

Effect of Organic Solvents on the Synthesis and Characterization of Carboxymethyl Cellulose from Sawdust

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Abstract

Sawdust generated as waste by-product from timber industries finds limited industrial applications and is mostly discarded or incinerated, causing environmental problems. This research work was carried out with a view of utilizing sawdust to synthesize Carboxymethyl cellulose (CMC). Cellulose was isolated from sawdust of commercially used hardwood (Mahogany- *Khaya ivorensis*) and softwood (Silk cotton- *Eriodendron orientale*) by alkali-acid and bleaching treatments. Using ethanol, butanol, isobutanol and isopropanol as solvent media, the isolated cellulose samples were converted to CMC through mercerization with sodium hydroxide (NaOH) and etherification with sodium monochloroacetic acid (SMCA). The products obtained were characterized using Degree of Substitution (DS), Fourier Transform Infrared (FTIR) Spectroscopy and Thermogravimetric Analysis (TGA).

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Studies revealed that optimum DS of 0.54 could be reached when isopropanol is used as solvent medium. The presence of carboxyl and methyl functional group at wavenumber 1580-1590 and 1380-1415 cm^{-1} respectively on the FTIR spectra confirmed the conversion of cellulose to CMC. TGA showed that the thermal stability of CMC is lower than that of the parent cellulose. The results obtained demonstrate a simple method for the conversion of sawdust to a high quality water-soluble cellulose derivative which has applications in the food, textile, cosmetics and pharmaceutical industries.

Keywords: Sawdust; Cellulose; Carboxymethyl cellulose; Synthesis; Characterization.

1. Introduction

In the world today, any green product, which will ensure the utilization of waste product, for the production of valuable material (resources recovery) and the conservation of the energy in the industrial process with the view of reducing carbon emission and global warming, is a welcome development. Sawdust is an agricultural waste product obtained in the process of smoothing plant and timber. Plant cell wall is the backbone structure of all plant materials, and cellulose is the chief constituent of plant cell wall and perhaps the most abundant organic matter available in the world today. About 1015 kg of cellulose is synthesized and degraded on Earth each year. Cellulose makes a large fraction of the plant dry weight, being typically in the range of 35-50%. It gives stability to the plants even in the absence of water and makes them more resistant. Cellulose is a linear polysaccharide consistency of several D-glucose units linked together by β , 1-4 glycosidic bond. 2,3,4 it is tasteless, odorless, white crystalline material, they are about 2000 to 4000 glucose units all linked by β , 1,4 glycoside bond hence the chain length is not constant. Cellulose is a linear and high molecular weight polymer as well as natural, renewable and biodegradable material [1] 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 [2]. In order to increase the cellulose applicability, an alternative pathway is to convert the cellulose to its derivatives such as carboxymethyl cellulose (CMC) through chemical derivatization reaction [3]. CMC is important for its water-soluble properties where great applications are applied throughout the food industry, detergents, cosmetics, pharmaceuticals, textiles, paper, adhesives as well as ceramics [4]. Physical and chemical properties of CMC are mainly determined by the degree of substitution (DS), distribution and degree of polymerization. Among these properties, DS has the greatest influence on the solubility, shearing stability and rheological behavior of CMC solution and its stability against temperature and low molecular additives. DS represents the number of the carboxymethyl groups in the molecular unit of the anhydroglucose units. In principle, all hydroxyl groups (HO-2, HO-3, and HO-6) in the anhydroglucose unit can be substituted, and the maximum degree of substitution (DS) is being 3 [5]. In this study, CMC was synthesized using extracted cellulose from sawdust and the effect of solvent parameters used in the synthesis was determined.

2. Materials and methods

2.1 Materials

Sawdust from hardwood (Mahogany- *Khaya ivorensis*) and softwood (Silk cotton- *Eriodendron orientale*) were

obtained from sawmills at Iyana-oba (Lagos State) and Ijoko (Ogun State) respectively. All chemicals used for the preparation and characterization of CMC were of analytical grade and include:

- Sodium hydroxide (NaOH)
- Sodium monochloroacetic acid (SMCA)
- Nitric acid (HNO₃)
- Glacial acetic acid
- Absolute methanol
- Isopropanol
- Ethanol
- Butanol
- Isobutanol
- Acetone

Instruments/equipment used include the following:

- Bruker Alpha FTIR spectrometer
- Perkin Elmer Pyris series- TGA6
- KS 500 Flask shaker
- Sartorius analytical balance
- Oven
- Stuart Magnetic stirrer
- Waterbath

2.2 Methods

2.2.1 Isolation of cellulose from sawdust

The freshly collected sawdust samples were sundried for a day and the dried samples were sieved into fine powder using a 1 mm mesh size. Cellulose was isolated using a modified method described by [6]. 1 kg of sawdust powder was delignified by heating with 5 L of 7 % nitric acid at 90 °C for 2 hours in a reaction vessel with automated stirring. The dark slurry obtained was washed several times with distilled water until the filtrate became neutral to litmus paper. The cellulosic material was further treated by heating with 4 L of 17.5 % sodium hydroxide for 2.5 hours at 70 °C with continuous stirring. The slurry obtained was again washed several times with distilled water until the filtrate became neutral to litmus paper. The isolated product was bleached by heating with 3.5 % sodium hypochlorite at 80 °C with continuous stirring for 30 minutes and then washed with distilled water. The bleaching stage was repeated to obtain white isolated cellulose which was air-dried for 5 days. The dried cellulose was ground and kept in polyethylene bag for the cellulose modification.

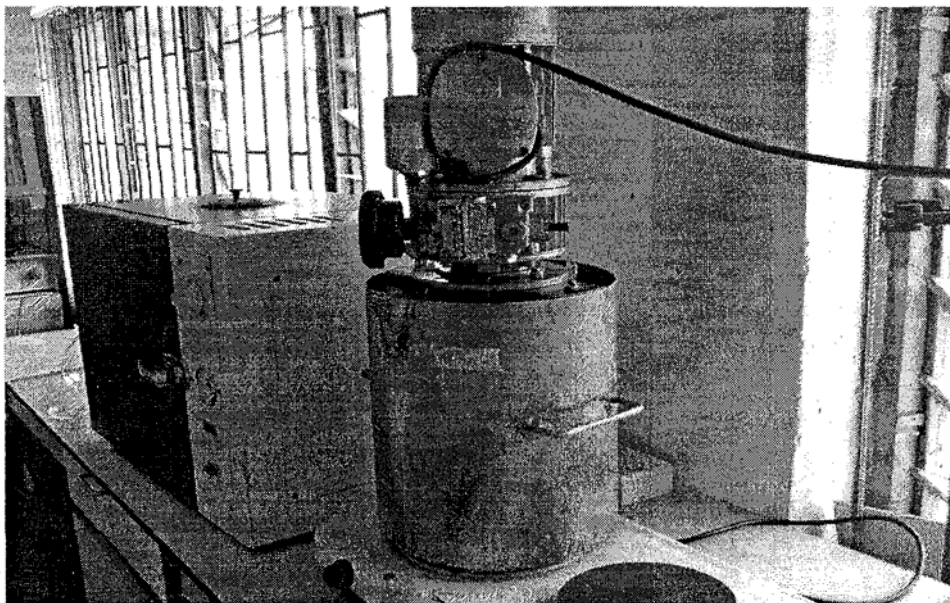


Figure 7: Set-up for the isolation process.



Figure 8: Set-up for the bleaching process.

2.2.2 Synthesis of Carboxymethyl cellulose from sawdust cellulose

CMC from sawdust cellulose was synthesized according to the procedure described by [7]. 8g of NaOH was added to 20 mL of water in a 1L beaker placed on a flask shaker, the mixture was stirred at 250 rpm until complete dissolution of sodium hydroxide was observed. 250 mL of the organic solvent was added to the solution (the organic solvents used in this experiment are butanol, ethanol, isobutanol and isopropanol). 20 g of cellulose was added to the mixture and after stirring for 1 hr, 15 g of SMCA was added to the mixture. Stirring was continued for 2 hr and thereafter the mixture was placed on a water bath at 60 °C for 2 hr with manual stirring. The slurry obtained was filtered and suspended in 300 mL of aqueous methanol overnight. The next

day, the slurry was neutralized with acetic acid. The product obtained was washed three times with of 80% (v/v) aqueous methanol and subsequently, it was suspended in acetone, stirred for 20 min, and dried in an oven at 60 °C for 24 hr.



Figure 9: Synthesized CMC from sawdust cellulose

2.2.3 Proximate analysis

1- Moisture content

This was determined by drying the sample to constant weight at 105 °C. Cleaned, dried and weighed evaporating dishes were used for this purpose. About 2 g of the powdered sample was taken into the dish and dried in an oven at 105 °C, after 2 hours of drying, the sample was cooled in a dessicator and then weighed. The process of drying, cooling and weighing was repeated until a constant weight was obtained. The weight of moisture present was found by difference and expressed in percentage as follows:

$$\text{Percentage moisture content} = \frac{W_1 - W_2}{W_1} \times 100$$

W_1 = weight of sample taken (g)

W_2 = weight of sample after drying (g)

2- Determination of Total Ash

Five (5) g of the sample was weighed into a previously dried, cooled and weighed silica crucible. The crucible and content was ignited, first gently over a low flame until charred, and then in a muffle furnace at 550 °C until a white ash was obtained. The ash was moistened with distilled water, dried on

a steam bath and then on hot-plate and re-ashed at 550 °C to constant weight. The weight of ash was obtained by difference and expressed in percentage of the sample as described by [8].

3- Determination of crude fibre

Freshly prepared 1.25 % H₂SO₄ (200 ml) was added to 2 g of sample which has been defatted by extraction with ether and brought to boil quickly. The residue was then transferred quantitatively into a digestion flask; 200 ml of 1.25% NaOH (0.313M) was added and boiled for 30 mins. The mixture was then filtered and the residue washed free of alkali with water. The residue was then transferred into a weighed silica dish and dried to a constant weight at 105 °C. The organic matter of the residue was burnt off by igniting for 30 mins in a muffle furnace at 600 °C. The ash left behind was cooled and weighed. The loss in weight on ignition was reported as crude fibre [8].

2.2.4 Determination of free swelling capacity

Free swelling capacity (FSC) was determined using the teabag method [7]. 0.4 g of sample was weighed and packed inside the teabag (Tea Gschwendner, Meckenheim, Germany). It was soaked in distilled water in a test tube rack connected to a thermostat in which the water was circulated at 40 °C. After 1 hour, the sample was removed from water and allowed to drain for 5 mins to ensure uniformity. The swollen tea bags were then weighed. The weight of empty tea bag and amount of water absorbed by the empty tea bag were predetermined. The FSC was determined as follows:

$$FSC = \frac{W_{ss}}{W_{cs}}$$

$$W_{ss} = W_4 - W_2 - W_1$$

$$W_{cs} = \frac{W_3 - (W_3 \times W_t)}{100}$$

W_{cs} = corrected weight of sample

W_{ss} = weight of swollen sample

W_t = % moisture content of sample

W₁ = weight of empty teabag

W₂ = Weight of water absorbed by empty tea bag

W₃ = weight of sample taken

W_4 = total weight after swelling

2.2.5 Determination of degree of substitution

Titrimetry was used for the determination of the DS. CMS (5 g) was dispersed in acetone (150 ml) and 5 M HCl (15 ml) was added to the dispersion which was stirred for 30 min. During this process, the CMC which was in sodium form was converted to the H-CMC (carboxymethyl cellulose in hydrogen form). H-CMC was washed four times with 80 % (v/v) methanol until the solution became neutral with pH test. The neutral dispersion was filtered again, suspended in acetone and it was stirred for another 15 min, filtered, and dried for 24 hr in a desiccator over silica gel. 1 g of H-CMC was dissolved in 50 ml of 1 % (w/v) NaCl solution and it was titrated with 1M NaOH. The DS was determined as follows:

$$DS = \frac{nNaOH \times Mo}{mc - nNaOH \times MR}$$

$$mc = mp - \frac{mp \times F}{100}$$

Mo = molar mass of the anhydroglucose unit = 162 g/ mol

MR = molar mass of carboxymethyl residue = 58 g/ mol

$nNaOH$ = quantity of sodium hydroxide used (mol)

mp = weight of polymer taken (g)

mc = corrected weight of polymer (g)

F = moisture (%)

2.2.6 FT-IR spectroscopy

The IR spectra of isolated and modified celluloses were run on ALPHA BRUKER FTIR spectrometer in the frequency range 4000 – 500 cm^{-1} .

2.2.7 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of the samples was carried out using a Parkin Elmer Pyris series- TGA 6. The cellulose and CMC samples were analyzed over a continuous increase in temperature from 30 – 600 $^{\circ}C$ at a heating rate of 20 $^{\circ}C min^{-1}$. The analyzer was purged with Nitrogen at a flow rate of 20 $mLmin^{-1}$.

3. Results

3.1 Proximate Analysis

The results of the proximate analysis of the hardwood and softwood sawdusts, and their products (CMC and cellulose) are presented in Table 3.

Table 3: Proximate composition of sawdust, cellulose and carboxymethyl cellulose.

Sample	Moisture (%)	Ash (%)	Crude Fibre (%)
HR	10.8	12.93	6.02
HC	6.7	2.94	5.59
H1	7.4	11.80	6.28
H2	7.4	9.42	6.24
H3	8.8	15.36	5.94
H4	7.6	13.25	5.62
SR	17.9	13.30	6.22
SC	6.2	1.16	7.01
S1	7.6	8.63	5.90
S2	6.6	7.70	6.17
S3	7.8	11.70	6.21
S4	7.5	11.52	5.85

The samples used are denoted as follows:

HR: Raw hardwood sawdust

HC: Isolated cellulose from hardwood sawdust

H1: CMC from hardwood sawdust synthesized with Butanol.

H2: CMC from hardwood sawdust synthesized with Ethanol.

H3: CMC from hardwood sawdust synthesized with Isobutanol.

H4: CMC from hardwood sawdust synthesized with Isopropanol.

SR: Raw softwood sawdust

SC: Isolated cellulose from softwood sawdust

S1: CMC from softwood sawdust synthesized with Butanol.

S2: CMC from softwood sawdust synthesized with Ethanol.

S3: CMC from softwood sawdust synthesized with Isobutanol.

S4: CMC from softwood sawdust synthesized with Isopropanol.

The moisture content of both the isolated and modified cellulose were found to be lower than the raw sawdust samples (Tables 3). A similar trend was also observed for the Ash content. This implies that the isolated and modified cellulose samples contains more minerals and will have a longer shelf life than the sawdust.

3.2 Free Swelling Capacity of Cellulose And Cmc

The free swelling capacity (FSC) of cellulose and CMC obtained from both hardwood and softwood sawdusts is given in Table 4.

Table 4: Free swelling capacity of cellulose and CMC

SAMPLES	FREE SWELLING CAPACITY
HC	6.20
H1	9.73
H2	9.63
H3	9.74
H4	10.96
SC	6.96
S1	10.87
S2	9.93
S3	10.92
S4	11.74

From the results shown in Table 4, native cellulose (HC and SC) has the least swelling capacity while isopropanol-modified Carboxymethyl cellulose (H4 and S4) exhibits the maximum free swelling capacity.

3.3 Degree of Substitution (Ds) of Cellulose and CMC

The degree of substitution (DS) of cellulose and CMC from hardwood and softwood sawdusts is shown in Table 5.

Table 5: Degree of substitution of CMC from hardwood and softwood sawdusts

SAMPLES	DS
H1	0.40
H2	0.35
H3	0.45
H4	0.54
S1	0.40
S2	0.35
S3	0.41
S4	0.45

The organic solvent for carboxymethyl cellulose process is expected to have good miscibility with water to prevent phase separation and provide good solubility for the etherifying agents, good selectively for carboxymethylation. The optimal DS was obtained in isopropanol reaction medium (i.e. H4 and S4) as shown in Table 5. A similar result was reported for pigeon pea starch in isopropanol-water reaction medium (Lawal and his colleagues 2008).

3.4 Ftir Spectra Cellulose and CMC

FT-IR spectroscopy was used to identify the functional groups present in each sample. Figures 10 (a-j) show the FT-IR spectra obtained for the various cellulose and CMC samples.

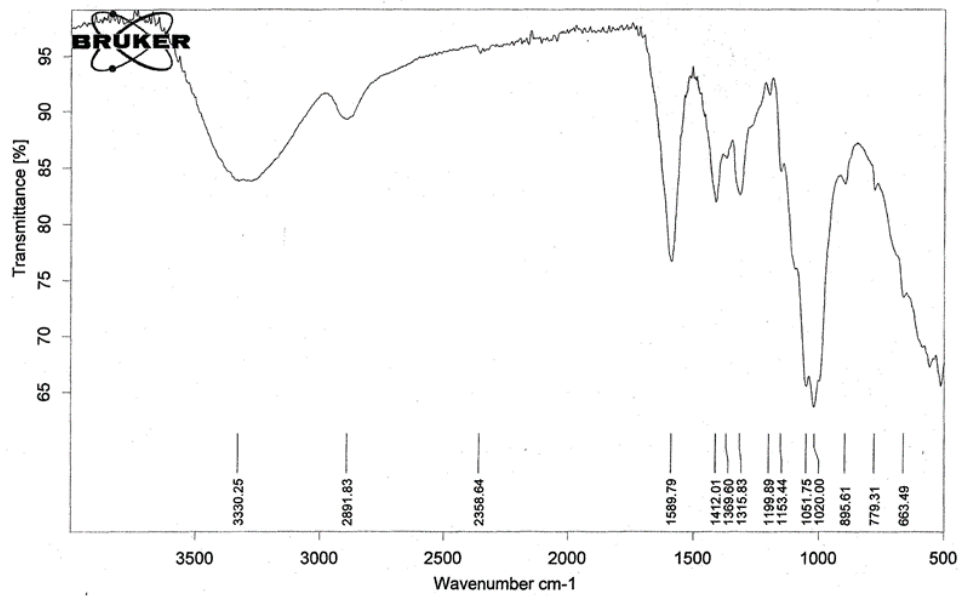


Figure 10a: FT-IR spectrum of H1

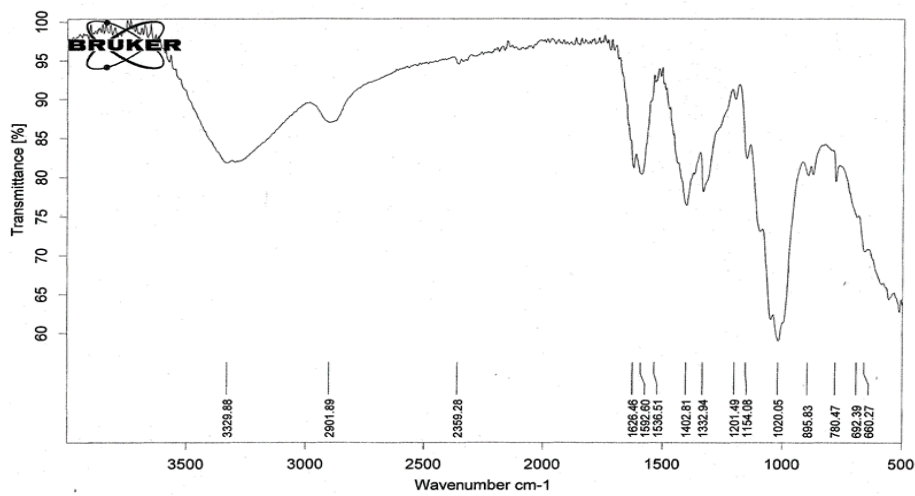


Figure 10b: FT-IR spectrum of H2

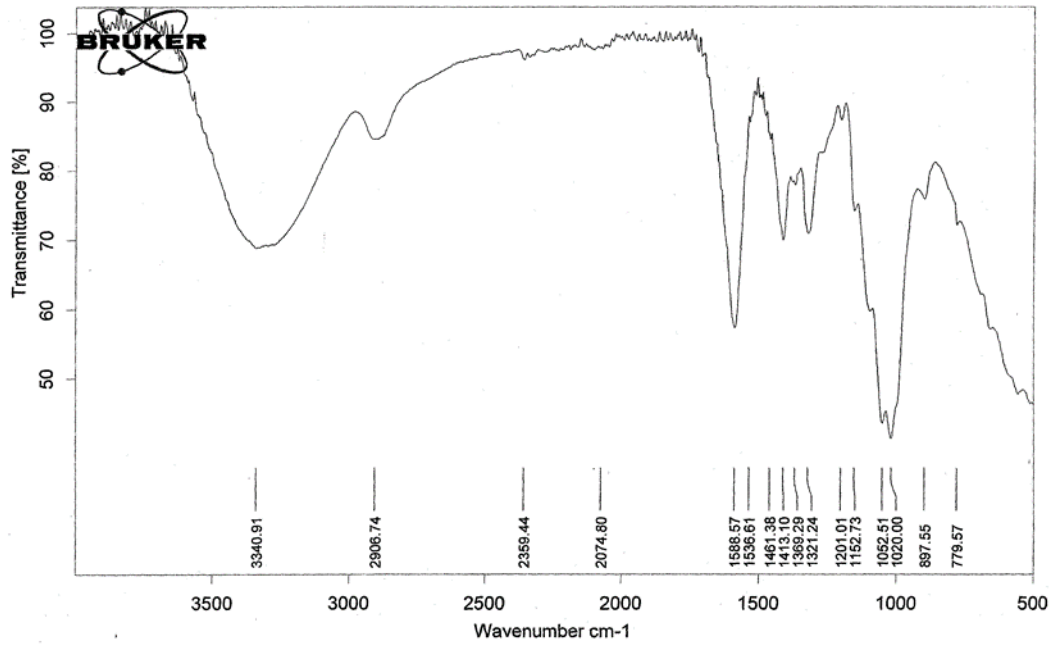


Figure 10c: FT-IR spectrum of H3

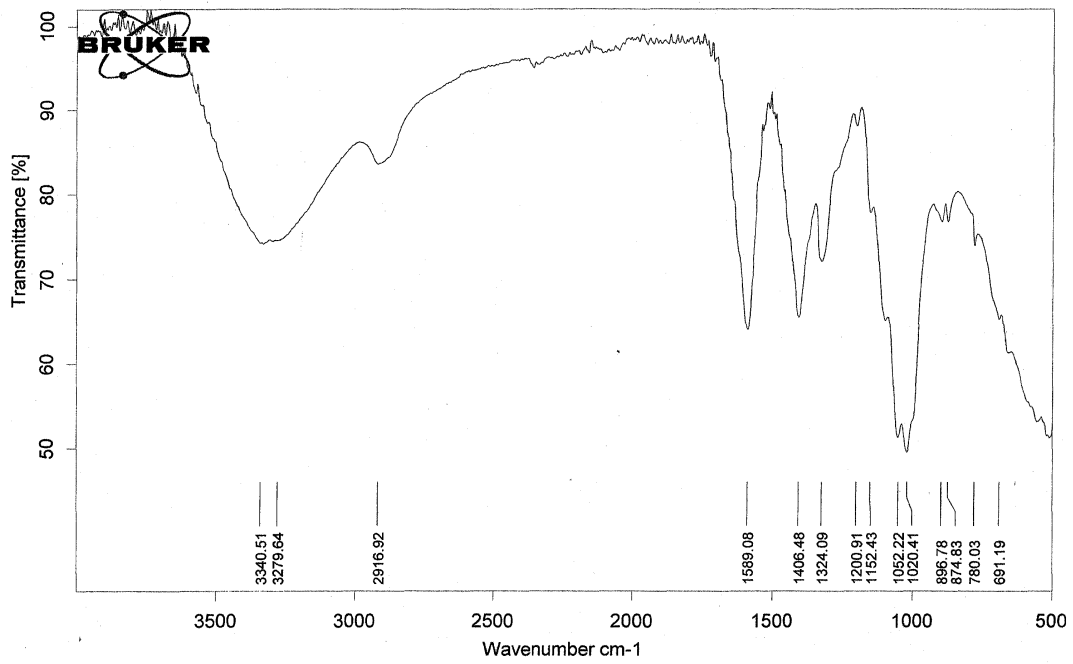


Figure 10d: FT-IR spectrum of H4

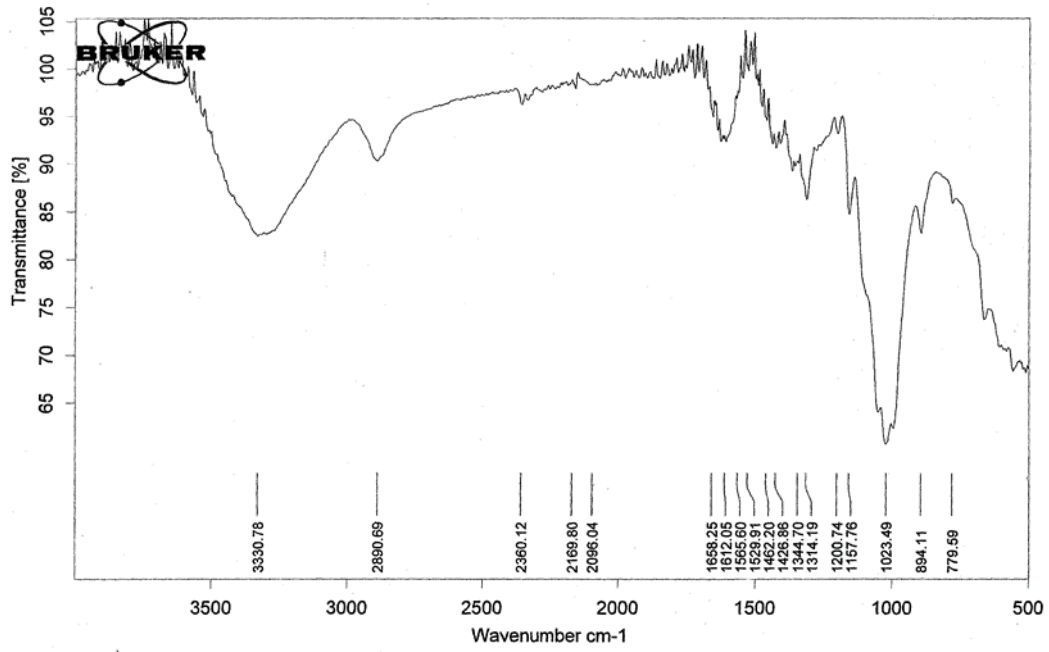


Figure 10e: FT-IR spectrum of HC

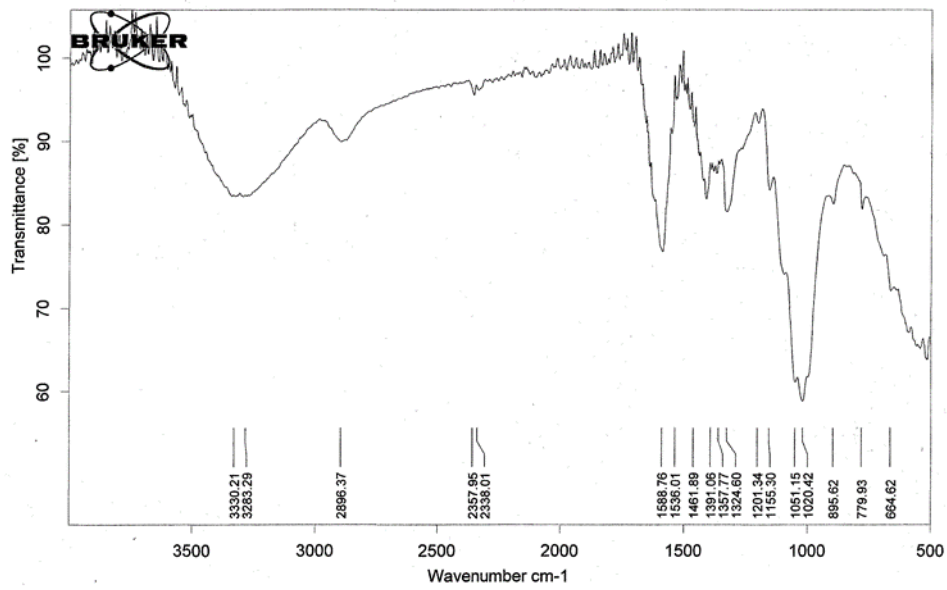


Figure 10f: FT-IR spectrum of S1

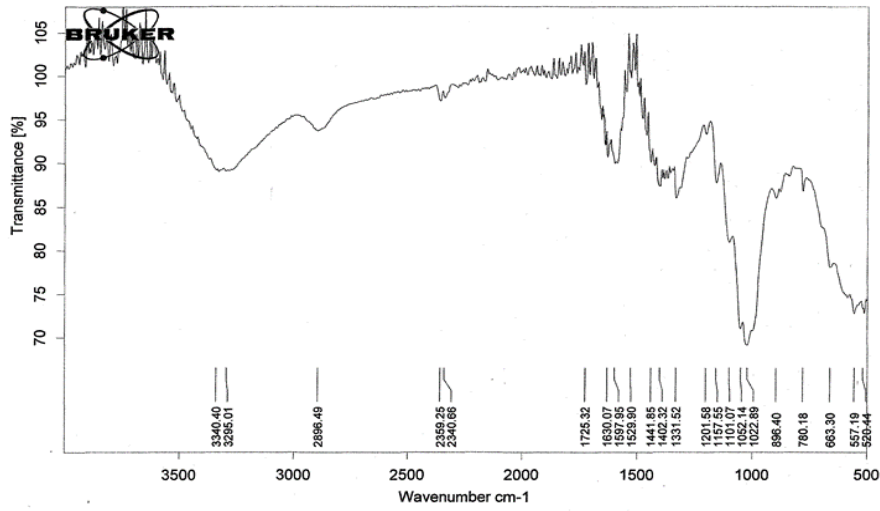


Figure 10g: FT-IR spectrum of S2

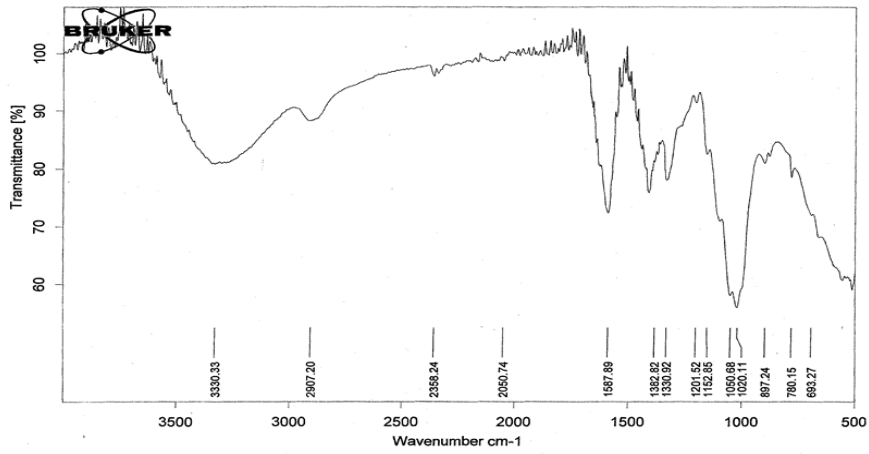


Figure 10h: FT-IR spectrum of S3

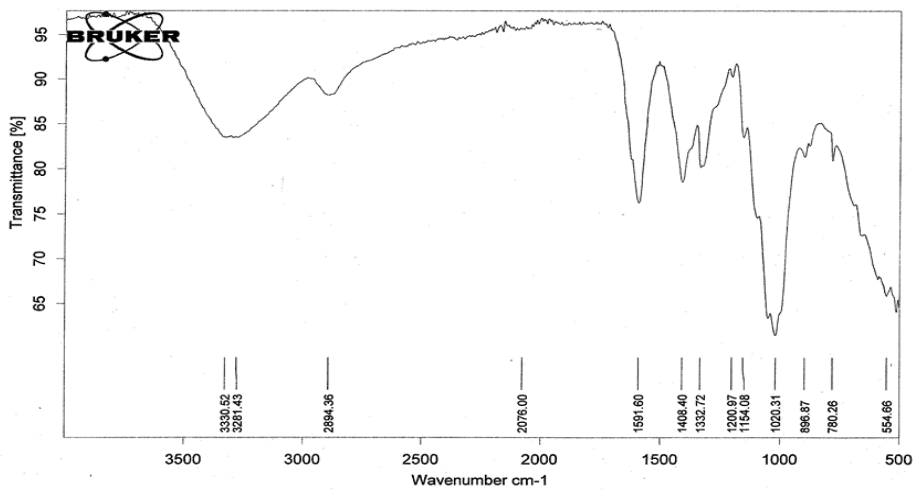


Figure 10i: FT-IR spectrum of S4

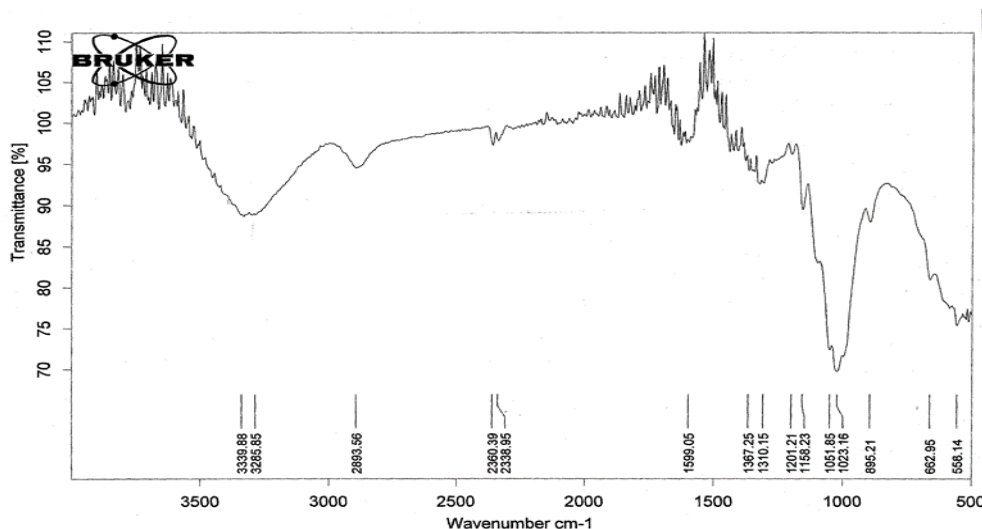


Figure 10j: FT-IR spectrum of SC

Figure 10: FT-IR spectra of Cellulose and CMC

In addition to the typical absorption of cellulose backbone, new bands were found on the spectra of the CMC samples at wavenumbers 1580-1590, 1390-145 and 1320-1225 cm^{-1} which can be attributed to carboxyl, methyl and hydroxyl functional groups respectively. This indicates that carboxymethylation process was successful. Low peak intensity was however recorded for H2 and S2 at the carboxyl region while H4 and S4 gave the highest peak intensity at this region. This suggests that isopropanol is a suitable solvent medium for etherification of cellulose.

3.4 Thermogravimetric Analysis of Cellulose and CMC

Thermogravimetric analysis (TGA) is a process in which a material is decomposed by heat, which causes bonds within a substance to be broken. TGA plays an important role in determining the thermal stability of the substance. TGA curves of samples analyzed are presented in Figures 11(a-j)

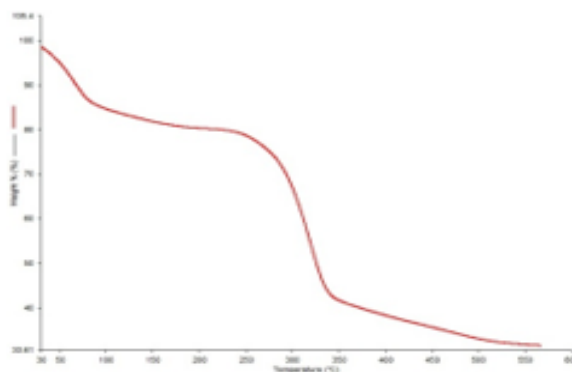


Figure 11a: TGA curve of H1

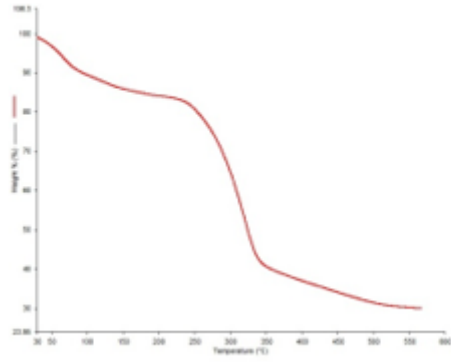


Figure 11b: TGA curve of H2

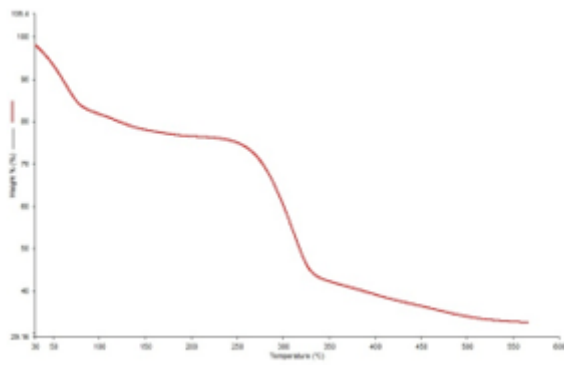


Figure 11c: TGA curve of H3

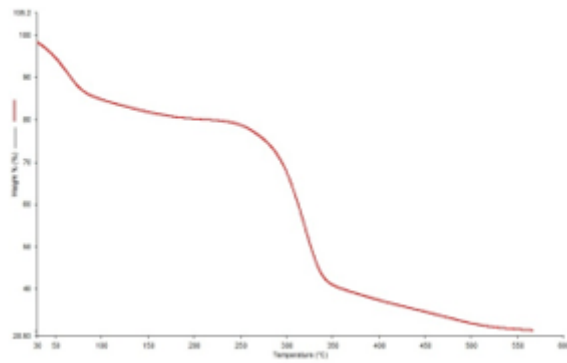


Figure 11d: TGA curve of H4

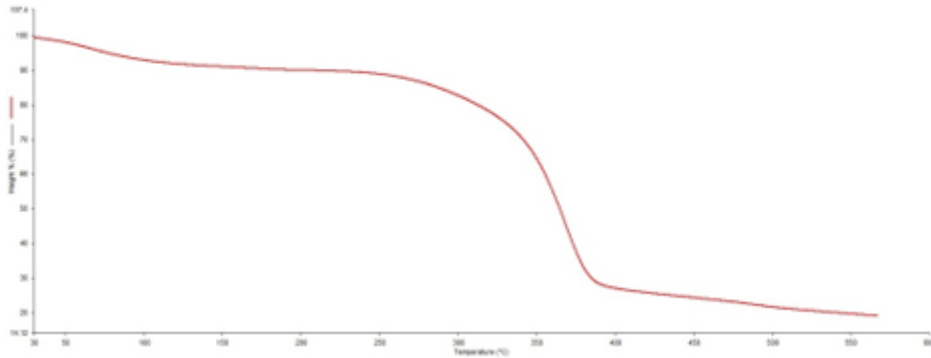


Figure 11e: TGA curve of HC

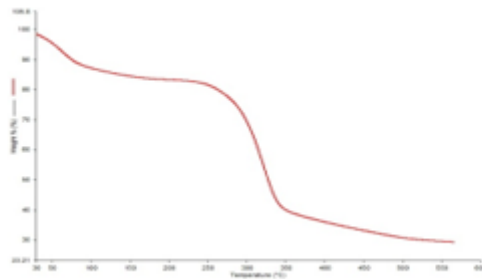


Figure 11f: TGA curve of S1

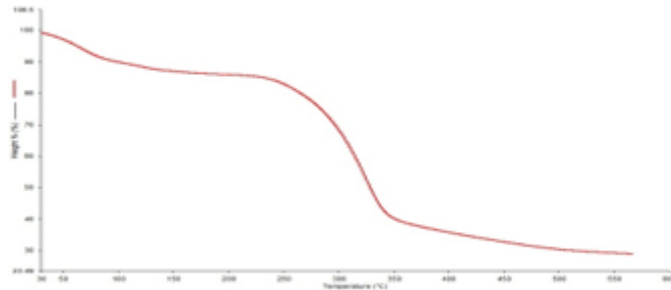


Figure 11g: TGA curve of S2

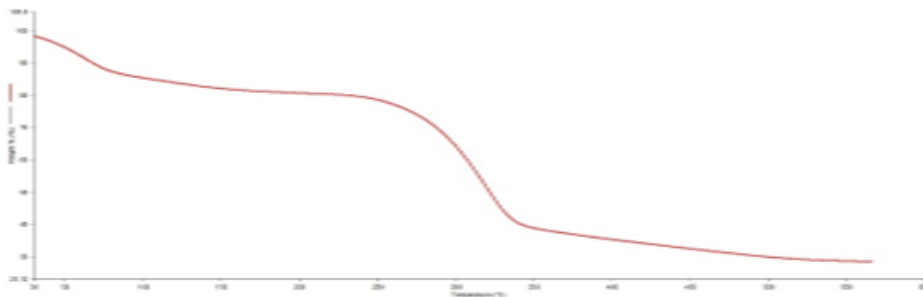


Figure 11h: TGA curve of S3

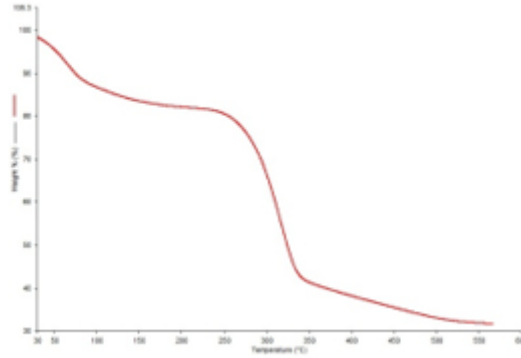


Figure 11i: TGA curve of S4

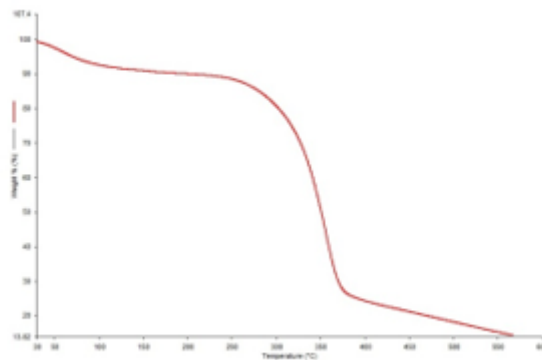


Figure 11j: TGA curve of SC

Figure 11: TGA curves of Cellulose and CMC

The TGA curves exhibit two distinct weight decreasing steps for all samples during thermal degradation. The first weight decrease, due to evaporation of moisture, occurred at 30-85 °C with a weight loss of 10 % and 15 % for cellulose and CMC samples respectively. The second weight was observed at 250-400 °C with maximum decomposition temperature around 350 °C and 310 °C for cellulose and CMC samples with weight loss of about 35 % and 37 % respectively. The second stage of weight loss was due to thermal degradation of carbohydrate polymers (Reddy and Rhim, 2014). The final weight loss after thermal degradation was approximately 20 % and 31 % for cellulose and CMC samples respectively. In all stages of thermal degradation, cellulose samples showed lesser weight loss than CMC samples. This indicates that cellulose samples exhibit higher thermal stability than CMC samples. The decrease in thermal stability of CMC as compared to parent cellulose is justified by the presence of negatively charged carboxymethyl groups (Danilo and his colleagues 2015).

4. Conclusion and Recommendation

4.1 Conclusion

Cellulose was successfully isolated from sawdust of hardwood and softwood using alkali-acid pretreatment and

bleaching processes. The isolated cellulose was converted to carboxymethyl cellulose using Butanol, Ethanol, Isobutanol and Isopropanol as organic solvent media. The FT-IR spectroscopy confirmed the conversion of cellulose to carboxymethyl cellulose by the presence of carboxyl and methyl functional groups at wavenumber of 1580-1590 and 1380-1415 cm^{-1} respectively on the FT-IR spectra. The degree of substitution of CMC was determined by titrimetry method and the values obtained ranged from 0.35 to 0.54 with CMC synthesized using Isopropanol solvent medium having the optimal DS and Ethanol having the least. Hence, Isopropanol is a suitable solvent medium for the synthesis of CMC. Thermal analysis showed that carboxymethyl cellulose exhibits lower thermal stability than the parent cellulose.

4.2 Recommendations

Government and Entrepreneurs should invest on conversion of sawdust (waste) to carboxymethyl cellulose (source of wealth) due to its many applications in order to boost the nation's economy and also to reduce the environmental and health hazards caused by improper disposal of sawdust

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