Synthesis and Application of Carboxymethyl Cellulose from *Gliricidia sepium* and *Cola gigantea*

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Carboxymethyl cellulose (CMC) was prepared from *Gliricidia sepium* and *Cola gigantea* cellulose with yields of 1.59 g/g and 1.76 g/g, respectively. The pH of the products were weakly acidic (6.47 and 6.54, respectively). The sodium chloride content was 0.22 for *C. gigantea* CMC and 0.27 for *G. sepium* CMC, while the degree of substitution was 0.46 and 0.51, respectively. The swelling capacity of *G. sepium* CMC was 802%, which was higher than the 519% of *C gigantea* CMC. Fourier transform infrared (FTIR) spectroscopy confirmed that the products were CMC, and a thermogravimetric analysis (TGA) confirmed that *C. gigantea* CMC was more stable than *G. sepium* CMC. Detergent fortified with *G. sepium* CMC had better performance than *C. gigantea* CMC in terms of cleaning action and emulsion index, and it competed favorably with a detergent fortified with commercial grade CMC.

Keywords: Carboxymethyl cellulose (CMC); Polysaccharide; Fourier transform infrared (FTIR) spectroscopy; Detergent; Gliricidia sepium; Cola gigantea

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INTRODUCTION

Carboxymethyl cellulose (CMC) is an organic polymer synthesized from a natural polysaccharide that is non-toxic, renewable, abundant, biocompatible, and biodegradable. It is of great value to many industrial sectors, including processed foods, textiles, paper, adhesives, paints, pharmaceuticals, cosmetics, and petroleum and mineral processing (Bahramparvar and Mazaheri 2011; Stanford 2012). The CMC has a hydrophobic skeletal backbone that has many hydrophilic carboxyl and hydroxyl groups attached; thus, CMC can be prepared *via* many processes such as homogeneous carboxymethylation (Heinze *et al*. 1999), fluidized bed reactor (Durso 1981), sheet carboxymethylation (Collings *et al*. 1942), without organic solvents (Edelman and Lindroos 1990), and paddle reactor (Holst *et al*. 1978). Ladish (1989) established that the alkali used in the preparation of CMC, such as NaOH, caused the native cellulose fibers to swell; this disrupts the crystalline structure of cellulose to increase the accessibility of reagents to react with amorphous sites, which promotes swelling and solubilization of the formed CMC (Batelaan *et al*. 2014). Carboxymethyl cellulose is a linear polyelectrolyte with anionic characteristics, which makes it soluble in both cold and hot water to form clear and colorless solutions. Specific properties of CMC are strongly affected by the solution concentration, ionic strength, and pH. These characteristics make CMC a favoured surfactant material in the formulations of detergents. At a low pH, CMC polymer chains can crosslink with one another through lactonization among the carboxylic acid and free hydroxyl groups attached to the skeletal backbone (Kästner *et al.* 1997; Chaplin 2007). Calcium and sodium salts of CMC in the form of polycarboxymethyl (CH_2COOX, where X = Ca or Na) ether are also used in drug compounding (Charu *et al*. 2012). Raw materials that have been used for CMC synthesis include: raw cellulose, wood, paper, cotton linters, *Lantana camara*, banana plants, and sugar beet pulp (Jardeby 2004; Varshney *et al*. 2006). In this work, CMC was synthesized from *Gliricidia sepium* and *Cola gigantea* cellulose *via* a two-step reaction method using alkali and chloroacetic acid (Togrul and Arslan 2003).

Carboxymethyl cellulose is used in various industries as a raw material for processed food and drug production, where CMC acts as a viscosity modifier or thickener by forming a gel (Kamel *et al*. 2008). It has different functions in various formulated products, such as lowering the freezing point of ice cream, reducing fats in food products (Bahramparvar and Mazaheri 2011; Stanford 2012), encapsulating drugs for ingestion and chemical release, and stabilizing drug formulations. At higher concentrations, CMCs of intermediate-viscosity grades form gels that are employed as the foundation base for cosmetics or other drug formulations (Bettini *et al*. 1994). It is useful in non-food applications, such as water-based paints, detergents, textile sizing, and strength-enhancing additives for paper (Olaru *et al*. 1998; Xue and Ngadi 2009). The CMC is also used in drilling mud for oil drilling production (Dolz *et al*. 2007), dye thickening in the textile industry (Fijan *et al*. 2009), and for protection of fibers surface (Mohanty *et al*. 2003). This study is aimed at utilizing CMC prepared from the cellulose of fast growing, abundant and underutilized *Gliricidia sepium* stalk and *Cola gigantea* saw-dust in fortifying liquid detergent. The application of *Gliricidia sepium* stalk CMC and *Cola gigantea* saw-dust CMC in liquid detergent is not only germane to our growing economy but a means of reducing environmental pollution and soil erosion cause by burning these waste materials. The prepared CMC and its fortified detergent will be characterized using standard wet- and instrumental- methods.

EXPERIMENTAL

Materials

The biomaterials used in this study were *Gliricidia sepium* stalk and *Cola gigantean* sawmill dust. These materials were sourced from the area around Akure, Ondo (Nigeria). All of the samples were authenticated at the Department of Crop, Soil and Pest Management, Federal University of Technology located in Akure, Ondo (Nigeria). *G. sepium* stalk materials were harvested at 20 cm above ground level and chipped to 0.5 cm to 1.0 cm in length, while *C. gigantea* sawdust materials were collected from Daramola sawmill, Ondo Road (Akure, Nigeria). All samples were screened to remove dust, sand, dirt, and contaminations, and then dried at ambient temperature to uniform moisture content prior to milling. Conditioned samples were milled to a 0.25-mm particle size according to TAPPI T264 om-88 (1988). The milled samples were stored separately in labeled polyethylene bags for subsequent experiments conducted at room temperature. Analytical grade chemical reagents used were sodium hydroxide (BDH, Poole, England), monochloroacetic acid (Sigma-Aldrich, St. Louis, USA), ferric ammonium sulfate ($NH_4Fe(SO_4)_2 \cdot 12H_2O$; BDH), nitric acid (BDH), potassium isocyanate (BDH), dimethyl sulphoxide (DMSO; Sigma-Aldrich), silver nitrate (Sigma-Aldrich), iron (III) chloride (Sigma-Aldrich), magnesium sulphate (BDH), calcium chloride (BDH), alkylbenzene sulphonic acid (Industrial grade, Pursuit Pharma, New Delhi, India), sodium monochloroacetate (BDH), and cupriethylenediamine (CED; Sigma-Aldrich).

Preparation of cellulose

Extractive free *Gliricidia sepium* and *Cola gigantean* biomass sample was obtained by refluxing in a soxhlet extractor using an ethanol (95%) and toluene mixture (1: 2) on a heating mantle for 4 h. This was followed by three successive extractions with 500 mL of distilled water for one hour in a hot water bath at 100 ^{o}C. The sample was later washed with 500 mL of boiling distilled water and oven dry the sample at 103 ^{o}C to a constant weight (TAPPI T204om-97). Cellulose was obtained from the dried extractive free biomass subjected to pulping and bleaching following Jonoobi *et al*. (2009) with little modification. Cooking was with of 17.5% (w/w) sodium hydroxide (1:7) for 180 min using thermostatic shaking water bath at 90 ^{o}C. The solids were filtered and washed with distilled water until the filtrate pH became neutral. The pulps were bleached with 2% sodium chlorite ($NaClO_2$) in acetic acid (3%) for 3 h followed by 15% sodium hydroxide in H_2O_2 (1%) for 2 h and sodium chlorite (1.5%) / acetic acid (3%) for 2 h. The samples were washed with hot distilled water within successive chemical treatment and oven-dried at 105 ^{o}C for 4 h.

Synthesis of sodium carboxymethyl cellulose

Sodium carboxymethyl cellulose (Na-CMC) was synthesized using the method described by Ida and Aliya (2013). Cellulose (5 g) was suspended in 92.5 g ethanol with 3.7 g water in a 500-mL two-neck flask, and then 50 mL of 62.5% sodium hydroxide solution at room temperature was added to this suspension *via* mechanical stirring. Afterwards, 25 mL of 40% NaOH was added to the flask, and the mixture was then stirred for 90 min. The obtained alkali cellulose was then reacted with sodium monochloroacetate ($ClCH_2COONa$). The carboxymethylation reaction was conducted at 60 °C for 3 h. After the reaction time, 100 mL of 70% methanol solution was added to the flask to precipitate the CMC and to wash the other chemical byproducts from the CMC, such as sodium glycolate and sodium chloride. The crude Na-CMC was neutralized with 90% acetic acid. The neutralized Na-CMC was then washed with 100 mL of 96% ethanol solution. The CMC yield (g/g) was calculated by the following expression,

$$\mathrm{CMC} = \frac{a}{b} \tag{1}$$

where *a* is the mass of the CMC sample (g) obtained after drying and *b* is the mass of the dried cellulose sample (g) used in the carboxymethylation reaction.

Methods

Moisture content

The moisture content of the CMC was measured in accordance with TAPPI T550 om-03 (2008). An empty crucible with its cover was oven-dried at 105 °C and then cooled in a desiccator; afterwards, its mass was measured. Exactly 2 g of the prepared CMC was then added to the pre-weighed crucible, oven-dried for 3 h at 105 °C, then cooled in a desiccator, and then the mass was measured. The crucible and its contents were returned to the oven for 1 h, then cooled, and then the mass measured. This was repeated several times until constant mass was attained (*i.e.*, no more than ± 0.002 g change). Moisture measurements on the CMC samples were conducted in triplicate and the reported values were the averages of the measurements. The moisture content was calculated as follows,

$$\%\ \text{Moisture Content} = \frac{w_1 - w_2}{w_1} \times 100 \tag{2}$$

where w_1 is the initial mass of the sample (g) and w_2 is the mass of the oven-dried sample (g).

Determination of moisture sorption capacity

A total of 2 g of the CMC material was accurately measured and evenly distributed over the surface of a 70-mm Petri dish of known mass. The sample was then placed in a large desiccator that contained distilled water in its reservoir at room temperature. The mass gained by the exposed CMC samples at the end of a five-day period was recorded. The amount of water sorption by the CMC was calculated based on the mass difference before and after the five-day exposure period (Ohwoavworhua *et al.* 2004).

Determination of swelling capacity

Swelling capacity measurements of CMC samples were carried out using the method of Okhamafe *et al.* (1991). Approximately 1.0 g of each sample was placed into a 20-mL graduated plastic centrifuge tube, and 10 ML of distilled water was added. The tube was sealed and its contents were agitated for 2 min. The mixture was allowed to stand for 10 min, and the tube was immediately centrifuged at 1000 rpm for 10 min. The supernatant was carefully decanted and the volume of the hydrated swelling material was measured. The swelling capacity (S (%)) of the sample was determined from the initial volume (V_1 (mL)) and final volume (V_2 (mL)) of the sample by Eq. 3:

$$S = \frac{V_2 - V_1}{V_1} \times 100 \tag{3}$$

Swelling capacity measurements were replicated four times for each sample, and the reported value for the sample was the average from these determinations.

Determination of true density

The true density, D_t, of the sample was determined by the liquid displacement method (Alfa *et al.* 2000) using xylene as the immersion fluid. The sample density was computed according to Eq. 4,

$$D_t = \frac{w}{\{(a + w) - b\}} \times SG \tag{4}$$

where w (g) is the mass of the sample used, SG is the specific gravity of the immersion fluid (xylene), a (g) is the mass of the bottle with immersion fluid, and b (g) is the mass of the bottle with immersion fluid and sample.

Determination of bulk and tapped densities

For the bulk and tapped density determinations (Bean *et al.* 1997), 20 g of the sample was carefully measured into a dry 100-mL graduated cylinder and the volume occupied by the sample without tapping (V_0 (mL)) was recorded. The graduated cylinder was mechanically tapped 500 times, and the new volume occupied by the sample after

500 taps ((V_{500} (mL)) was recorded. The bulk (B_d (g/mL)) and tapped (T_d (g/mL)) density values were calculated based on the sample mass used (W (g)):

$$B_d = W/V_0 \tag{5}$$

$$T_d = W/V_{500} \tag{6}$$

Determination of CMC ash content

A 1 g sample was ashed by igniting it in a muffle furnace at 550 °C. It was kept in the oven until the organic matter was decomposed completely (Pomeranz and Meloan 1994). The ash content (%) was calculated using Eq. 7,

$$\%\ \text{Ash Content} = \frac{A}{B} \times 100 \tag{7}$$

where A (g) is the mass of the ash and B (g) is the mass of the moisture-free test specimen.

Determination of CMC pH

The pH of the CMC sample was determined with a calibrated pH meter (FAO 1997). The CMC powder (2 g) and distilled water (100 mL) was mixed for 10 min. The pH of the resulting supernatant after standing was measured and recorded.

Determination of CMC sodium chloride content

The sodium chloride (NaCl) content of the CMC was determined as follows. Approximately 5 g of the sample was weighed into a pre-weighed porcelain crucible. The sample was then ashed in a furnace at approximately 550 °C. After ashing, the crucible was cooled in a desiccator, and the ashed sample was pulverized. The pulverized sample was extracted several times with hot water. The extracts were filtered into a 500-mL volumetric flask, acidified with nitric acid, and diluted to the mark. Next, 100 mL of this solution was mixed with 25 mL nitric acid (1:3) and added to 50 mL of 0.01 M silver nitrate and 1 mL of saturated ferric ammonium sulfate solution (*i.e.*, 8 g $NH_4Fe(SO_4)_2 \cdot 12H_2O$ mixed with 20 mL distilled water and a few drops of concentrated HNO_3) as an indicator. The treated aliquot was titrated with a 0.01 M potassium thiocyanate (KSCN) solution to the first appearance of a dark red colour, which was attributed to the formation of a ferric thiocyanate complex. The above procedure was repeated several times until concordant results were obtained. The amount of NaCl (%) was calculated according to Eq. 8,

$$\%\ \text{NaCl} = \frac{a \times 0.001169 \times 5}{b} \times 100 \tag{8}$$

where a is the amount of titrate used (mL) (*i.e.*, 0.01 M potassium thiocyanate solution), and b is the mass (g) of the CMC sample used (*i.e.*, 5 g)

Determination of degree of substitution

The degree of substitution (DS) of the prepared CMC was determined by the ASTM D1439-03 (2008) standard for direct titration. Exactly 2 g of the sample was dissolved into 10 mL of DMSO *via* stirring at 75 °C for 30 min. After cooling the solution, 5 to 6 drops of phenolphthalein indicator were added. This solution was titrated against 0.01 M NaOH solution until a permanent pale pink color was seen. The DS was calculated using the following equation,

$$\text{Degree of substitution } (DS) = \frac{162 \times V_{\text{NaOH}} \times C_{\text{NaOH}}}{m - 100 \times (V_{\text{NaOH}} \times C_{\text{NaOH}})} \tag{9}$$

where m is the mass of the sample used (2 g), C_{NaOH} is the concentration of the titrant solution (0.01 M NaOH), and V is the volume of titrant used (mL).

Instrumental analysis

Fourier transform infrared spectroscopy with attenuated total reflectance (ATR–FT-IR) was performed with a FT-IR system 2000 from Perkin-Elmer (Waltham, MA, USA), using the SplitPea™ accessory (Harrick Scientific), provided with a silicon internal reflection element and configured for external reflectance mode. The membranes were previously dried at 60 °C in a vacuum oven for 12 h. The spectra were obtained from a 200 µm diameter sampling area, after the accumulation of 200 interferograms, at a 4 cm^{-1} spectral resolution. All spectra were corrected for the ATR characteristic progressive increase in the absorbance at lower wave numbers, using the equipment software. Peak identification was obtained from the correspondent second-derivative spectra in the range between 1250 and 800 cm^{-1}. Prior to the thermogravimetric analysis, the sample was dried at 105 °C under vacuum.

A first scanning was run from 30 to 105 °C to erase any thermal events that might have occurred during the preparation and storage of the samples. After rapid cooling to 30 °C, the temperature was scanned. The resolution of this instrument is 0.02 µg as a function of temperature. Runs were carried out at linear multiple heating rates 10 °C min^{-1} from 30 °C to 800 °C under high purity nitrogen (99.999%) at a flow rate of 20 ml min^{-1} using 6 mg sample. Before starting each run, nitrogen was used to flush the furnace for 30 minutes to create an inert atmosphere so as to avoid unwanted oxidation in the pyrolysis zone. The TG/DTA analyzer was calibrated before recording thermograms. Dried alumina powder was used as a reference material, and a ceramic sample holder was employed for taking thermograms. In order to ensure the uniformity of temperature of the sample and good reproducibility, small amounts (3 to 6 mg) were taken. Three runs of the same sample were conducted under the same set of experimental conditions.

Preparation of standardized liquid detergent formulated with CMC

Sodium hydroxide was mixed with water in a ratio of 1-to-3 to yield a solution with a density of 1257 g/dm^3. The resulting solution was allowed to sit for 24 h. A 50 mL sample of this NaOH solution was added to 100 mL linear alkylbenzene sulphonic acid and stirred with 500 mL of water. To this base was added 2% of the CMC sample *via* stirring; the pH of the mixture was adjusted to 6.5 using a 5% linear alkylbenzene sulphonic acid solution.

Liquid detergent pH determination

The pH of the prepared liquid detergent was determined using a pH meter (827 pH lab model, Metrohm AG CH-9100 Herisau, Switzerland). The liquid detergent (10 g) was diluted with distilled water in a 100 mL volumetric flask. This made a 10% liquid detergent solution. The electrode of the pH meter was inserted into the 10% liquid detergent solution. The pH was recorded as described by Umar (2002).

Liquid detergent emulsification index

The liquid detergent emulsification index was determined by the method described by Mabrouk (2005). Approximately 4 drops of kerosene was added to a test tube that contained 2 mL of the 10% detergent solution (as made in pH determination). The test tube was shaken briefly and the extent of emulsification was denoted as the height of emulsified layer (mm) divided by the total height of the liquid column (mm) expressed as a percentage.

Standardized soiled fabric test specimen

The cleaning action of detergent was based on a procedure reported by Kumar and Mali (2010), which is a modification of a method described by Aghel *et al*. (2007). The procedure uses a standardized soiled fabric sample. Exactly 3 g of cotton fabric (previously dried to a constant weight) was immersed in 150 mL of 10% (w/v) of soil medium (in hexane) for 20 min. The soil medium was composed of coconut oil (31.3 g), carbon black (23.7 g), red oil (15 g), and liquid paraffin (15 g); these ingredients were thoroughly mixed into a thick paste with a pestle in a mortal. The cotton fabric was then removed and dried at room temperature for 2 d. The mass of the soiled fabric was determined to calculate the soil load.

Determination of cleaning action of liquid detergent solution

To determine the cleaning action of the formulated liquid detergent, a 0.1% liquid detergent solution was prepared using tap water. A 150 mL sample of the diluted detergent solution was measured into a 250-mL beaker; to this was suspended the soiled fabric. The fabric and solution were agitated for 5 min using a mechanical stirrer, and then allowed to rest for 15 min. The fabric was then removed and suspended in 100 mL tap water for 10 min. The fabric was removed and dried at room temperature for 2 d, then oven dried for 2 h at 40 °C. The washed fabric mass after oven drying was then determined. A control wash sample was prepared using the same procedure above, but without liquid detergent added. The cleaning action (*CA* (%)) was calculated using Eq. 10,

$$\%\,CA = \left(1 - {}^{T}\!/_{B}\right) \times 100 \tag{10}$$

where *T* (g) is the mass of soil remaining in the test sample after washing and *B* (g) is the mass of soil remaining in the control sample after washing. Physical examination of the composite fabric after soiling and after washing was quantified according to the ISO 105-A02 (1987) standard, which uses a gray scale to measure color changes of the test fabric.

CMC viscosity measurements

The viscosity of the CMC was measured by adapting TAPPI T230 (1999), which uses a capillary viscometer (Ubbelohde-type). The CMC sample (0.5000 g) was dissolved into 25.00 mL 1.0 M cupriethylenediamine (CED) solution that was diluted with 25.00 mL of deionized water to form a 1% CMC solution. Viscosity was measured at a constant temperature (25 °C). Measurements were performed in triplicate, and reported values were the averages of the replicates. A washed, clean and dry Ubbelohde viscometer was prepared with one end closed, and 25 mL of the solution was measured into the capillary viscometer. The closed end was opened, and the efflux time estimated in seconds. Five measurements were made, and an average of three measurements was taken after discarding both the lowest and highest readings. The viscometer was carefully cleaned with nitric acid, water, and acetone and dried between measurements. The viscosity [η] in cP was calculated from the efflux time of the sample solution (t) and the blank solution (t_o), using the equation of Solomon and Gatesman represented by Eq. 11,

$$[\eta] = \frac{\left[2\left(\eta_{sp} - \ln\eta_r\right)\right]^{\frac{1}{2}}}{C} \tag{11}$$

where [η] is the intrinsic viscosity (cP), η_{sp} is the specific viscosity = $\frac{\eta_{solution} - \eta_{solvent}}{\eta_{solvent}}$, $\eta_{\text{solution}} = t_{\text{solution}} \times \rho_{\text{solution}}$, $\eta_{\text{solvent}} = t_{\text{solvent}} \times \rho_{\text{solvent}}$, η_{r} is the relative viscosity = $\frac{t_{solution}}{t_{solvent}}$, C is the concentration of the sample. (1.052 g/cm^3), ρ_{solution} is the density of solution (g/cm^3), ρ_{solvent} is the density of solvent (g/cm^3), t_{solution} is the solution flow time (s), and t_{solvent} is solvent flow time (s),

The viscosity was converted to the degree of polymerization (Morton 1996) as follows,

$$\text{D.P.} = 598.4\ln[\eta] + 118.02(\ln[\eta])^2 - 449.6 \tag{12}$$

The molecular weight was calculated using the equation of Hong *et al*. (1978) as follows,

$$\text{DP} = \frac{162}{M} \tag{13}$$

where DP is the degree of polymerization, M is the required molecular weight, and 162 is the molecular weight of an anhydroglucose (AGU) unit.

Liquid detergent specific gravity measurement

The weight of a cleaned and dried 25-mL specific gravity bottle was determined. The specific gravity bottle was filled with the liquid detergent sample to the mark. The mass of the 25 mL liquid detergent was then determined. A similar measurement was performed using distilled water in place of the liquid detergent. The specific gravity was determined by dividing the mass obtained for the liquid detergent by that of distilled water at 25 °C. Measurements were conducted in triplicate and reported values were the averages of the replicates.

Brightness determination

Colour change expressed as the brightness index was determined using gray scale. Five standard pairs were used. The loss of colour using the gray change scale was evaluated by comparison to five pairs of gray standards. The fabric washed with individual detergent was compared to the soiled fabric using the grey scale. One half of the grey scale had identical chroma to the starting specimen. The second half ranges from the starting chroma (no loss of color) to white (loss of all color). The amount of contrast between the treated and untreated fabric is related to one of the standard pairs to yield the gray scale rating. On this scale, 5 indicate no difference while 1 indicates the most difference and that most of the color had been removed by the washing (ISO 105-A02 1987).

Biodegradability test of liquid detergents

The biodegradability of the four standardized liquid detergents (three fortified with prepared CMC and one fortified with a commercially available CMC) was measured according to the APHA 5210:B (1999) standard. A total of 5 g of the liquid detergent was measured into a biological oxygen demand (BOD) bottle. Exactly 1 mL solution of phosphate buffer (phosphate buffer: Dissolve 8.5g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g $NaHPO_4.7H_20$ and 1.7g NH_4Cl in 1 L), magnesium sulphate, calcium chloride, and iron (III) chloride each was added to 1000 mL of distilled water. This solution was added to top up the contents in the BOD bottle. This was left to stand for 2 h before the dissolved oxygen was measured. After incubation in the dark at 20 °C for 5 d, the dissolved oxygen of the treated sample was measured. The BOD (mg/L) of the sample was calculated from the dissolved oxygen levels before (DO_0 (mg/L)) and after (DO_d (mg/L)) five-day incubation.

$$\mathrm{BOD} = (\mathrm{DO_0} - \mathrm{DO_d}) \times \left(\frac{\text{Volume of BOD bottle}}{\text{Volume of liquid detergent sample}}\right) \tag{14}$$

Statistical Analysis

The data obtained in triplicate were analyzed by Probit Analysis using Duncan's Multiple range Test (DMRT) and analysis of variance (ANOVA).

RESULTS AND DISCUSSION

Carboxymethyl Cellulose

The physicochemical properties of carboxymethyl celluloses (CMCs) prepared from *Gliricidia sepium* and *Cola gigantea* cellulose are presented in Table 1. The yield of 1.76 g/g CMC obtained from the cellulose of *Gliricidia sepium* (WGCMC) after the final CMC products was dried at 105^{o}C, was higher than that of *Cola gigantea* sawdust (WSCMC), 1.59 g/g, although both CMCs were off-white in color, tasteless, and odorless. The CMC yield of WGCMC was higher than the 1.66 g/g yield reported for palm cannel cake CMC (Bono *et al*. 2009), whereas the WSCMC yield was of lower value. It has been reported that yield obtained in the production of CMC could be affected by reaction temperature, concentration of NaOH used, and the etherifying reagent (*e.g*., monochloroacetic acid (MCA)) (Silva *et al*. 2004).

Table 1. Physicochemical Properties of Prepared Carboxymethyl Cellulose

Parameter	**Material**	
	WSCMC	**WGCMC**
Yield (g/g)	1.59 ± 1.40	1.76 ± 1.84
Colour (HTML colour)	Off-white	Off-white
Moisture (%)	6.224 ± 0.17	6.56 ± 0.49
Moisture sorption (%)	72.26 ± 0.47	77.26 ± 0.55
Swelling capacity (%)	749.17 ± 1.44	801.73 ± 14.92
Bulk density	0.48 ± 0.00	0.49 ± 0.01
Tap density	0.61 ± 0.01	0.66 ± 0.02
True density	0.74 ± 0.00	0.68 ± 0.07
Ash content (%)	0.46 ± 0.07	0.41 ± 0.02
pH	6.47 ± 0.02	6.53 ± 0.05
NaCl (%)	0.22 ± 0.01	0.27 ± 0.01
Degree of substitution	0.46 ± 0.05	0.51 ± 0.02
Viscosity (cp)	262.21 ± 5.21	285.14 ± 4.74
Degree of polymerization x 100	7.84 ± 18	8.65 ± 17
Molecular weight x 1000 kg/mol)	127± 30	140 ± 27

Mean values listed of three replicates with ± standard deviation values;
WSCMC - *C. gigantea* carboxymethyl cellulose; WGCMC - *G. sepium* carboxymethyl cellulose

The moisture contents of WGCMC and WSCMC sieved to particle size of 1.70 mm were 6.56% and 6.22%, respectively. The values obtained were higher than the 2.56% to 4.16% values reported by Latif *et al.* (2007) for the CMC derived from six different samples. The moisture content of CMC samples of this study were below the upper limit of 12% as prescribed by Resolution OIV/OENO 366/2009 (2009) by the International Organisation of Vine and Wine (OIV). This indicated that the CMC from this study would be able to resist degradation that could be caused by moisture sorption.

A pH of 6.47 was recorded for WSCMC. Although this seems lower in value than 6.55 of WGCMC, both are in a very week acidic medium. These values were within the recommended pH range of 6 to 8.6 for CMC as stated by Resolution OIV/OENO 366/2009 (2009). Lower CMC pH values than the recommended limit could indicate a lower purity of the product with non-reacted reagents (*e.g.*, monochloroacetic acid) and reaction by-products.

The WGCMC had a higher swelling capacity of 802%, whereas WSCMC had a value of 749%. The moisture sorption capacities of 77.3% and 72.3% were recorded for WGCMC and WSCMC, respectively. The swelling capacity, moisture sorption capacity, and DS values for WGCMC were higher than for WSCMC. Latif *et al.* (2005) had reported earlier that the DS of CMC is directly proportional to the swelling ability and sorption capacity. The swelling capacity and moisture sorption of the CMC could have been influenced by their DS (Waring and Parsons 2001); WGCMC had a higher moisture content, which could indicate its higher moisture attractiveness. Hence, it seems that WGCMC absorbed moisture faster than WSCMC. The difference in determined properties of CMC content might be as a result the source of cellulose used; plant species, age and source affect the cellulose content compositions (Chandra *et al*. 2007; Carere *et al*. 2008).

The degree of substitution of WSCMC was 0.46, whereas it was 0.51 for WGCMC. This suggests that the two cellulose did not react in the same way, resulting in differences of degree of substitution; these DS values were similar to CMC made from sugar beet pulp cellulose (0.11 to 0.67) (Togrul and Arslan 2003), cotton linters (0.15 to

0.70) (Heydarzadeh *et al*. 2009), water hyacinth (0.24 to 0.73) (Barai *et al*. 1996), banana pseudo-stems (0.26 to 0.75) (Adinugraha and Marseno 2005), seaweed – 0.51, Pomelo peel – 0.54, sugarcane – 0.43 (Lakshmi *et al.* 2017), and sago waste (0.33 to 0.82) (Pushpamalar *et al*. 2006). Commercial carboxymethyl cellulose has DS values that range from 0.4 to 1.5, but most available CMCs have DS values that range from 0.4 to 0.8 (Bono *et al*. 2009). The chemical composition of CMCs is strongly influenced by the DS, *i.e.* degree of substitution of CMC is one its most important characteristics, which can be influenced by the available number of replaceable hydroxyl groups on its cellulose chain, with the number of replaceable hydroxyl groups being 3 (Varshney and Naithani 2011). Carboxymethyl cellulose with a DS less than 0.4 can swell but will be insoluble, whereas higher DS values indicate a CMC that is more soluble due to the hydrophilic nature of the substituted carboxyl group (Waring and Parsons 2001; Varshney *et al*. 2006).

The sodium chloride level in CMC is an important parameter, as it is a reaction by-product and it is considered a contaminant. The CMC produced contained 0.22% and 0.27% NaCl for WSCMC and WGCMC, respectively. These values were within the specified limits of CMC (*i.e.*, < 5%) as is noted in Resolution OIV/OENO 366/2009 (2009). Reported NaCl levels for CMC in the literature are: 0.19% for *Picea smithiana* and 0.29% *Eucalyptus globulus* CMC (Latif *et al.* 2007); 0.62% for cotton linter CMC (Latif *et al.* 2007); and 0.14 to 0.16% for *Pennsetum purpurem*, *Ananas comosus*, and *Chromolaena odorata* CMC (Oluwasina and Lajide 2015). The differences in NaCl levels in CMC reported in the literature could be a function of reaction conditions, such as the reaction media used (ethanol or isopropanol), the purity of the monochloroacetic acid used, and the method of CMC washing used.

Density (bulk, tap, and true) is an important parameter for the powdered CMC sample, as it will affect the commercial transport of the material. The bulk densities of both CMC are in close agreement, having values of 0.48 and 0.49 for WSCMC and WGCMC respectively. A higher true density value was recorded for the WSCMC (0.74) *versus* that of the WGCMC (0.68). The difference observed in the tap density of WGCMC(0.66) and that of WSCMC (0.61), could be because WSCMC packed densely together inside the cylinder when been tapped to determine the tapped density, which could be as a result of it smaller particle size (Zou and Yu 1996a,b).

The viscosity of 1% CMC in 0.5 M CED solution was 262.2 cP for the WSCMC sample and 285.1 cP for the WGCMC sample. The CED viscosity values obtained in this work were lower than the values reported by Latief *et al*. (2005) for CMC made from rayon grade wood pulp and from cotton linters (500 cP to 600 cP); these cellulose sources underwent one or two etherification reactions to create the CMC. The degree of polymerization (DP) of the WGCMC was 865, which corresponded to a molecular weight of 140,100 g/mol. In contrast, the WSCMC had a DP of 784, which corresponded to a molecular weight of 127,000 g/mol. The DP and molecular weight values of the CMCs of this study were within the values reported by Oluwasina and Lajide (2015) of 77.7 to 976.0 and 115,000 g/mol to 158,000 g/mol, respectively, for CMC synthesized from different lignocellulosic materials. DP and molecular weight values of cellulose from pulped material depend on it viscosity resulting from its level of bleachability; the research result are within DP of 300 to 1700 (Alfred and Hurter 1998). Cupriethylenediamine would influence the viscosity of such CMC; this would in turn affect the DP and molecular weight. Thus, the chemical make up of cellulose precusor for the preparation of CMC (this may have been influenced by methods for the isolation of cellulose, preparation of CMC, concentration of cupriethylenediamine) may have affected the dissolution (Oluwasina and Lajide 2015).

The introduction of strong peak at 1593 cm^{-1} was attributed to the presence of a carbonyl group (C=O). This suggested that the cellulose from *Gliricidia sepium* and *Cola gigantea* was modified into CMC (Brusau *et al*. 2004; Staurt 2004; Rachtanapun *et al*. 2007) as shown in Figs. 1 and 2. The observed carbonyl group (C=O) peak in this work was consistent with the findings of Chen *et al*. (2013) regarding CMC. Also, Ida and Aliyu (2013) as well as Wang and Wang (2010) presented water hyacinth's carboxymethyl cellulose and other plant materials. The absorption peak at 1592.4 cm^{-1} and 1593.6 cm^{-1} indicated the presence of carbonyl groups, whereas the absorption peaks at 1420.3 cm^{-1} and 1422.8 cm^{-1} indicated the presence of the methylene group of carboxymethyl moiety (asymmetric stretching vibration modes) (Adnugraha *et al*. 2005; Mario *et al*. 2005; Bono *et al*. 2009; Luna-Martinez *et al*. 2005). The grafting of carboxylate groups onto the cellulose structure by carboxylmethylation accounted for the presence of strong peaks at around 1593 cm^{-1} in the CMC samples, which represented the symmetric stretching modes of carbonyl groups (C=O). According to Latif *et al*. (2007), carboxylate groups have wavenumbers that range from 1600 cm^{-1} to 1640 cm^{-1} and 1400 cm^{-1} to 1450 cm^{-1}. The absorbance values at 1420 cm^{-1} and 900 cm^{-1} are sensitive to the amount of crystalline *versus* amorphous cellulose structures in the material; thus, the broadening of these bands reflected a more disordered structure (Carmen-Alice *et al*. 2014). The peak between 1650 cm^{-1} to 1550 cm^{-1} was associated with carboxylate anion (COO^-) found in carboxymethyl cellulose (Olieira *et al*., 2011; Ruzene *et al*., 2007; Biswal and Singh 2004; Pantze 2006).

The FTIR spectra provided evidence that the hydrogen from the hydroxyl groups of cellulose were replaced with carboxymethyl moities ($–CH_2COOH$) during the carboxymethylation reaction (Bono *et al*. 2009).

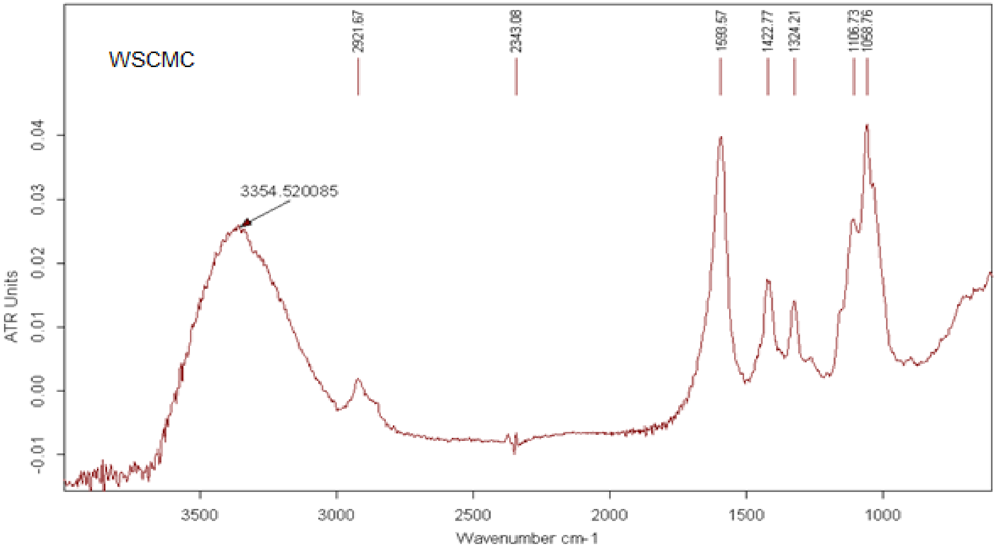

Fig. 1. FTIR spectra of caboxymethylcelluloses made from *C. gigantea* (WSCMC)

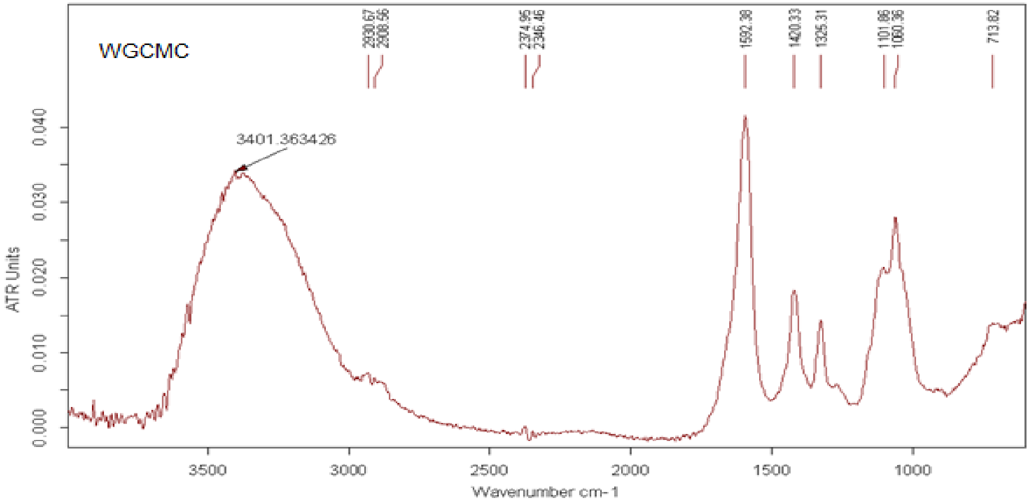

Fig. 2. FTIR spectra of caboxymethylcelluloses made from *G. sepium* (WGCMC)

The thermogravimetric mass losses for WSCMC and WGCMC at 100 °C were 3.24% and 4.68%, respectively (Figs. 3 and 4); this was attributed to the moisture loss from the samples. The mass loss at 289 °C was 10.4% for WSCMC and 10.9% for WGCMC. This was attributed to the thermal degradation of cellulose. The final degradation temperature of 793.1 °C for WSCMC and 789 °C for WGCMC was observed. This revealed that WSCMC was thermally more stable than WGCMC. The WSCMC had a residual of 7.69%, whereas WGCMC had a residual of 6.67%. These results revealed that there could be inorganic matter in the WSCMC.

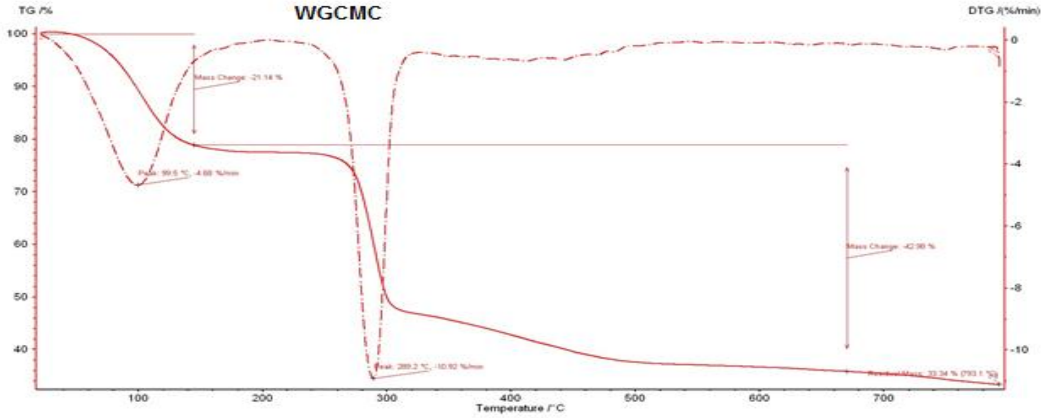

Fig. 3. TG and DTG curves from WGCMC

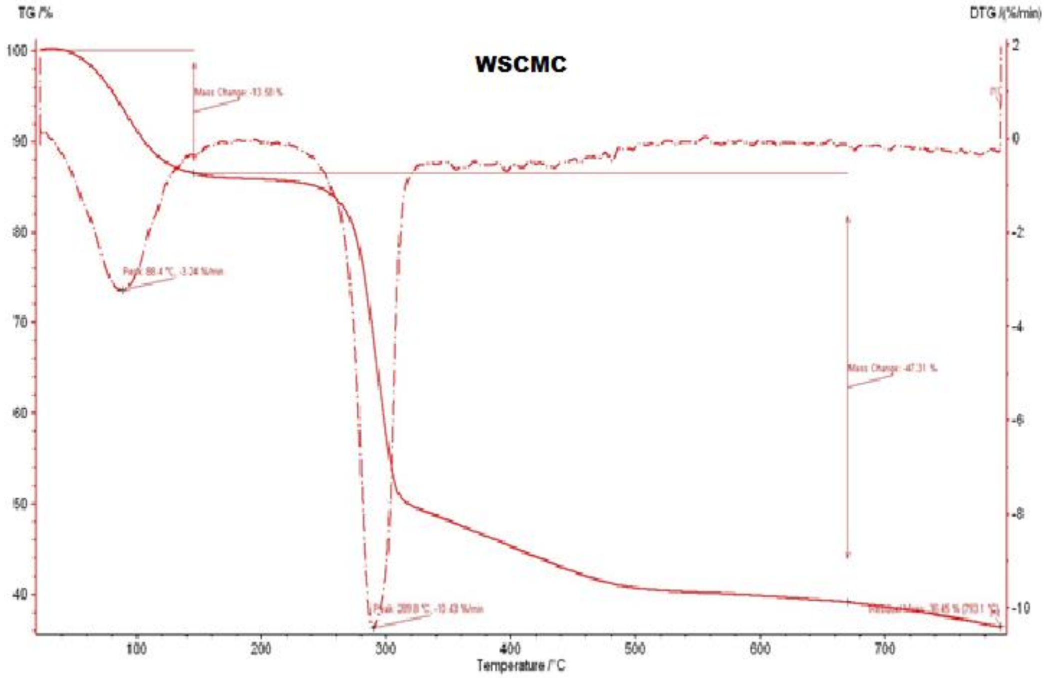

Fig. 4. TG and DTG curves from WSCMC

The ash contents recorded for WSCMC and WSCMC were 0.46% and 0.41%, respectively; these values were lower than the residuals obtained from the thermogravimetric analysis. The result obtained here differed from that reported by Oluwasina *et al*. (2014) in which the thermographic ash was higher than the gravimetric ash content, but Chen *et al*. (2011) has suggested that the presence of sodium oxalate could increase the ash content.

Application of CMC in Liquid Detergent Formulation

Table 2 shows that the standardized liquid detergents made with the CMC of this study had viscosities approximately twice that of the liquid detergent without CMC (*i.e.*, “water detergent”). This observation confirmed that the liquid detergent’s viscosity depends on the CMC added. Commercial based CMC detergent had the highest viscosity value of 5.012 cP, which was closely followed by the detergent produced from WGCMC (4.293 cP) and WSCMC (4.327 cP). The higher viscosity of commercial-based CMC detergent could be attributed to the high degree of substitution of methylcarboxylate substituents (0.4 to 1.5) on the CMC (Heinze and Koschlla 2005). These degrees of substitution are higher than those produced in this research work for WSCMC (0.46) and WGCMC (0.51). Differences in the viscosity values of standardized liquid detergents made with various CMCs have been reported by Jardeby (2004).

Table 2. Physicochemical Properties of the Detergents

Sample	Viscosity (cP)	Specific Gravity	Brightness	Cleaning Action (%)	Emulsion Index (%)	March BOD (mg/L)	June BOD (mg/L)	Sept BOD (mg/L)
WSCMC Detergent	4.293^{c} ± 0.01	1.049^{a} ± 0.01	2.00^{a} ± 0.00	46.517^{a} ± 0.26	89.417^{b} ± 0.35	1.533^{b} ± 0.15	0.233^{a} ± 0.06	0.023^{a} ± 0.01
WGCMC Detergent	4.327^{c} ± 0.04	1.046^{a} ± 0.01	1.00^{a} ± 0.00	42.623^{c} ± 0.42	88.181^{c} ± 0.15	2.267^{c} ± 0.06	0.300^{a} ± 0.10	0.017^{a} ± 0.01
CBCMC Detergent	5.012^{a} ± 0.01	1.023^{b} ± 0.00	3.00^{a} ± 0.00	44.016^{b} ± 0.01	90.881^{a} ± 0.77	2.133^{c} ± 0.06	0.233^{a} ± 0.06	0.043^{a} ± 0.03
Water Detergent	2.387^{d} ± 0.03	1.023^{b} ± 0.01	4.00^{a} ± 0.0	25.466^{e} ± 0.27	58.278^{e} ± 0.47	0.13^{c} ± 0.06	0.033^{b} ± 0.01	0.017^{a} ± 0.01

Values are means of three replicates ± standard deviation; column means values followed by different letters are significantly different (at $p < 0.05$ level); CBCMC - Commercial carboxymethyl cellulose-based detergent; water detergent - Distilled water-based detergent

The specific gravities of liquid detergents made with WSCMC and WGCMC were not statistically different from one another at the $p < 0.05$ level (Table 2), but both were statistically different from the detergent made from a commercial-based CMC and the detergent made without CMC ("water detergent"). The specific gravity of liquid detergents made with WSCMC and WGCMC were not statistically (at $p < 0.05$) different as indicated in Table 2, but was different from the detergent prepared without the addition of CMC. Although all the detergents have low specific gravity, this could be attributed to the dilution with 200 mL of water.

The cleaning ability of the detergent prepared with CMC was better than that without CMC, as shown in Table 2. The results showed that WSCMC-based detergent had the highest cleaning value of 46.5%, which was followed by commercial-based CMC detergent (44.0%) and by WGCMC-based detergent (42.6%). The cleaning action of the CMC-based detergent was attributed to the anti-dirt depositional action of CMC. This would have prevented the dirt from adsorbing onto the fabric again. Kumar and Mali (2010) reported a similar explanation for the use of CMC in different shampoo formulations that had cleaning actions of 24.2%, 32.5%, 18.8%, 33.6%, and 32.1%.

The brightness is the clarity or shade value obtained by comparing the composite fabric after washing to the soiled cloth using gray scale according to ISO 105-A02 (1987). The brightness results of the washed fabrics revealed that the fabrics washed with WGCMC-based detergent had the highest brightness as a result of its ability to remove dirt, whereas soiled fabrics washed with WSCMC- and commercial-based detergent had a brightness value of 3. The lowest brightness was observed for soiled fabrics washed with the detergent without CMC (Table 2).

The emulsification index indicated the ability of the detergent to emulsify hydrocarbons. The emulsification indexes recorded in this research were 89.4%, 88.1%, and 90.9% for WSCMC, WGCMC, and CBCMC respectively, all of which were higher than the 58.3% obtained for water based detergent, these demonstrated that the detergent fortified with CMC to remove all form of dirt. All the emulsification indexes reported in this research were higher than the 54% reported by Abouseoud *et al.* (2007). The higher emulsification indexes recorded in this study may be attributed to the anti-redeposition ability of the CMC added to the detergent

The biochemical oxygen demand (BOD) indicates the amount of oxygen utilized by microorganisms within a 5-day period to convert the organic matter in wastewater to carbon dioxide and water. It could be used to establish the degradation shelf-life of a liquid detergent. The highest onset BOD of 2.27 mg/L was recorded for WGCMC-based detergent (Table 2), which was followed by a commercial-based CMC detergent with 2.133 mg/L. The BOD result revealed that all the detergent experienced degradation, although the CMC based detergents are slow to degradation than water based detergent. The degradation revealed that the inclusion of CMC made the detergent to be environmentally friendly

CONCLUSIONS

1. The rising needs for an alternative source for non-biodegradable, petroleum-based industrial raw material required urgent action. *Gliricidia sepium* cellulose and *Cola gigantea* cellulose offered a potential alternative source of which carboxymethyl-cellulose (CMC) was produced.
2. High yields of *Cola gigantea CMC* and *Gliricidia sepium CMC* were achieved, as veritable sources of carboxymethyl cellulose with yields of 1.59 g/g and 1.76 g/g.
3. The detergent fortified with carboxymethyl cellulose performed credibly well in terms of cleaning action and emulsion index. It also competed favorably with detergent fortified with commercial grade CMC.
4. The high yield of CMC from the two sources suggested that CMC from *Cola gigantea* and *Gliricidia sepium* with a good swelling capacity low sodium chloride content could be commercialized.

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