Synthesis of Sodiumcarboxymethylcellulose from BorassusAethiopum Pulp, and it's Applications

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Abstract. Soduimcarboxymethylcellulose (Na-CMC) which is a water soluble gum was synthesizedfrom thelignocellulosic fibrous trunk and frond parts of*Borassusaethiopum* palm. Ziess electronic microscope was used to determine the lengths of the isolated trunk and frond fibres as 1.98 ± 0.0071 mm and 4.5±0.01 mm respectively. Digestion of the plant chips to isolate the pulp was chemically carried out under an elevated temperature of 102 ^{0}C using concentrated Nitric acid as pulping liquor. The trunk's pulp yield of 55.18 ± 0.75 %; moisture content of 68.38 ± 1.6 %; relative density of 0.14 ± 0.002 g/cm^3; and ash content of 1.22±0.50%, were considered as good grades for commercial Na-CMC. The characteristic whiteness of the cellulose gum was achieved at different concentrations using sodium hypochlorite. Alpha-cellulose was converted to cellulose gum by reacting with 17.5 % NaOH before the acid hydrolysis. The values for the acidity or alkalinity, viscosity, and binding strength tests of the research samples compared were determined. The effect of the Na-CMC on the binding strength, flexibility, and smoothness of washing soap, ceramic plates, papers, etc, were compared to the commercial Na-CMC grade.

Key words: Sodiumcarboxymethylcellulose, *Borassusaethiopum*, pulping, cellulose, characterization, applications.

1. INTRDOUCTION

Cellulose ($C_6H_{10}O_5$)n, is a biopolymeric substance and the world's most abundant naturally occurring polysaccharide, found mainly in higher green plant's cell walls. Studies had shown that plant woods contain about 40-50% cellulose, bast fibers like flax contain about 80-90 % cellulose (Klemm et al, 2005; Afrostburg, 2005). Cellulose which is a polymer composed of repeating cellobiose units having two anhydroglucose units (β-glucopyranose residues) that can be substituted to derive other cellulosic materials.

Cellulose from various sources have the same molecular structures though different glucosidic bonding position (Finar 1996; Chaure et al, 2010). Cellulose had been studied as one of the major source of biofuel, through the hydrolysis of lignocellulosic biomass(Chaure et al 2010).

BorassusaethiopumMart is one of the lignocellulosic fibrous wood material of the family of Palmyra palms, commonly called "African fan-palm or giant-fish tree". The palm is a priority socio-economic ligneous tree specie, naturally widespread in Africa, found mainly in Nigeria, Cameron, Senegal, etc. It grows better in semi-arid to sub-humid regions, (Kumar et al, 2008). The palm is easily recognised by the huge fan-shaped fronds which are about 16.80 cm long, broadly shaped and divided at the middle into numerous narrow segments. It also has an impressive smooth gray trunk that is swollen in the middle and is about 30 m (100 ft) tall (Ahmed et al, 2010). Propagation is possible through the fruits which are greenish and later orange in colour when matured. The seeds contain a lot of minerals and could be eaten as food (Paul, 2011). Report had shown that wine from the *B.aethipum*'s trunk sap is good, but threatens the sustainability of the species population (Grivetti, 1978).

Maigari,(2012), had investigated on the production of red wine from the riped fruit of *B.aethiopum using* calyces as colorant and proved it to be acceptable as compared to some imported bottled wine. The timbers from the wood trunk, were used in the past mainly for building houses and the tender fronds for making hand fans, mats, handbags or baskets, etc. Wood pulps could be derived from the timber of this palm and had been a good source of pulp for kraft or paper boards, while the frond fibres had been used in fine paper and paper products Akpabio (1998).

Wood generally are organic fibrous materials consisting of cellulose units embedded in a matrix of lignin which ensure strength and compression resistant to plants,(Briffa, 2008). Biosynthetic analysis had shown that wood from different plants vary in properties, due to the atmospheric conditions, locations and growth conditions (Boergan, 2003). Wood chips consist of cellulose, used in the isolation of pulps, lignin and three dimensional polymer that binds cellulose chains together (hemicelluloses), the shorter branched carbohydrate polymer (Britt, 1981). Wood pulp is the lignocellulosic fibrous material prepared by delignification of the wood chips and had been reported as the major component in paper productionAkpabio (1998), (Wang, 1986). They consistof cellulose chains of glucose unit having three hydroxyl groups that can be substituted to derive other compounds. Reports had shown that disruption of the hydrogen bonds leads to derivatization of cellulose esthers or ethers which are the basis for most industrial products (Sjöstrom, 1993). The anhydroglucose unit of cellulose contains three hydroxyl groups that could be substituted by carboxymethyl groups to derive sodium carboxymethylcellulose. The average number of hydroxyl groups substituted per anhydroglucose unit is known as the “degree of substitution”.

SodiumCarboxyMethylcellulose (Na-CMC) is a cellulose derivative obtained by chemical modification of natural cellulose. Na-CMC can be produced by reacting alkali cellulose with sodium monochloroacetate under rigidly controlled conditions.

The enzymatic and acid hydrolysis of cellulose had shown that cellulose from different sources could still maintain the same molecular structure but different crystalline structures(Nam, 2009). The breakthrough in the synthesis of Na-CMC from*Borassusaethiopum* pulps will not only have enormous impact on the world food supply, economic, and geopolitical growth, it will also positively influence some classes of industrial products.

It had also been proved that wide range of these cellulose gums could be used in a lot of products as thickeners for example in tobacco, paper, yogurt, paints, mining, etc. Cellulose gum had found applications in thermal stabilization, enzyme resistance, emulsification and in medicine, to influence drug release (Kamd et al, 1971). A large quantity of cellulose gum is used in oil-drilling industries to modify and control the viscosity of drilling mud.

As part of my contribution to the dynamic industrial technology, I investigated on the production of this semi-synthetic sodium salt of carboxymethylcellulose, in order to improve both the quality and quantity of commercial products. Also to reduce the huge resources on the importation of foreign cellulose gum for our local industrial or domestic products.

2.0. MATERIALS AND METHODS

2.1 *Borassusaethiopum raw materials*

The fullymatured Borassus*aethiopum* palm was obtained from the vicinity of NnamdiAzikiwe University Awka. The palm was felled, barked and logged. The logs and fronds were further reduced into smaller chips of about 1 cm long using a sharp knife. The wood chips and fronds were allowed to dry for seven days under atmospheric conditions.

2.2. Morphological analysis of the frond and trunk chips.

The morphological analysis was carried out on the trunk and frond chips of *B.aethiopum* using Ziess microscope with ocular micrometer guage fitted in. The relative density, ash, and moisture contents of the materials were determined according to TAPPI, USA (Tappi 212m-54), standard (Casey, 1980).

2.3 PULPING METHODS

2.3.1 Nitric Acid (HNO_3) Pulping

This method was carried out by stuffing 290 g of the oven-dried trunk and frond chips into an earthen-ware pot respectively. 450 ml of concentrated HNO_3 were added to the chips and the mixture heated at the temperature range of 80-100 ^{0}C. The digestion of the chips lasted for hundred and fifty minutes, (2 ½ hours). The fibres were neutralized using 0.5 M NaOH solution. The isolated fibres were washed repeatedly with distilled water until a clear solution was achieved...

2.3.2 Bleaching of the Pulp

The pulps were bleached to a characteristic whiteness of Na-CMC by using two batch methods. In the first batch, 20 g of sodium hypochlorite was added to the pulp slurry at the consistency of 10 % at 25 ^{0}C for hundred and eighty minutes (3 hours) while stirring at regular time intervals. The pulps were later washed with distilled water. In the second batch, 10 g of sodium hypochlorite was added at the same consistency. The pulps were washedrepeatedly to a whitepulp and allowed to dry.

2.3.3 Pulp refining and percentage yield determination

Refining of pulp in distilled water helps it to swell, fibrillate and cut the cellulosic fibres, in order to increase the bonding properties. This was done by beating the pulp in a Hollander beater until a homogeneous phase is achieved. The mixture was later screened to remove pulp lumps and other impurities.

The percentage yield of the pulpswere determinedby drying the sample at 80 ^{0}C and the percentage yield calculated for three determinations.

$$\%\ \text{Yield} = \frac{\text{wt. of oven-dried pulp}}{\text{wt. of oven-dried chips}} \times \frac{100}{1}$$

2.3.4 Preparation of Sodiumcarboxymethylcellulose(Na-CMC)

100 g of the bleached *Borassusaethiopum* trunk and frond pulps were soaked in 4 % sodium hydroxide solution for 180 minutes. The pulps were thoroughly washed with distilled water. Further bleaching was carried out by adding 5 g of sodium hypochlorite in each of the pulp slurry and allowed to stand for 5 hours to ensure a characteristic whiteness of sodium carboxymethylcellulose. Apha-cellulose was isolated from the bleached pulps by treating with 17.5 % sodium hydroxide solution at 30 ^{0}C. Alpha-cellulose was converted to alkali-cellulose by treating with 35 % sodium hydroxide solution 80 ^{0}C while stirring. The alkali cellulose was allowed to dissolve completely at a reduced temperature of 40 ^{0}C. 75 % chloroacetic acid was added to the alkali cellulose while stirring. The temperature of the reacting system was maintained at 40 ^{0}C by using ice crystals, and reaction was allowed to stand for 15 hours. The sodium carboxymethylcellulose formed was dried in an oven at 105 ^{0}C, and packaged in air-tight containers. Different grades of the cellulose gums, from the trunk and frond pulps were prepared by altering the concentration by mass of the reactants.

2.3.5 Quality Tests on the Na-CMC Sample

2.3.5.1 Viscosity Test:

The viscosity was carried out using ASTMD- 1439 Standard Test for Na-CMC todetermine the resistance of fluid to flow or thickness of the sample. Accurate viscosity of Na-CMC solution was carried out using Brookfield viscometer specification. 5 g of the research sample was dissolved in 100 ml of distilled water, transferred into the viscometer cup with covers and was monitored using a stopwatch. The viscosity was calculated using the formular

$$V = \frac{P}{T}$$

Where: V is viscosity, P is density of solution, T is temperature

2.3.5.2 Solubility Test

This was carried out by dissolving 5 g of each scmc grades in , (a) 1 % NaOH, (b) 10 ml of hot (100 ^{0}C), (3) cold water at the temperature of 27 ^{0}C . The solubility was calculated using the formula;

$$\textbf{Solubility} = \frac{\textbf{Mass of Na-CMC}}{\textbf{Volume of Solvent}} \times \frac{\textbf{100}}{\textbf{1}}$$

2.3.5.3 BondingStrength Test

20 g of the research NA-CMC sample was dissolved into washing soap formulation and compared to Na-CMC free soap after allowing the soap to set. The smoothness and bonding strength effect of the sample was investigated on fine paper slurry and ceramic plate preparations. The properties of the research samples were examined by comparing the Na-CMC free samples and the commercial samples under the same condition.

3.0RESULTS AND DISCUSSION

Results of the morphological analysis on the wood and frond fibres were stated on Table 1. The values are very suitable for sodiumcarboxymethylcellulose synthesis. The solubility values in different solvents for both the trunk and frond falls are within range, since Na-CMC is mostly used in solution forms. The percentage yield of the trunk and frond pulps of 55.18±0.73 and 23.94± 5.33 respectively are profitable for the commercial purpose according to Grant, (1978). The ash content and relative density as stated on table 1 **are** good qualities Enos (1999).

TABLE 1: Physical properties of the Borassus*aethiopumtrunk* and frond Fibre

Parameter	Trunk	Frond
Relative density(g/cm^3)	0.141 ± 0.002	0.058 ± 0.015
Solubility (g/ml) :		
a. 1 % NaOH,	0.04 2± 0.050	0.024 ± 0.003
b. In hot water (100^{0}C),	0.0113 ± 0.002	0.015 ± 0.001
c. Cold water(20^{O}C),	0.004 ± 0.003	0.005 ± 0.011
Moisture contents(%)	60.38 ± 1.160	42.08 ± 2.88

Ash content(%)	1 .22 ± 0.050	1.75 ± 0.040
% yields of pulps	55.18 ± 0.730	23.94 ± 5.330

Values are mean ± S.D of three determinations.

Table 2 :Composition of different grades of Na-CMC from the palm trunk and frond alpha- cellulose

Research samples	**1**	**2**	**3**	**4**	**5**
Apha-cellulose (g)	10	20	30	40	50
Sodium hydroxide (g)	2	4	6	8	10
Water (ml)	5	10	15	20	25
Chloroacetic acid (g)	5	5	5	5	5
Alpha-cellulose : Chloro-acetic acid ratio	2: 1	4 : 1	6: 1	8 : 1	10: 1

Various composition of alpha-cellulose and chloroacetic acid

Table 2, Shows the composition of different grades of sodiumcarboxymethylcellulose (Na-cmc), from different ratios by mass of alpha-cellulose(trunk and frond); sodium hydroxide; water and chloroacetic acid. Various concentrations by mass of these reactants were chosen in order to determine the best grade to compare the commercial Na-CMC grade.
The theoretical, actual and the percentage yields of 68.67 %, 67.53 % of Na-cmc from trunk 's and 48.77 % , 49.61 % of the frond s' alpha-cellulose, as shown on table 3, gave a higher percentage yield of sodium carboxymethylcellulose. This higher yield could be attributed to the higher density of cellulosic carbohydrate content of the trunk fibre against the fronds. Sjöstrom (1993) who suggested that the trunk is a profitable bulk raw material for the commercial production of Na-CMC. It was observed that the percentage yield of sodiumcarboxymethylcellulose reduced drastically with the increase in the concentration of the NaOH, and this could be due to the further hydrolysis or degradation action of sodium hydroxide on the cellulosic polymer chains Nam, Sung Wang et al, (2009).

Table 3 :*Shows results of the theoretical, actual and percentage yields of the sodium carboxymethylcellulose from trunk and frond's alpha-cellulose.*

Alphacellulose and chloroacetic ratio	**Theoretical yield of the trunk alphacellulose (g)**	**Actual yield of the trunk 's Alphacellulose (g)**	**Theoretical yield of the frond 's alphacellulose (g)**	**Actual yield of the trunks alpha - cellulose (g)**	**% yield of trunk 's alpha-cellulose(%)**	**% yield of trunk 's alpha cellulose (%)**
2:1	22	15.12	22	10.29	68.72	48.77
4:1	39	26.34	39	19.35	67.53	49.61
6:1	56	30	56	23.57	53.57	42.08
8:1	73	45.23	73	30.51	61.95	41.79
10:1	90	52.13	90	35.45	57.92	39.38

Values for the theoretical, actual and percentage yields of the sodiumcarboxymethylcellulose from the trunk and frond fibres.

Table 4, Results of the quality tests on the different grades of SCMC based on the ratios by mass of Alpha-cellulose /chloroacetic acid respectively :

α-cellulose :Chloroacetic acid	**2:1**	**4:1**	**6:1**	**8:1**	**10:1**
pH	3:35	5.00	7.10	8.34	9.95

Viscosity	0.12	0.15	0.56	0.69	0.75
Solubility (g/ml)	0.15	0.19	0.1	0.09	0.07
Bonding strength of scmc soap	86.36	105.49	299.98	316	328.56
Soap washability	Fair	Good	Good	Fair	Poor
Smoothness on ceramic plates	Good	Good	Good	Good	Fair

Values for viscosity, solubility, pH, bonding strength, soap washability and smoothness, determination for the different grades of sodium carboxymethlycellulose from trunk's alpha-cellulose/ chloroacetic acid ratios:

From the results on the quality tests as shown on table 4, it was observed that pH of the sample sodium carboxymethylcellulose between the ranges of 7.10 and 8.34 gave the characteristic neutral pH range of Na-CMC, Slavin, et al (1981). The viscosity of the grades at 6:1alphacellulose/chloroacetic acid ratio, compared well to the commercial grades. The bonding strength of the washing soap mixed with research sample Na-CMC exhibited better bonding characteristic than the commercial soap. It was observed that Na-CMC combined ceramic plate gave smoother and outstanding appearance than that of the Na-free type.

(4)CONCLUSION

The percentage yield of pulps isolated from *borassusaethiopum*palm had been observed to be a profitable source material for the production of high grade Na-CMC. Soduimcarboxymethylcellulose can be synthesised from the trunk and frond fibres of *borassusaethiopum* palm using acidic hydrolysis.

Carboxymethylcellulose from *Borassusaethiopum*pulps can improve the qualities and quantities of our local industrial products. The huge resources on the importation of foreign cellulose gum for our local industrial or domestic products can be used for other developmental purposes.

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