \frac{56.11\left(\frac{\text{g}}{\text{mol}}\right)*0.1085\left(\frac{\text{mol}}{\text{l}}\right)*(5.72-3.18)\text{(ml)}}{\frac{1.271\text{ (g)}}{5}}$$

$$\text{Saponification value}\left(\frac{\text{mgKOH}}{\text{g refined wax}}\right) = 60.831\ \text{mg}\frac{\text{KOH}}{\text{g refined wax}}$$

c) Iodine numbers

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{Liter of solution}} = \frac{\text{weight of solute}}{\text{molar weight of solute}} = \frac{1}{\text{volume (L)}}$$

$Na_2S_2O_3 . 5H_2O$ = 248.17 g/mol

$$C = \frac{m}{V * MM} \rightarrow m = C * MM * V = 0.1 * 248.17 * 1L = 24.817g$$

The following iodine number calculation is based on the values depicted on Table A6 - 3, Appendix A6 (SM-01-RW-ID-01),

From equation 3-1, and the raw data provided in Appendix A1, table A1-4, the normality of sodium thiosulfate was calculated as below;

$$N = 20.394 * \left(\frac{W}{V}\right)$$

Where W (average $Cr_2K_2O_7$ weight (g)) = 0.226

V (Average titre volume) (ml) = 43.67, thus;

$$N = 20.394 * \left(\frac{W}{V}\right) = 20.394 * \left(\frac{0.226}{43.67}\right) = 0.1055\ N$$

$$\text{Iodine number} = \frac{\text{Nx(B−T) x 12.69}}{\text{w}} = \frac{0.1055*(46.00-37.00)*12.69}{0.253} = 47.6\frac{\text{g}}{\text{100 g refined wax}}$$

iv. Density of sugarcane wax

Data used for calculations was for vessel number 13, at a temperature of 25 ˚C. Water was used as a standard or reference liquid to determine density of crude wax, Table A7 - 1, Appendix A7

Vessel no. 13

Vessel weight (g) = 58.519

Water density at 26.7 ˚C (g/ml) = 0.997 g/ml (Fierro, Jr & Nyler, 2019)

Mass of water & vessel (g) = 66.905 g

$$\text{Mass of water (g)} = \text{Mass of contents (g)} - \text{Vessel \&lid(g)} = 66.905\ \text{g} - 58.519\ \text{g} = \mathbf{8.386\ g}$$

$$\text{Vessel volume (ml)} = \frac{\text{Mass of water (g)}}{\text{density of water g/ml}} = \frac{8.386\ \text{g}}{0.997\ \text{g/ml}} = 8.411\ \text{ml}$$

Mass of wax & vessel (g) = 65.97 g

$$\text{mass of wax (g)} = \text{Mass of wax \& vessel (g)} - \text{Vessel weight (g)} = 65.97 - 58.519 = 7.451\text{g}$$

$$\text{density of wax}\left(\frac{\text{g}}{\text{ml}}\right) = \frac{\text{mass of wax(g)}}{\text{vessel volume (ml)}} = \frac{7.451\ \text{g}}{8.411\ \text{ml}} = \mathbf{0.886\ g/ml}$$

Similar procedure was followed for density calculation of other vessels containing crude and refined wax from different batches.

v. Mass balances for future economic evaluation of the proposed process

D101: Dryer

- basis DAF mud 614.385 kg to get output of 100 kg refined wax/day
- assumption that 58% water content
- ➢ F1: DAF mud (58% water, 5% fibre, 37% wax)

Mass balance:

Water : $\mathrm{F1_w = x1_w * F1} = 614.385 * 0.58 = 356{,}34$ kg

Fibre : $\mathrm{F1_f = x1_f * F1} = 614.385 * 0.58 = 30{,}72$ kg

Wax : $\mathrm{F1_{wax} = x1_{wax} * F1} = 614.385 * 0.58 = 227{,}32$ kg

- ➢ F2: water out
- Assuming complete removal of water from DAF mud

Water out: $\mathrm{F2_w} = F2 = \mathrm{x2_w * F1w} = 1 * 356{,}34 = 356{,}34$ kg

- ➢ F3 =F4 crude wax

Fibre : $\mathrm{F4_f = F1_f} = 30{,}72$ kg

Wax : $\mathrm{F4_{wax} = F1_{wax}} = 227{,}32$ kg

F3 = F4 (Total): $\mathrm{F4_{wax} + F4_f} = 227{,}32$ kg $+ 30{,}72$ kg $= 258{,}04$ kg total

Crude wax percentage composition in F4

$$fibre : x3_f = \left(\frac{x1_f}{x1_f + x1_{wax}}\right) * 100 = \left(\frac{5}{5+37}\right) * 100 = 11{,}90\%$$

$$wax : x3_{wax} = \left(\frac{x1_{wax}}{x1_f + x1_{wax}}\right) * 100 = \left(\frac{37}{5+37}\right) * 100 = 88{,}10\%$$

V-101: Decanter

- ➢ F5: crude wax of F4
- assumption that 55% of crude wax is contained in F4
- assumption that 10% of the fibre are contained in the crude wax

crude wax of F4: $\mathrm{F5} = 0.55 * \mathrm{F4} = 0.55 * 258{,}04 = 141{,}92$ kg

fiber in crude wax : $F5_f = 0.10 * \mathrm{F4} = 0.10 * 30{,}72 = 3{,}07$ kg

wax in crude wax: $F5_{wax} = \mathrm{F5} - F5_f = 141{,}92$ kg $- 3{,}07$ kg $= 138{,}85$ kg

- ➢ F6: residue to X-101
- Assumption: 45% F4

$\mathrm{F6} = 0.45 * \mathrm{F4} = 0.45 * 258{,}04 = 116{,}12$ kg

fibre in residue: $F6_f = F4_f - F5_f = 30{,}72$ kg $- 3{,}07$ kg $= 27{,}64$ kg

wax in residue: $F6_{wax} = F4_{wax} - F5_{wax} = 227{,}32$ kg $- 138{,}85$ kg $= 88{,}47$ kg

X-101: Extractor

Incoming streams: F6 (residue)
: F13 ethanol

- Total residue: F6 = 116,12 kg total

wax in residue: $\mathrm{F6_{wax}} = 88,47\ \mathrm{kg}$
fibre in residue: $\mathrm{F6_{f}} = 27,64\ \ \mathrm{kg}$

- $\mathrm{F13} = \text{all ethanol in}\ \mathrm{F24} = 829\ \mathrm{kg}$

Outgoing streams: F12 (residue)
: F14 (ethanol wax)

- F12 (residue):

Assumptions:

- 7% ethanol relative to solids in residue F6
- 2% wax lost relative to residue F6

ethanol out: $\mathrm{F12_{ethanol}} = 0.07 * (\mathrm{F6_{f}} + \mathrm{F6_{wax}}) = 0.07 * (\ 27,64\ \ + 88,47\ ) = 8,128\ \mathrm{kg}$
wax out: $\mathrm{F12_{wax}} = 0.02 * (\mathrm{F6_{f}} + \mathrm{F6_{wax}}) = 0.02 * (27,64\ \ + 88,47\ ) = 2,322\ \mathrm{kg}$
fibre: $\mathrm{F12_{f}} = \mathrm{F6_{f}} = 27,64\ \mathrm{kg}$

- F14 (Ethanol-wax):

wax: $\mathrm{F14_{wax}} = \mathrm{F6_{wax}} - \mathrm{F12_{wax}} = 27,64 - 2,322\ \ = 86,15\ \mathrm{kg}$
ethanol: $\mathrm{F14_{ethanol}} = \mathrm{F13_{ethanol}} - \mathrm{F12_{ethanol}} = 829 - \ 8,128 = 820,87\ \mathrm{kg}$

$$\mathrm{x13_{ethanol}} = \left(\frac{\mathrm{F14_{ethanol}}}{\mathrm{F14_{wax}} + \mathrm{F14_{ethanol}}}\right) * 100 = \left(\frac{820,87}{86,15\ + 820,87}\right) * 100 = 90,5\%\ \text{, thus,}$$

F14 contains ~90% ethanol.

C-101: Agitated vessel 01

- F5: crude wax of F4

crude wax of F4: $\mathrm{F5} = 0.55 * \mathrm{F4} = 0.55 * 258,04 = 141,92\ \mathrm{kg}$
fiber in crude wax : $F5_{f} = 0.10 * \mathrm{F4} = 0.10 * 30,72\ = 3,07\ \mathrm{kg}$
wax in crude wax: $F5_{wax} = \mathrm{F5} - F5_{f} = 143,22\ \mathrm{kg} - \ 3,10\ \mathrm{kg} = 138,85\ \mathrm{kg}$

- F14 (Ethanol-wax):

wax: $\mathrm{F14_{wax}} = \mathrm{F6_{wax}} - \mathrm{F12_{wax}} = 27,64 - 2,322\ \ = 86,15\ \mathrm{kg}$
ethanol: $\mathrm{F14_{ethanol}} = \mathrm{F13_{ethanol}} - \mathrm{F12_{ethanol}} = 829 - \ 8,128 = 820,87\ \mathrm{kg}$

- F8: fresh ethanol required to give a total of 4x of crude wax

Fresh ethanol: $\mathrm{F8} = (F5_{wax} + F14_{wax}) * 4 - F14_{ethanol} = (138,85\ +\ 86,15\ ) * 4 - 820,87 = 79,13\ \mathrm{kg}$

F7: activated charcoal required to give 1:1 ratio to inlet crude wax

- activated charcoal: $F7 = F5_{wax} + F14_{wax} = 138{,}85 + 86{,}15 = 225\ \mathrm{kg}$

F10: slurry out (ratio wax: ethanol: charcoal is 1:4:1)

- Total slurry out: $F10 = F5_{wax} + F8 + F7 + F14_{wax} + F14_{ethanol} = 138{,}85 + 79{,}13 + 225{,}00 + 86{,}15 + 820{,}87 = 1353{,}07\ \mathrm{kg}$

wax: $F10_{wax} = F5_{wax} + F14_{wax} = 225\ \mathrm{kg}$
fibre: $F10_{f} = 0.10 * F4 = 0.10 * 30{,}72 = 3{,}07\ \mathrm{kg}$
ethanol: $F10_{ethanol} = F14_{ethanol} + F8 = 820{,}87 + 79{,}13 = 900\ \mathrm{kg}$
activated charcoal: $F10_{charcoal} = F7 = 225\ \mathrm{kg}$

The ratio is $= \frac{F10_{wax}}{F10_{wax}} : \frac{F10_{ethanol}}{F10_{wax}} : \frac{F10_{charcoal}}{F10_{wax}} = \frac{225}{225} : \frac{900}{225} : \frac{225}{225} = 1:4:1$

$x10_{wax} = \left(\frac{F10_{wax}}{F10_{total}}\right) * 100 = \left(\frac{225}{1353{,}07}\right) * 100 = 16{,}629\ \%$

$x10_{fibre} = \left(\frac{F10_{fibre}}{F10_{total}}\right) * 100 = \left(\frac{3{,}07}{1353{,}07}\right) * 100 = 0{,}227\ \%$

$x10_{ethanol} = \left(\frac{F10_{ethanol}}{F10_{total}}\right) * 100 = \left(\frac{900}{1353{,}07}\right) * 100 = 66.515\ \%$

$x10_{charcoal} = \left(\frac{F10_{charcoal}}{F10_{total}}\right) * 100 = \left(\frac{225}{1353{,}07}\right) * 100 = 16{,}629\ \%$

F-101: Filter 01

- F17: Residue

Assumptions:

- contains 10% ethanol
- 33.3% of wax is lost to charcoal.

ethanol: $F17_{ethanol} = 0.10 * F10_{ethanol} = 0.1 * 900 = 90\ \mathrm{kg}$

fibre: $F17_{f} = F10_{f} = 3{,}07\ \mathrm{kg}$

activated charcoal: $F17_{charcoal} = F10_{charcoal} = 225\ \mathrm{kg}$
wax: $F17_{wax} = \frac{F17_{charcoal}}{3} = \frac{225}{3} =$ 75 kg wax lost on activated charcoal

- F18: refined wax

refined wax: $F18_{wax} = F10_{wax} - F17_{wax} = 225 - 75 = 150\ \mathrm{kg}$
ethanol: $F18_{ethanol} = 0.90 * F10_{ethanol} = 0.90 * 900 = 810\ \mathrm{kg}$

C-102: Agitated vessel 02

- F19: activated charcoal

$activated\ charcoal: F19_{charcoal} = F18_{wax} = 150\ \mathrm{kg}\ 1\ \mathrm{to}\ 1\ \mathrm{ratio, on\ wax\ present}$
$ethanol: F19_{ethanol} = 0.90 * F10_{ethanol} = 0.90 * 900 = 810\ \mathrm{kg}$

- F20: Slurry out

$activated\ charcoal$: $F20_{charcoal} = F19_{charcoal} = 150$ kg

$ethanol$: $F20_{ethanol} = F19_{ethanol} = 810$ kg

refined wax: $F20_{wax} = F18_{wax} = 150$ kg

Total F20 = $F20_{wax} + F20_{ethanol} + F20_{charcoal} = 150 + 810 + 150 = 1110$ kg

$The\ ratio\ is = \frac{F20_{wax}}{F20_{wax}} : \frac{F20_{ethanol}}{F20_{wax}} : \frac{F20_{charcoal}}{F20_{wax}} = \frac{150}{150} : \frac{810}{150} : \frac{150}{150} = 1{:}\,5.4{:}\,1$

F-102: Filter 02 (for refined wax colour upgrade)

- F21: residue

Assumption:

- 10% loss of ethanol in residue
- 33.3 % of wax loss relative to charcoal

$activated\ charcoal$: $F21_{charcoal} = F20_{charcoal} = 150$ kg

ethanol: $F21_{ethanol} = 0.1 * F21_{charcoal} = 0.1 * 810 = 81$ kg

wax: $F21_{wax} = \frac{F20_{charcoal}}{3} = \frac{150}{3} = 50$ kg

- F22: filtrate

wax: $F22_{wax} = F20_{wax} - F21_{wax} = 150 - 50 = 100$ kg

$ethanol$: $F22_{ethanol} = 0.90 * F20_{ethanol} = 0.90 * 810 = 729$ kg

Total $F22 = F22_{wax} + F22_{ethanol} = 729 + 100 = 829$ kg

E-102: Evaporator

Assumption:

- 99.9% recovery of ethanol in the evaporator

$ethanol$: $F24_{ethanol} = F22_{ethanol} = F13 = 729$ kg

wax: $F25_{wax} = F22_{wax} =$ **100 kg refined wax**