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Synthesis of Cellulose Acetate From Cashew Nut Shell Cellulose

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Abstract

Cashew nut was divided into its three constituent parts viz: the kernel, the testa and the shell. The shell was grated, and extracted with n-hexane using Soxhlet extractor. The Soxhlet extraction lasted for 12 hrs. The relative percent of the shell, kernel and the testa to the cashew nut were 65.49, 29.02 and 1.80 % respectively. The Deffated cashew nut shell was weighed into a thimble and extracted with eighty percent (80 %) ethanol; the extraction process was done exhaustively until the solution was colorless to yield 17.9 and 82.10 % of alcohol extractives and cashew nut shell respectively. The defatted and alcohol extracted Cashew Nut Shell was de-lignified with 17.5 % sodium hydroxide. After drying, about 2 g of the de-lignified Cashew Nut Shell cellulose was reacted with acetic acid and acetic anhydride in the presence of sulfuric acid to yield cellulose acetate. The cellulose acetate obtained was found to be soluble in acetone.

Key words: Cellulose acetate obtained; Acetic anhydride; Acetic anhydride

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INTRODUCTION

Cellulose acquires a unique place in the annals of polymers. Payen, 1838 recognised cellulose as a definitive substance and coined the name 'cellulose'. Cellulose as a precursor for chemical modifications has been used even before its polymeric nature was recognised and well understood.

Milestones on this pathway were the discovery of cellulose nitrate (commonly misnamed nitrocellulose) by Schonbein in 1846, the preparation of Schweizer's reagent, i.e. a cuprammonium hydroxide solution representing the first cellulose solvent. Partially functionalized cellulose nitrate mixed with camphor as softener was one of the first polymeric materials used as a plastic and is well known under the trade name of celluloid. Cellulose nitrates of higher N-content have been used extensively for military purposes. Today, cellulose nitrate is the only inorganic cellulose ester of commercial interest (Balser *et al.,* 1986).

Cellulose is the most abundant polymer on earth, which makes it also the most common organic compound. Annual cellulose synthesis by plants is close to 10^{12} tons (Klemm *et al.,* 1998). Plants contain approximately 33 % cellulose whereas wood contains around 50 % and cotton contains 90 %. Most of the cellulose is utilised as a raw material in paper production. This equates to approximately 10^{8} tons of pulp produced annually. From this only 4 million tons are used for further chemical processing annually (Hermanutz *et al.,* 2006). It is quite clear from these values that only a very small fraction of cellulose is used for the production of commodity materials and chemicals.

The main sources of cellulose are the occurrence of this polysaccharide in different types of plants often combined with other biopolymers. Of great scientific importance is access to cellulose using enzymatic and chemical methods, respectively, developed during the last decade.

The primary occurrence of cellulose is the existing lignocellulosic material in forests, with wood as the most important source. Other cellulose-containing materials include agriculture residues, water plants, grasses and other plant substances. Besides cellulose they contain hemicelluloses, lignin, and a comparably small amount of extractives (Hon, 1996).

In recent years, there has been an increase in the level of research on the development of new biodegradeable materials for use in packaging, agriculture, medicine and other areas. Generally, biodegradeable polymer materials are increasingly important as environmental contamination and waste disposal problems associated with plastics and related products from synthetic polymers become more severe. Natural polymers have various advantages over synthetic polymers due to their low-cost, great availability and biodegradability Zhou, *et al.,* (2008). Furthermore, oil prices have increased significantly due to the limited nature of fossil fuels, especially petroleum resources. In respect to this situation, lignocelluloses biomass from plants has become the main focus of the developing bio-refining industry. Commonly, all plant biomass consists of cellulose, hemicelluloses, lignin, pectin and protein Singh and Khatri, (2012). Most of the plant biomass consists of about 33 % of cellulose as the major component of the rigid cell walls Singh and Singh, (2012).

Cellulose is a linear and high molecular weight polymer as well as natural, renewable and bio-degradable material Rachtanapun, (2009). However, due to its high crystallinity and strong inter and intra-molecular hydrogen bond, cellulose neither melts nor dissolves in the most common organic solvents, therefore, reduces its applicability. In other to increase the cellulose applicability, an alternative pathway is to convert the cellulose to its derivatives such as cellulose acetate Hattori *et al.,* (2004). From the foregoing it should be possible to produce derivatives of cellulosic component of plant by-product such as cashew nut shell.

The cashew tree (*Anacardiumoccidentale L*) is a valuable cash crop that is a native of Brazil and the lower Amazons Frankel, (1991). The tree was introduced in the Americas, the West Indies, Madagascar, India, West Africa and Malysia Frankel, (1991). The economic importance of this special tree is such that while the tree is native to Central and South America, it is now widely distributed throughout the tropics, particularly in many parts of Africa and Asia. The cashew nut, often simply called a cashew, is widely consumed. It is eaten on its own, used in recipes, or processed into cashew cheese or cashew butter. The shell of the cashew seed yields derivatives that can be used in many applications including lubricants, waterproofing, paints, and arms production, starting in World War II. The shell of the cashew nut contains oil compounds which may cause contact dermatitis similar in severity to that of poison ivy, primarily resulting from the phenolic lipids, anacardic acid and cardanol Frankel, (1991).

The cashew plant contains a large quantity of shell which constitute between 70 and 75 percent of the nut. The shell also contains about 30 % of cashew nut shell liquid which is currently being extracted for end users. The remaining 70 % is not currently being exploited, aside from its being used for fuel, as potential source of useful raw material. This research plans to lay emphasis on the derivatives of cellulose, and how they can be utilised efficiently for production.

Cashew nut has become an important cash crop to the extent that people from abroad come into Nigeria during harvesting period to buy for shipment to their country. It is not convincing that the kernel which is just about 25 % of the nut is the only thing that attracts them to the nut. If that be the case, they would have set up a factory to remove the kernel from the shell, which constitute about 75 % of the nut, here in order to reduce cost of shipment. Therefore it makes sense to do a research to see the possible application to which some of the constituents of the shell can be put.

This research is interested in looking into waste agricultural products as a potential supply of the raw material to the industry. This is in line with the current global strategy of shifting emphasis from hydrocarbon to more renewable resources in a sustainable way.

This study, aims to investigate and explore the versatility of cashew nut shell cellulose as a starting material for the synthesis of cellulose-based materials.

Cashew nut shall be divided into its three constituent parts viz: the kernel, the testa and the shell. The shell shall then be extracted of its lipid content using organic solvent like n-hexane. This shall be followed by the use of ethanol to remove other extractives. The resulting shell shall be subjected to processes of delignification to give cellulose. Further, cellulose derivative was also produced from the delignified cashew nut shell cellulose.

Cellulose is a versatile starting material for several applications. It is directly linked to the paper industry in which cellulose is used in a conventional way, as a structural material for paper and cardboard products. However, even though this is the current major use of cellulose, only the imagination is the limit for the utilisation of this extremely versatile and adaptable material. Cellulose can be chemically modified to yield derivatives which are used widely in different industrial sectors in addition to conventional applications. As an example, in 2003, 3.2 million tons of cellulose was used as a raw material in the production of regenerated fibres and films in addition to cellulose derivatives Klemm *et al.,* (2005). Derivatives are further used as coatings, laminations, optical films and absorbents. Additionally, cellulose derivatives can be found as additives in building materials and also in pharmaceutical, food and cosmetic products.

Cellulose derivatives are a class of compounds that originated with nitrate (celluloid), the first man-made thermoplastic to be industrialized in the 19th century and still retain their industrial importance because of their spin ability, film formability and transparency, strength and tenacity, sorption performances and other useful properties. Currently the conversion of cellulose to advanced materials has attracted considerable attention in connection with green and sustainable industrial development Swatloski *et al.,* (2002).

The most important cellulose esters are cellulose acetate (CAc), and the co-esters cellulose acetate-propionate, and cellulose acetate-butyrate. Among these, cellulose acetate is by far the most important cellulose ester. It was first used for photographic film and later as a coating for fabric on airplanes. Like cellophane it is made from cellulose but has very different properties. Unlike cellophane, it is thermoplastic, that is, it will soften and melt when heated Holt-Gimenez, (2007)

The most common source of cellulose is cotton linters. The fibers are mixed with glacial acetic acid and acetic anhydride with sulfuric acid as a catalyst. This results in cellulose triacetate. In a subsequent step water is added to stop the reaction and to partially hydrolyze the triacetate:

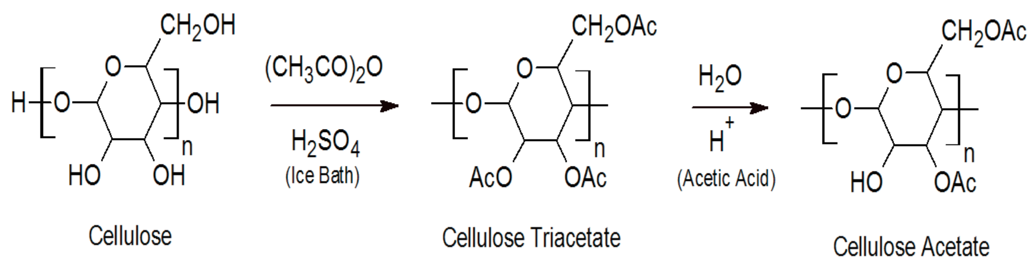

Figure 1
Production of cellulose triacetate from cellulose

Cellulose acetate is a crystal clear, tough, and flexible plastic and is the most stable cellulose derivative. It has excellent chemical resistance to organic and inorganic weak acids, hydrocarbons, vegetable oils, and the like. Often plasticizers are added to further increase its flexibility or mixed ester of cellulose like butyrate-acetate and propionate-acetate are produced which have improved flexibility, toughness, and moisture resistance Hobgood, (2011).

METHODOLOGY

A sample of cashew nut was obtained from Anyigba, Kogi State. The nut was separated into its three components: shell, kernel and testa. Then in a similar way, the shell was defatted, and then, every other component was extracted until the cellulose was left intact. The cellulose was then used to derive cellulose acetate.

Materials/reagents/apparatus

Materials and reagents

Cashew nut sample, thread, thimble, 11 cm filter paper, N-hexane, 80 % ethanol,distilled water, sodium hydroxide 17.5 %, sulphuric acid, acetone, acetic anhydride, glacial acetic acid.

Sample Collection and Preparation

Cashew nuts were bought at Anyigba market. A floatation test was carried out on the cashew nuts to collect the sunken ones from the floats. The sunken nuts were collected and washed, and dried in the sun for a week. The nuts were split into two half to allow for the separation of the kernel, the testa and the shell. The shell was grated in a blender prior to its extraction in a Soxhlet extractor.

Extraction of Cashew Nut Shell Liquid (CNSL)

The grated shell wrapped up with a pre-weighed thimble. Soxhlet extraction was carried out on it. The Soxhlet extraction lasted for 12 hrs using the n-hexane solvent.

The thimble was then cut open, after extraction, to allow the defatted residue to dry. The residual dried sample was weighed with the thimble. The difference between this weight and the sum of the weight of the thimble and thread was taken as the weight of the defatted cashew nut shell.

Extraction of Soluble Extractives From the Defatted Shell

Eighty percent (80 %) ethanol solution was prepared. Forty grams (40 g) of DCNS was weighed separately in four places, wrapped and then tied using a white thread to make a thimble. Cold extraction was then carried out on these samples for three days (after each day, a fresh solvent was used). After the cold extraction, the samples were then placed in a Soxhlet extractor, 200 ml of 80 % ethanol solution was poured into the round bottom flask underneath, and the extraction process commenced. The extraction was done until the solution in the chamber was colourless.

The samples were then removed, and the thimble cut open to dry. After complete drying, the samples were weighed, and the recorded value represented the weight of the Defatted and Alcohol Extracted Cashew Nut Shell (DAECNS).

Delignification of Cashew Nut Shell Cellulose

Sodium hydroxide (17.5 %) solution was prepared. Four samples each weighing 2 g were weighed and wrapped in glass wool. The samples were treated with the 17.5 % NaOH solution in the ratio of 1:20 (gram: volume basis) of sample to solution. They were heated at 100 ^oC for an hour and then decanted repeatedly for 30 times.

Preparation of Cellulose Acetate

Two gram (2.0 g) of the dried sample was mixed with 35 ml of glacial acetic acid. The solution was kept in water bath between 50-55 ^oC for one hour with frequent stirring. An acetylating mixture of 0.5 ml conc. H_2SO_4 and 10 ml of acetic anhydride were gradually added to the glacial acetic acid-pulp mixture at the temperature between 55-65 ^0C. The resulting mixture was kept in water bath for an hour at 50-55 ^oC with occasional stirring until a clear solution was obtained. 12 ml of acetic acid and 3.5 ml of distilled water were added with vigorous stirring to avoid precipitation. The mixture was kept at 50-55 ^oC for one hour and was poured into a large volume of distilled water. The precipitates formed were filtered, washed, air dried and subjected to solubility test in acetone to confirm their presence Juvy *et al*., (2016).

RESULTS

Table 1
Relative Proportions of the Components of the Cashew Nut

S/N	Sample (Cashew)	Mean weight of components	% relative weight of components of the sample
1	CN	2508 g	100
2	CNS	1650 g	65.49
3	CNK	727.8 g	29.02
4	CNT	45.23 g	1.80

KEYS
CN= Cashew nut
CNS= Cashew nut shell
CNK= Cashew nut kernel
CNT= Cashew nut testa

Table 2
Result From the Cold Extraction

S/N	Sample (Cashew)	Mean weight of components	% relative weight of components of the sample
1	CNS	1000g	100
2	CNSL	239.2g	23.92
3	DCNS	760.8g	76.08

KEYS
CNS= Cashew nut shell
CNSL= Cashew nut shell liquid
DCNS= Defatted cashew nut shell

Table 3
Results Obtained Using Soxhlet Extraction Method

S/N	Sample (Cashew)	Mean weight of components	% relative weight of components of the sample
1	CNS	615g	100
2	CNSL	193g	31.38
3	DCNS	422g	68.62

Table 4
Estimation of the Proportion of DAECNS in DCNS

S/N	Sample (Cashew)	Mean weight of components	% relative weight of components of the sample
1	DCNS	39.38	100
2	DAECNS	32.33	82.10

KEYS
DCNS= Defatted cashew nut shell
DAECNS= Defatted and alcohol extracted cashew nut shell

Table 5
The Relative Proportion of the DLCNS to the DAECNS

S/N	Sample (Cashew)	Mean weight of components	% relative weight of components of the sample
1	DAECNS	2.00g	100
2	DLCNS	0.85g	42.50

KEYS
DAECNS= Defatted and alcohol extracted cashew nut shell
DLCNS= De-lignified cashew nut shell

DISCUSSION

The result of the analysis (Table 1) shows the relative composition of the cashew nut. The components of the cashew nut examined were: the cashew nut shell, the cashew kernel and the cashew testa. The cashew nut shell component constitutes the highest portion of the cashew nut 65.5 %, this was followed by the cashew nut kernel with relative percentage weight of 29.02 % and finally the cashew nut testa, which had a relative weight of 1.80 %.

According to USEPA, 1999, the weight of the cashew nut shell was found to be 67 % while that of this research work is 65.5 %, in line with that of the USEPA. The difference that occur may have resulted from variation in sampling points of cashew nut obtained and also loss of weight during the grinding/grating process.

Table 2 shows the relative composition of cashew nut shell liquid (CNSL) and defatted cashew nut shell (DCNS) in the cashew nut shell obtained through cold extraction. This estimated that about 23.92 % of the CNSL and 76.08 % of the DCNS was contained in the CNS.

Table 3 shows the relative composition of cashew nut shell liquid (CNSL) and defatted cashew nut shell (DCNS) in the cashew nut shell obtained through Soxhlet extraction method. This estimated that about 31.38 % of the CNSL and 68.62 % of the DCNS was contained in the CNS.

Table 4 shows result of the extraction of DCNS with ethanol solution in which 39.38 g of the DCNS sample was taken. The product; Defatted and Alcohol Extracted Cashew Nut Shell (DAECNS) were 32.33 g and contained 82.10 % in composition of the DCNS.

Table 5 shows the relative composition of the Delignified Cashew Nut shell (DLCNS) in DAECNS. 2.0 g of the DAECNS sample was extracted with 17.5 % NaOH solution with a relative composition of 42.50 % of the DLCNS in the DAECNS.

CONCLUSION

Cellulose can be derived from wood; the tree must be fallen and processed in other to obtain the cellulose. Re-growing other trees take time and exposes the soil surrounding to erosion and other environmental hazards. Cellulose obtained from cashew nut shell is a valuable source of raw material for the industry. The advantage being that there will be no need to fall any tree.

Cellulose is mainly used to produce paper and paperboard. Only relative small quantities are converted to semi-synthetic cellulose derivatives, such as cellophane, rayon, and cellulose acetate and cellulose ethers Barkalow *et al.* (2014).

This project has demonstrated that cellulose acetate is obtainable from cashew nut shell cellulose. The most important cellulose ester is cellulose acetate. It is widely used for industrial applications. Important uses include textiles (fibres and threads for quality fabrics); plastic films such as optical film for anti-fog goggles; and consumer products such as cellulose based filters, window cartons, and labels Weiner *et al.*, (2000).

REFERENCES

Balser, K., Hoppe, L., Eicher, T., Wandel, M., Astheimer, H. J., Steinmeier, H., & Allen, J. M. (1986). Cellulose esters. In W. Gerhartz, Y. Y. Stephen, C. F. Thomas, R. Pfefferkorn, & F. James (Eds.), *Ullmann'Sencyclopedia of Industrial Chemistry*. New York: Wiley.

Barkalow, David G., & Whistler, Roy L. (2014). Cellulose. *Access Science*. Doi:10.1036/1097-8542.118200.

Frankel, E. (1991). *Poison ivy, poison oak, poison somac and their relative pistachios: Mangoes and cashew*. The Boxwood Press Pacific Grove CA 2, 15-16.

Hattori, K., Abe, E., Yoshida, T., & Cuculo, J. A. (2004). New solvents for cellulose II ethylenediamine/thiocyanate salt system. *Polymer Journal*, *36*(2), 123-130.

Hermanutz, F., Meister, F., & Uerdingen, E. (2006). *Chemical Fibres Int.*, *6*, 342-344.

Hobgood, R. K. (2011). Cars could run on recycled newspaper, Tulane scientists say. Tulane University news webpage. Tulane University. Retrieved March 14, 2012.

Holt-Gimenez, Eric (2007). Biofuels: myths of the Agrofuels transition. Backgrounder. Institute for Food and Development Policy, Oakland, CA. 13:2 "Archived copy". Archived from the original on 2013-09-05.Retrieved 2013-09-05."Archived copy".Archived from the original on 2013-09-06.Retrieved 2013-09-05.

Hon, D. N. S. (1996). *Chemical modification of lignocellulosic material,* Marcel Dekker, New York.

Juvy, J., Monserate, J. R., Salazar, A. M., Tuates, J. R., & Ofero, A. C. (2016). *Synthesis and characterization of nanocomposites from coconut waste* (coconut husk).

Klemm, D., & Fink, H. P. (2005). *Angew. Chem. Int. Ed. 44*, 3358.

Klemm, D., Philipp, B., Heinze, T., Heinze, U., & Wagenknecht, W. (1998). *Comprehensive Cellulose Chemistry*, *Volume 1, Fundamentals and Analytical Methods*. Wiley-VCH, Weinheim,

Krassig, H. A. (1993). Cellulose, structure, accessibility and reactivity. Gordon and Breach Publishers, 5301 Taconystreet, Philadelphia, PA.

Payen, A. (1838) Mémoire sur la composition du tissu propre des plantes et du ligneux. (Memoir on the composition of the tissue of plants and of woody [material]). *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sci-ences*, *7*, 7.

Rachtanapun, P. (2009). Blended films of carboxymethyl cellulose from papaya peel (CMC_p) and corn starch. *Kasetsart Journal (Natural Sciences)*, *43*(5), 259-266.

Singh, R. K., & Khatri, O. P. (2012). A Scanning electron microscope based new method for determining degree of substitution of sodium carboxymethyl cellulose. *Journal of Microscopy*, *246*, 43-52.

Singh, R. K., & Singh, A. K. (2012). Optimization of reaction conditions for preparingcarboxymethyl cellulose from corn cobic agricultural waste. *Waste Biomass Valor.*

Swatloski, R., Spears, S., & Holbrey, J. J. (2002). *Am. Chem. Soc.*, *124*, 4974.

USEPA. (1999). Determining the Adequacy of Existing Data. *Guidance for the HPV Challenge Programme*. Draft dated 2/10/99.

Weiner, M. L.; & Kotkoskie, L. A. (2000). *Excipient toxicity and safety.* New York: Dekker. P. 210 ISBN 0-8247-8210-0

Zhou, R., Mo, Y., Li, Y., Zhao, Y., Zhang, G., & Hu, Y. (2008). Quality and internal characteristics of Huanghua pears (*Pyruspyrifolia* Nakai, cv. Hanghua) treated with different kinds of coating during storage. *Postharvest Biology and Technology, 49*, 171-179.