

Synthesis and Characterization of Carboxymethyl Cellulose from Cassava Stem (*Manihot esculenta*)

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Cellulose was extracted from cassava stem (*Manihot esculenta*) and then was converted to sodium-carboxymethyl cellulose (Na-CMC). The cassava stem was dried, ground and sieved and allowed to pass through a 50 mesh sieve. Cellulose was extracted, delignified and bleached using sodium chlorite and glacial acetic acid. Carboxymethyl cellulose was consequently synthesized from the extracted cellulose by the use of isopropyl alcohol as solvent with the addition of 20% NaOH and monochloroacetic acid. The yield of CMC was 121.5%. The synthesized CMC was then subjected to FTIR test. Production of carboxymethyl cellulose was confirmed by bands at wave numbers of 1636.6 cm^{-1} and 1423.8 cm^{-1} which could have been attributed to the COO and $-\text{CH}_2$ functional groups, respectively. A CMC with viscosity value of 43.4 cP at 2% concentration and a degree of substitution (DS) value equivalent to 0.64 was obtained during the conversion indicating that the product would be fully soluble in water.

Keywords: Cellulose, Carboxymethyl cellulose, Etherification, Cassava, Thickeners

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INTRODUCTION

Lignocellulosic biomass from forestry/agricultural practices has become an attractive raw material for many industrial applications due to its availability in enormous quantities at low cost and its richness in cellulose. These renewable raw materials for industrial biopolymer application such as bamboo, fibers, agricultural wastes cassava which are rich in cellulose are now gaining importance. They have become alternatives for synthetic materials as they contain cellulose which can be used for various chemical functionalizations. In addition to cellulose, lignocellulosic materials also contain lignin, hemicelluloses, fats and waxes, which are extractive components while the non-extractive components consist of silica, carbonates and others, (Kodali and Pogaku 2006). Cassava is normally cultivated for its root starch which is mainly used as food (48%), feed (34%), feedstock (18%) (FAO, 1990, 2008).

Cassava is mainly grown in tropical and sub-tropical areas where wet and dry seasons alternate, Africa, Asia, Latin America, and Australia. The biomass of cassava stem can be as much as 50% of the root mass, but the role of cassava stem in both cellulose and energy production has so far been overlooked. Cassava stems have a long history of being found mostly not useful because of their particularly woody nature. The stems have in many places been cleared from field, abandoned or burnt causing environmental problems.

Studies on maximizing the use of existing waste in energy production are therefore of importance (Parclack *et al.* 2006).

The chemical fictionalization of cellulose is aimed at altering properties which can be used for different purposes including producing different derivatives of cellulose which are useful in many applications, Varshney *et al.* 2011. These cellulose derivatives are grouped according to the process and substituent; esters (cellulose acetate through esterification) and ethers (carboxymethyl cellulose and cyanoethyl cellulose through etherification).

Water-soluble cellulose derivatives exhibit useful properties of thickening, thermal gelation, surfactancy, film formation, and adhesion. Further they are kinetically and thermodynamically more stable and appear easy to prepare and characterize. With these characteristics, they merit applications such as pharmacy, cosmetics, food, oil drilling, paper, paint, textiles, construction, and adhesives.

Among cellulose derivatives, cellulose ethers constitute the only food-allowed group of modified celluloses. Purified CMC is a white to cream coloured, tasteless, odourless, free-flowing powder. Various work has been done on CMC by (Togrul *et al.* 2003; Adinugraha *et al.* 2005; Pushpamalar *et al.* 2006; Isreal *et al.* 2008; Bono *et al.* 2009; Onigbide *et al.* 2015). There has not been any report on the synthesis of carboxymethyl cellulose using cellulose from cassava stem. However, cassava stem has been converted to ethanol (Klinpratoom *et al.* 2014).

The present work aims at reducing waste of cassava stem by the extraction of the cellulosic component. The obtained cellulose was used to synthesize carboxymethyl cellulose by the use of isopropyl alcohol as solvent and monochloroacetic acid with sodium hydroxide. The solvent helps to swell up the cellulose thereby allowing miscibility and accessibility of the etherifying reagent to the reaction center of the cellulose chain (Barai *et al.* 1997).

EXPERIMENTAL

Materials

Cassava stem supplied from Faculty of Agriculture, Nnamdi Azikiwe University, Awka, Nigeria was used in this study. Glacial acetic acid, sodium chlorite salt, sodium hypochlorite salt, sodium hydroxide, Isopropyl alcohol (Isopropanol), monochloroacetic acid, methanol and ethanol were of analytical grade and were used as received.

Methods

Extraction of cellulose from cassava stem

Cassava stem chips were air and oven dried and then ground into powder. It was then sieved to a particle size of 300 microns. The delignification of cassava stem powder (CSP) was done according to a modified method outlined by (Kumar *et al.* 2013), which was based on acid-chlorite treatment.

10g of the dried cassava stem powder was placed in a beaker and 160ml of tap water was added to it (ratio of 1g CSP to 16ml of water). Afterwards, 15g of sodium chlorite was added to the mixture (1.5g NaClO₂/g CSP). 120ml of Glacial acetic acid

(12ml CH₃COOH/g CSP), was added slowly with continuous stirring. The beaker was covered with aluminum foil and the mixture was then heated on an open water bath which was set at 70°C. The same quantities of NaClO₂ and CH₃COOH were then added to the mixture at 45-minute intervals for 3 hours. After 3 hours, the beaker containing the mixture was removed from the water bath. The mixture was sieved using a fabric sieve of approximately 150 micron, and the residue was thoroughly washed with tap water until neutral pH was obtained. The resulting white residue which is the delignified CSP, was then oven dried at 105°C and stored in a cool dried container. This procedure was repeated with different CSP weights as 15g, 20g, and 25g.

Physicochemical analysis of cassava stem powder (CSP)

The following proximate analysis was carried out on the cassava stem powder, (CSP) including moisture, ash, lignin, hemicellulose and cellulose contents according to ASTM International standards before and after delignification. Effect of temperature on delignification was studied and characterization of cellulose was also performed using FTIR spectroscopy.

Synthesis of Carboxymethyl cellulose

20g of cassava stem cellulose was added to a beaker containing 400ml of Isopropyl alcohol. 80ml of 20% NaOH (w/v) was added into the mixture and stirred. The mixture was heated at 40°C in a water bath with occasional stirring for 1 hour. The etherification reaction was done by adding 24g of monochloroacetic acid slowly into the mixture and stirred for 40minutes. The mixture was covered with aluminum foil and was placed into the water bath for 3 hours at 60°C. The slurry was then soaked in 400ml of methanol for 1 hour and was neutralized with 350ml of 90% acetic acid after which it was filtered. The CMC was washed four times with 80% ethanol, filtered and dried in the oven at 60°C. All tests on carboxymethyl cellulose were carried out according to ASTM International test standards.

Effect of delignification temperature on weight loss of CSP

To determine the effect of temperature on the delignification treatment of CSP, 25g of CSP was used for the delignification at different temperatures. This shows the effect of temperature on the efficiency of delignification and bleaching reactions expressed in terms of percentage loss in cassava stem powder (CSP) weight.

Determination of the production yield of CMC

The yield of CMC production was determined based on dry weight. The net dry weight of CMC was divided by dry weight of cassava stem cellulose incorporated in the carboxymethylation reaction.

Determination of the moisture content of CMC

The moisture content of CMC was determined using ASTM D 2216. 20g of CMC was dried at 60°C for 3 hours and allowed to cool for 3 minutes. The sample was then reweighed and the weight was recorded.

Determination of the viscosity of CMC

3g of CMC was weighed and was dissolved in 90ml of distilled water in a beaker. Then a Brookfield Rotational Viscometer was used to measure the viscosity of the dissolved CMC.

Determination of degree of substitution of CMC

The degree of substitution of CMC sample was determined by standard method, ASTM D1439. The values for the degree of substitution obtained from potentiometric titration were calculated using equations 1 and 2. Values obtained from potentiometric titration corresponded to the absolute values of the degree of substitution (Rosnah *et al.* 2004).

$$\text{Carboxymethyl content (\% CMC)} = \frac{BC-DE}{F} \quad (1)$$

$$\text{Degree of substitution (DS)} = \frac{0.162 \times \% \text{CMC}}{1 - (0.058 \times \% \text{CMC})} \quad (2)$$

In Eqs. 1 and 2, *B* is the volume of sodium hydroxide added, *C* is the concentration in normality of sodium hydroxide added, *D* is the volume of hydrochloric acid consumed, *E* is the concentration in normality of hydrochloric acid used, and *F* is the weight of the CMC sample. 162 is the molecular weight of the anhydrous glucose unit and 58 is the net increment in the anhydrous glucose unit for every substituted carboxymethyl group.

Fourier transform infrared (FT-IR) spectroscopy

The functional groups of the synthesized CMC were determined using a Perkin Elmer Spectrum, RXI Fourier Transform Infrared Spectrophotometer. The samples were dried in an oven at 60 °C to remove moisture. About 0.2 mg of sample and 2 mg of potassium bromide were mixed and ground finely before the mixture was compressed to form a transparent pellet. The infrared spectra of these samples were measured in the transmission of the wave numbers ranging from 4000 to 400 cm⁻¹.

RESULTS AND DISCUSSION**Proximate Analysis of Cassava Stem**

Table 1 gives the proximate composition of cassava stem cellulose extracted, its composition before and after treatment.

Table 1. Proximate Composition of Cassava Stem

Components	Cellulose	Hemicellulose	Lignin	Ash	Moisture
Composition before treatment (%)	43.25±0.76	13.42±0.03	34.5±0.16	5.33±0.02	3.6±0.03
Composition after treatment (%)	56.20±0.32	11.07±0.04	4.27±0.05	3.20±0.01	26.23±0.58

The Changes in chemical compositions of cassava stem before and after pretreatment are presented in Table 1. The untreated cassava stem consisted of 43.2% cellulose, 13.42% hemicelluloses, 34.5% lignin and others. After acid chlorite pretreatment, the content of lignin decreased to 4.27%, indicating that 87% of lignin from raw material could be removed after this pretreatment. This is comparable to the decrease in lignin content from 35% to 4% (87% from raw material) after acid chlorite treatment (Klinpratoom *et al.* 2014). It was also reported by that acid treatment followed by the NaOH treatment considerably reduced hemicellulose content and increased cellulose content, (Klinpratoom *et al.* 2014).

Effect of Delignification Temperature on Weight Loss of CSP

The effect of delignification temperature on weight loss of CSP is presented in Table 2 and illustrated graphically in Figure 1. This figure shows that at low temperature of 30°C, the bleaching reaction is almost insignificant with only 2.8% loss in CSP weight. Increasing the temperature to 50°C increases the loss in weight to 8%, at 70°C, the percentage loss in weight of CSP was 19.2%, while the loss in CSP weight for the delignification reaction obtained at a temperature of 90°C was 15.6%. The greatest percentage loss in weight occurred at 70°C. The curve obtained shows clearly that the delignification and bleaching reaction is better as temperature increases up to an optimum of 70°C but then decreased at 90°C. This observation is due to the improvement in activation and decomposition of sodium chlorite at high temperature which also helps to swell the CSP and allow for the accessibility of the particles themselves, resulting in faster diffusion of the bleaching agent inside the bulk of the particles. Although better bleaching was obtained with increase in temperature, the R^2 value of 0.75 indicated that the relationship between the percentage losses in weight of DLCSP and temperature was not completely linear as the value was not close to 1.

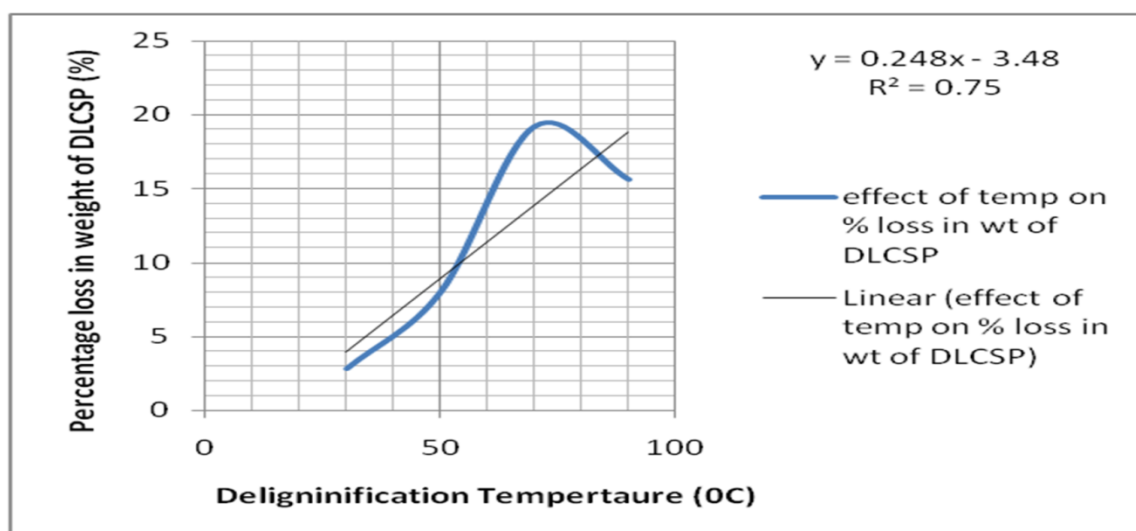


Fig.1. Effect of delignification temperature on Weight Loss of CSP

Table 2. Effect of Delignification Temperature on Weight Loss of CSP, Initial Weight of CSP= 25g

Temperature (°c)	Weight of DLCSP (g)	Loss in Weight of CSP (g)	Percentage loss in weight of CSP (%)
30	24.3	0.7	2.8
50	23.0	2	8.0
70	20.2	4.8	19.2
90	21.1	3.9	15.6

Yield of CMC Production

Using the basis of dry weight analysis, the net dry weight of CMC was determined using Eq.3.

$$\text{Yield of CMC (\%)} = \frac{\text{weight of dried CMC (g)}}{\text{dry weight of dil csp(g)}} \times 100 \quad (3)$$

The % yield of CMC in this research is 121.5% (24.3 g). Although the yield of cellulose from cassava stem is poor, this increase in mass of CMC is due to the swelling of the cellulose in alkaline medium during the mercerization stage of the carboxymethylation reaction.

Moisture Content of CMC

Carboxymethyl cellulose is a hydrophilic derivative of cellulose and the moisture content is calculated using Eq.4,

$$\text{Moisture content (\%)} = \frac{W_1 - W_2}{W_1} \times 100 \quad (4)$$

Where W_1 is the weight of the moist CMC, and W_2 is the weight of the dried CMC

The moisture content calculated for CMC is 76%. This shows that CMC has high moisture content owing to its hydrophilic nature. Due to this high water content, hydrogen bond is formed between water molecules and CH_2COONa in the polymer chain.

Viscosity of CMC

Viscosity provides information on flow characteristics of the fluid involved in processing operation and product. The commercial range for low viscosity CMC is between 20 and 50 cP in 2% concentration of solution.

The viscosity of CMC from this study is 43.4 cP. Viscosity can be affected by many factors such as NaOH used during synthesis. Even though the CMC was washed with alcohol, there was some residual NaOH which could not be washed away by ethanol and these resulted in extra NaOH being contained in the final product of carboxymethylation and thus decreased the viscosity. Also viscosity can be reduced by

the degradation of the polysaccharide. The viscosity of CMC is very essential so as to determine its possible application.

Degree of Substitution (DS) Value of CMC

The DS of most commercial CMC is from 0.4 to 1.4 and researchers are always looking for ways to increase degree of substitution (Sara and Lo 2005; Silva *et al.* 2004). When the DS is below 0.4, the CMC is swellable but insoluble, while above this value, CMC is fully soluble and its hydro affinity increases with increasing DS value (Varshney *et al.* 2011).

The degree of substitution, DS value for the CMC synthesized was 0.65. It is fully soluble in water and its solubility will increase with temperature. The carboxymethylation reaction efficiency is higher as a result of the use of high polarity solvent, isopropanol. A comparison between DS value of carboxymethyl cassava stem cellulose and other sources cellulose is shown in Table 3. Significant differences were observed in the DS values. However, the different experimental conditions and chemicals used can be attributed to the cause of the differences.

Table 3. Comparison of DS of CMC from Cassava Stem with CMC from Other Sources

Source of cellulose	Degree of substitution	References
Water hyacinth	0.24-0.73	Barai <i>et al.</i> 1996
Sago waste	0.33-0.82	Pushpamalar <i>et al.</i> 2006
Sugar beet pulp cellulose	0.11-0.67	Togrul and Arslan. 2003
Lantana camara	0.20-1.22	Varshney <i>et al.</i> 2006
Palm kernel cake	0.67	Bono <i>et al.</i> 2009
Cassava stem powder	0.65	This work

FT-IR Analysis of Cellulose and CMC

The FT-IR of cellulose from cassava stem and CMC can be seen in Figures 2 and 3 respectively. From Fig. 2, the cellulose spectra at the band on 3332.2 cm^{-1} are due to the stretching frequency of the $-\text{OH}$ groups as well as the intramolecular and inter-molecular hydrogen bonds in cellulose. The peak at wavenumber of 1032.5 cm^{-1} is due to $>\text{C}-\text{O}-\text{C}$. The C-H stretching vibration is shown at peak 2907.3 cm^{-1} . Other peaks appearing at wavenumbers of 1423.8 cm^{-1} and 1319.5 cm^{-1} can be attributed to $-\text{CH}_2$ scissoring and $-\text{CH}$ bending vibration, respectively. The peaks at 1636.3 cm^{-1} (COO) and 1423.8 cm^{-1} (CH_2 scissoring) indicate the presence of carboxymethyl substituent. According to Biswal *et al.* (2004) and Pescok *et al.* (1976), carboxyl groups and its salts have frequencies at wavenumbers of 1600 to 1640 cm^{-1} and 1400 to 1450 cm^{-1} .

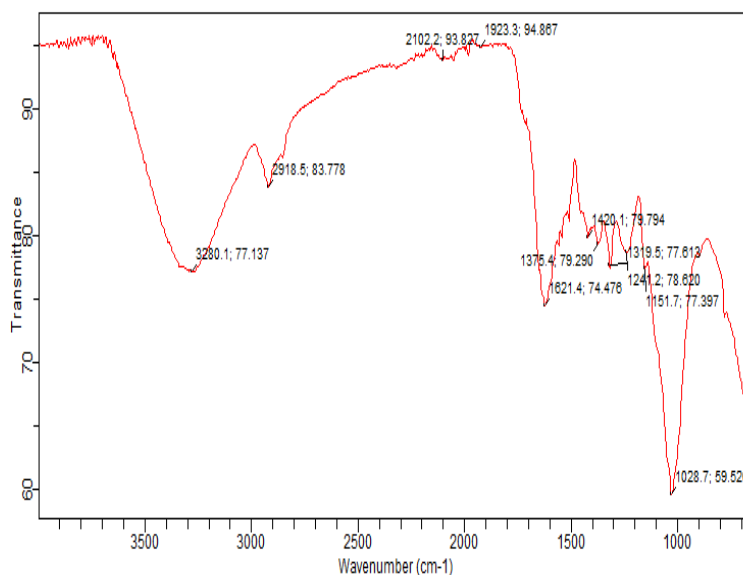


Fig. 2. FT-IR spectrum of cellulose from cassava stem

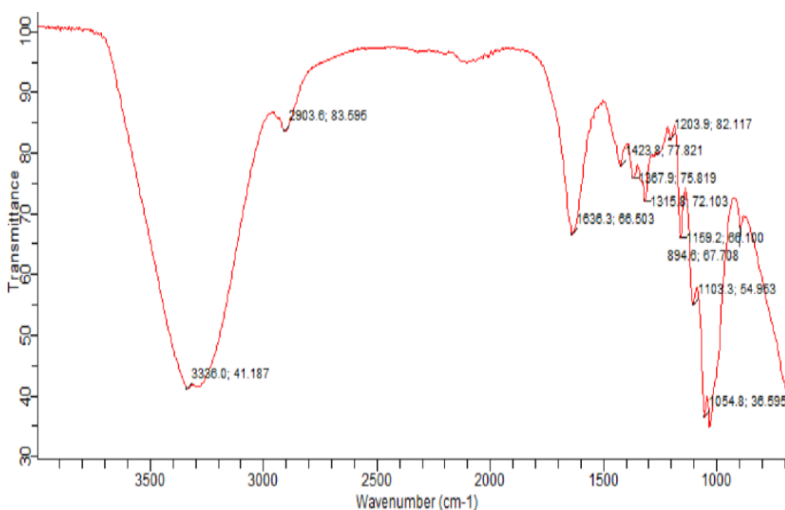


Fig. 3. FT-IR spectrum of CMC obtained from cassava stem

CONCLUSIONS

Cellulose from cassava stem was converted to carboxymethyl cellulose by mercerization with NaOH and treatment with Isopropanol followed by etherification with monochloroacetic acid.

1. High yield of CMC (121.5%) was achieved. This could be attributed to the use of isopropanol as solvent during the mercerization stage.
2. The degree of substitution of CMC was determined from potentiometric titration to give the value of 0.65 showing that the synthesized CMC is water soluble with viscosity of 43.4 cP.

3. FT-IR Spectroscopy of CMC confirmed the change of cellulose to CMC by the presence of carboxyl, COO group at the wavenumber of 1636 cm^{-1} and $-\text{CH}$ group at 1423.8 cm^{-1} . CMC can be used for various applications like thickeners in toothpastes, ice creams and paints, viscosity modifiers, as frozen desserts in food and etc.

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