

Cellulose Obtained From Agricultural Waste Subjected to Carboxymethylation

Sanjana Keshav¹, Archana Grover²

Assistant Professor¹, Student²

Department of Chemistry

A.D. Patel Institute of Technology

Corresponding Author's E-mail:- groverarchana5@gmail.com²

Abstract

We concentrated on leftover biomass, which is particularly plentiful in Slovenia and comes from corn and wheat harvesting. To begin, we chemically identified common biomass, such as maize stover, corn stems and peeled cobs, and wheat straw. We determined the cellulose, lignin, hemicellulose, extractives, and ash contents. Due to the rather high cellulose content in typical samples, which ranged between 35% and 44%, the materials were further delignified using an alkaline technique with NaOH as a reagent. Mechanical, morphological, and other aspects of isolated cellulose fibres were investigated. Simultaneously, we refined the delignification procedure to determine how delignification circumstances impact the qualities of isolated cellulose fibres. Furthermore, we investigated the conversion of isolated cellulose fibres into carboxymethyl cellulose (CMC) by Williamson ether synthesis under a variety of solvents and experimental circumstances. CMC was synthesised using cellulose fibres extracted from maize stover, corn stems and peeled cobs, and wheat straw. We also investigated prospective variations in CMC production utilising native (cellulose I) and regenerated (cellulose II) cellulose as starting materials.

Keywords: - *Agricultural residues, delignification process, cellulose, Williamson ether synthesis, carboxymethyl cellulose (CMC)*

INTRODUCTION

After yearly harvesting of cereal crops, large amounts of stem biomass are created; nevertheless, the latter are typically underutilised. Farmers use agricultural wastes as animal feed and litter in certain circumstances, but in most cases, they are left on the fields, composted, or simply burned. Because of the growing environmental problems produced by contemporary industry, we have begun to investigate the technical exploitation of agricultural wastes to develop added value goods. This type of biomass is very useful in the paper sector and, by extension, in packaging. The plant biomass is mostly composed of cellulose, hemicellulose, and lignin (Igdi, 1988), with cellulose fibres being the most significant. Cellulose is a high-molecular-weight linear macromolecule with 1,4-glucosidic linkages connecting glucose monosaccharide units (Hon and Shiraishi, 2001). Many people believe that cellulose is the most prevalent polymer on Earth, if not the most abundant organic stuff. It may be converted into a variety of valuable chemical feedstocks, including cellulose ethers and esters (Klemm et al, 1998). CMC is one of the most significant cellulose derivatives. It is a water-soluble, linear, long-chain polysaccharide with a high viscosity and polyelectrolyte property

that can be employed in the textile, food, paper, and pharmaceutical sectors (Singh and Singh, 2013).

EXPERIMENTAL

Biomass samples

Corn stover, stems and peeled cobs; wheat straw.

Chemical characterization of biomass

The typical biomass samples were ground to 0.5 mm diameter particles prior to chemical testing. The cellulose was determined using the Kürschner-Hoffer method (Kürschner and Hoffer, 1931), the hemicellulose using the chlorite method (Wise, Murphy, and D'Addieco, 1946), the lignin using Klason's method (TAPPI T 222 om 02), the ash using standard method TAPPI T 211 om-93, and the extractives using standard method TAPPI T 204 cm 97.

Delignification process

We began by cutting the biomass into smaller pieces. The delignification process was carried out in a 5 L laboratory delignificator at 160 °C and increased pressure using an 18% NaOH solution as reagent (18% reflects the proportion of NaOH relative to the amount of totally dry biomass). The mass ratio of totally dry biomass to water was one to five. The

delignification reaction lasted 3 hours and 1.5 hours following process optimization. When the procedure was finished, it was neutralised, disintegrated, screened, squeezed, and homogenised.

Determination of mechanical and morphological properties

Mechanical properties were measured from laboratory sheets which were prepared according to ISO 5269-2. Breaking length was determined according to ISO 1924-2. Average fiber length and width were determined on Valmet Fiber Image Analyser FS5 from dilute fiber suspensions.

Determination of lignin content in isolated cellulose fibers (Kappa number)

This parameter was determined according to the international standard method ISO 302:2015(E).

Synthesis of CMC

Syntheses were performed in different solvents, such as isopropanol, ethanol and HFIP (1,1,1,3,3,3-hexafluoro-2-propanol). For all reactions, 2.55 mmol NaOH mmol⁻¹ AGU (in the case of in situ formation of sodium chloroacetate 5.1 mmol NaOH mmol⁻¹ AGU) and 2.04 mmol sodium chloroacetate mmol⁻¹ AGU or 2.04 mmol chloroacetic acid mmol⁻¹ AGU were used.

First, we performed alkalization process using 4 mL of pure solvent, cellulose pulp (the mass of absolutely dry matter was 81 mg) and 1.275 mmol NaOH. In the case of isopropanol as solvent, about 100 μ L of distilled water was added to the solution to accelerate the dissolution of NaOH. The reaction was carried out for 1 hour at a temperature of 25 °C to 40 °C. This was followed by the etherification process with 1.02 mmol sodium chloroacetate or chloroacetic acid (in this case, we also added 1.275 mmol NaOH to the solution), which was mixed in advance with 2 ml pure solvent and about 400 μ L distilled water and added to previous solution. The etherification was performed from 1 hour to 23 hours at a temperature of 60 °C to 75 °C. Finally, we added an excess of acetic acid to the solution, filtered off the solid residue, washed with 70% methanol and dried at 100 °C to constant weight.

Additional analyses

Additional analyzes of isolated cellulose fibers and CMC cellulose fibers were performed with FTIR spectroscopy (FTIR spectra were recorded on Bruker FTIR Alpha Platinum ATR and Spectrum Two PerkinElmer). Microscopic images were obtained on the Nikon Eclipse 80i optical microscope and SEM images on scanning electron microscope Thermo Fisher

Scientific Quattro S. We also used commercial cellulose fibers as reference cellulose in the course of Williamson ether synthesis and compared the obtained FTIR spectra with FTIR spectra of a commercial CMC, where the degree of substitution (DS) was determined using the Eyler method (Eyler, Klug and Diephuis, 1947).

RESULTS AND DISCUSSION

The findings of biomass characterisation revealed that the materials (corn stover, maize stems and peeled cobs, and wheat straw) contain varying amounts of cellulose, hemicellulose, and lignin. The amount of cellulose and lignin in biomass varies depending on its composition. As a result, the concentration of these two components in wood biomass is larger than in agricultural biomass (Figure 1).

As seen in Figure 1, the cellulose concentration was rather high in all cases, so we chose to isolate it using the delignification technique, which is used to break down the chemical structure of lignin and make it liquid soluble. The characteristics of isolated cellulose fibres differed from one another. As a result of delignification, no cellulose fibres were recovered from peeled corn cobs. In reality, only extremely little cellulose pieces were produced (Figure 2a). The forms of cellulose fibres shown by scanning electron microscopy were intriguing (Figures 2b, 2c, 2d and 2e). Optical microscopy demonstrated the existence of trachea, parenchymal, and epidermal cells (Karlsson, 2006). (Figure 2f).

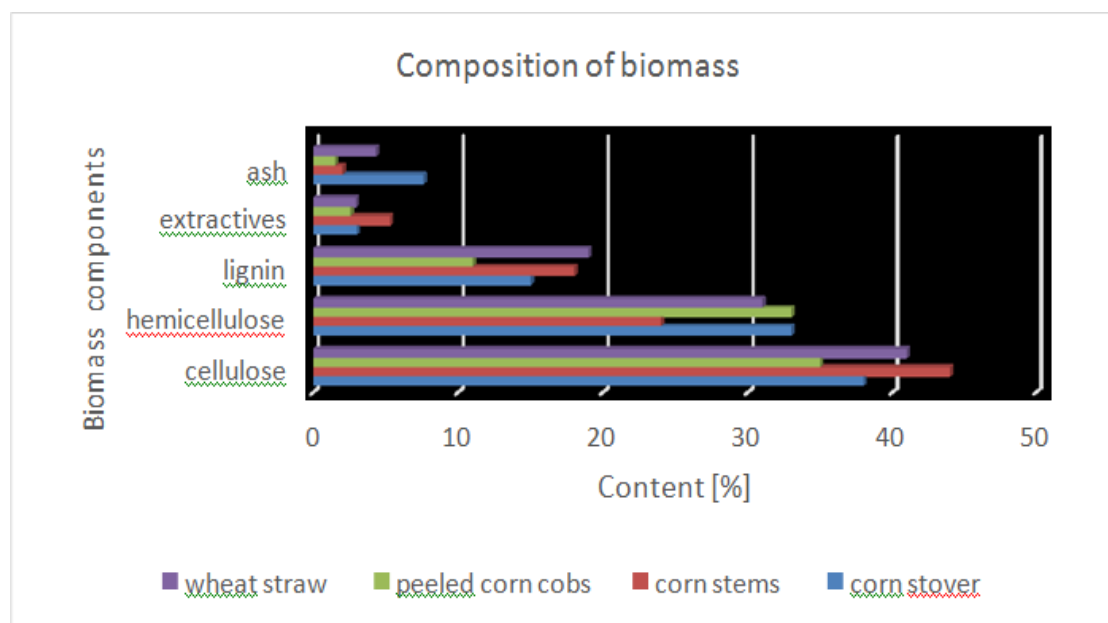


Figure 1: Composition of biomass

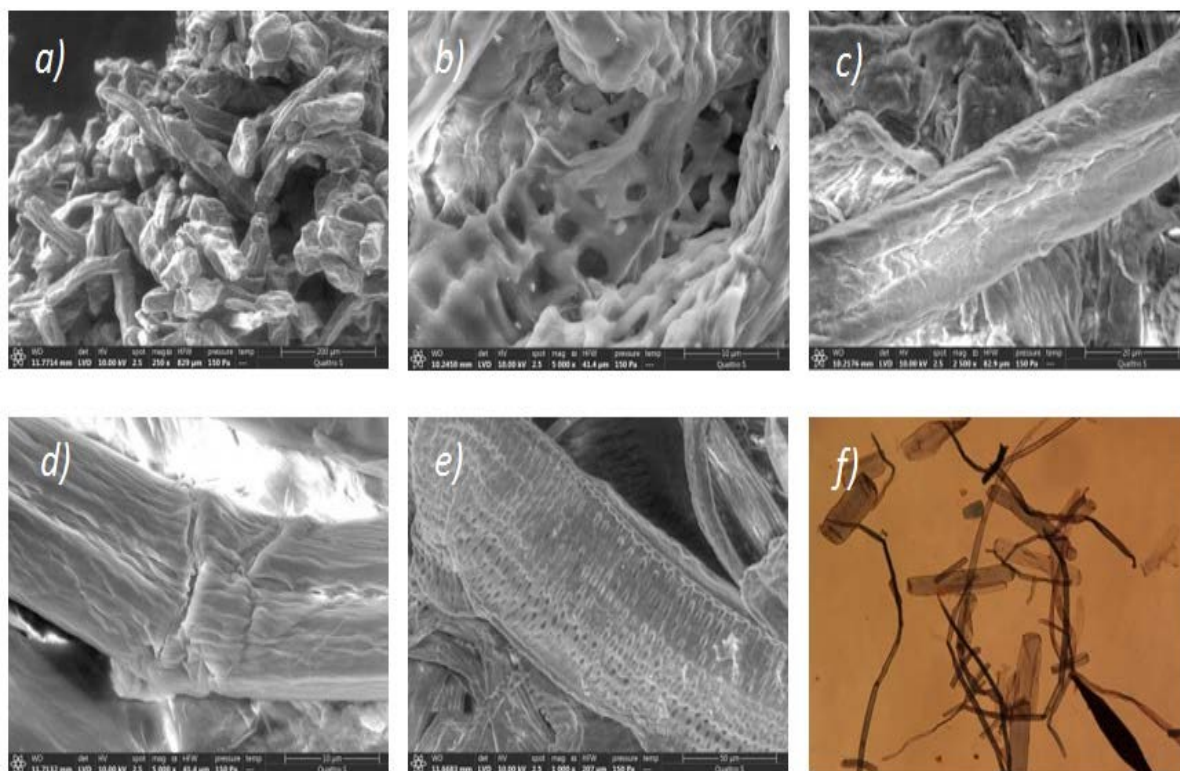


Figure 2: SEM and optical microscopic images of isolated cellulose fibers

The results reveal that the characteristics of cellulose fibres, particularly the breaking length as the most typical mechanical parameter, are highly dependent on the delignification process settings. As a result, the longer the delignification process, the lower the lignin content of fibres and the values of mechanical characteristics. The morphological features of fibres, on the other hand, are significantly less reliant on the delignification circumstances (Table 1).

Table 1: Dependence of the properties of cellulose fibers isolated from wheat straw on the conditions of delignification process

Property	Value at 3 h delignification	Value at 1.5 h delignification
Breaking length [m]	3530	5575
Fiber length (Lc(l) ISO)	0.697	0.808
Fiber width [μm]	15.27	15.72
Kappa number	8	16

We also investigated if isolated cellulose fibres might be used in the modification procedure. As a result, we used the Williamson ether reaction to create CMC. The data reveal that the reaction's path is determined by the solvent in which it occurs (Figure 3).

Such reactions, it turned out, worked effectively in ethanol and isopropanol at the conditions given in section Experimental, but not so well in HFIP. The use of regenerated cellulose (cellulose II)

has no effect on the reaction's outcome, except when the NaOH concentration in the alkalization process is high (Ambjörnsson, Schenzel, and Germgrd, 2013). Cellulose II is formed when cellulose I is agitated for 0.5 to 1 hour at room temperature in an 18% NaOH solution.

As a result, while executing such reactions, it is possible to employ native cellulose (cellulose I) without any pre-treatment.

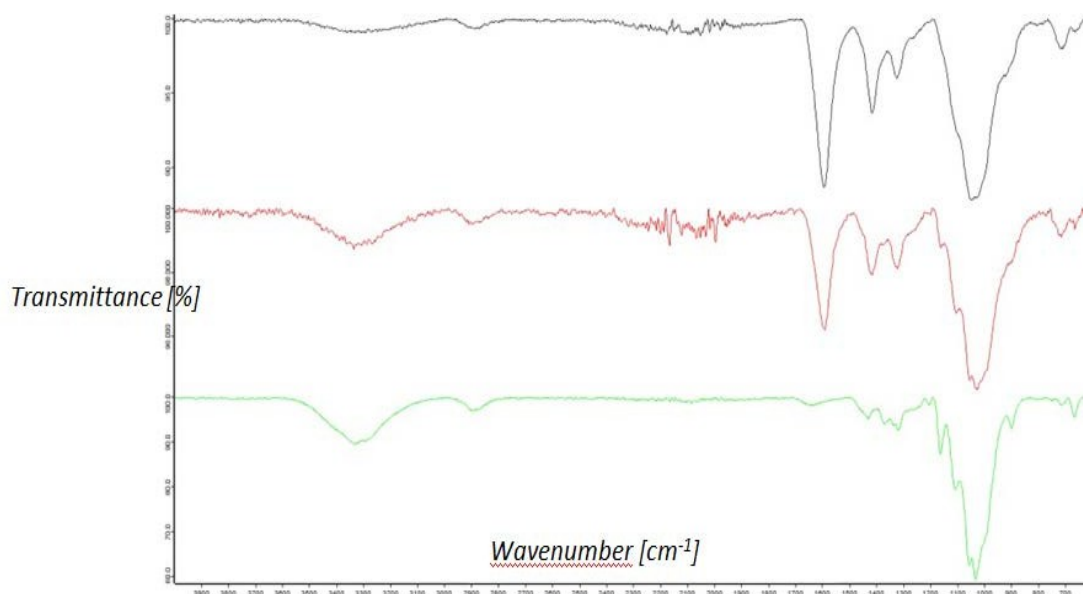


Figure 3: FTIR spectra of the products obtained in synthesis of CMC in isopropanol (black FTIR spectrum), ethanol (red FTIR spectrum) and HFIP (green FTIR spectrum) using cellulose fibers isolated from wheat straw (alkalization process was carried out at 40 °C for 1 hour and etherification at 70 °C for 7 hours)

Further study has revealed that CMC is generated after a short period of conducting the etherification phase, therefore this process may be completed in as little as one hour. Of course, whether we undertake the etherification process for less or more time, the FTIR spectrum of CMC alters significantly, indicating that the degree of substitution and other features of CMC vary with the period of execution of both steps of Williamson ether synthesis. The degree of substitution and other features of CMC are also highly dependent on other circumstances of CMC synthesis (e.g., reagent concentration, temperatures at which both phases occur,...). In addition to the foregoing, the

results reveal that, despite differences in mechanical, morphological, and other qualities, the responses of CMC production on isolated cellulose fibres of varied origin are relatively comparable. Because the appearance of the resultant CMC compounds produced in different solvents varies, we also did scanning electron microscopy investigation (Yanez-S et al, 2018). The cellulose fibres create various structures when exposed to isopropanol (Figure 4a), ethanol (Figure 4b), or HFIP (Figure 4c) as solvents, which is reflected in their varied characteristics. When CMC sodium salt was dissolved in water, a thick gel-like material began to develop (Figure 4d).

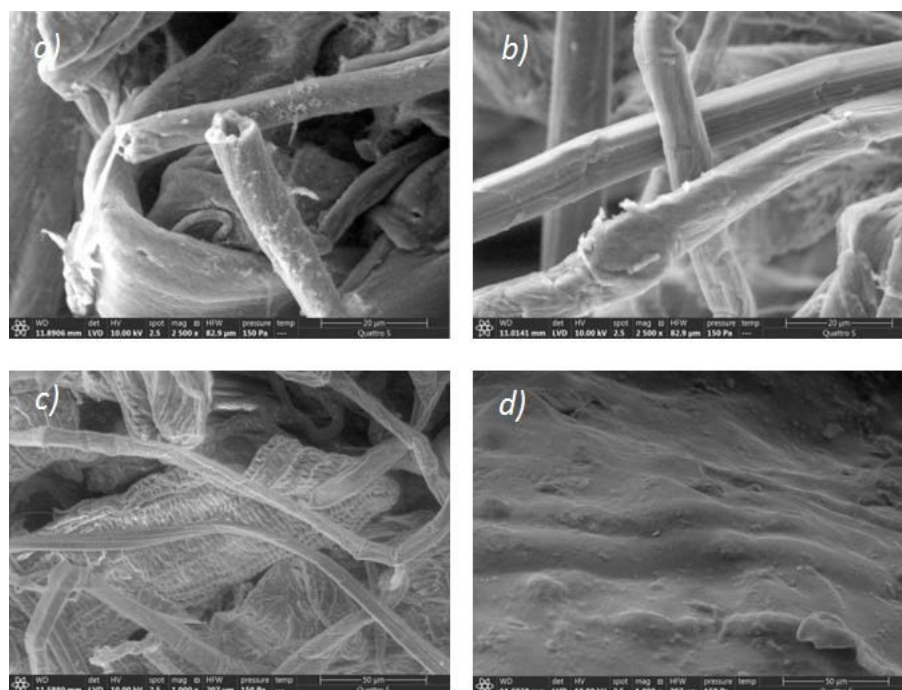


Figure 4: SEM microscopic images of CMC synthesized on the cellulose fibers isolated from corn stover

In the synthesis of CMC, it has also been established that there are some side reactions that could occur. Therefore, it is very important that CMC is well washed at the end of the synthesis with an aqueous alcohol solution, because the by-products are poorly soluble in anhydrous solutions.

CONCLUSION

It was discovered that the cellulose extracted from all of the biomass samples studied is appropriate for CMC production. The latter can be utilised as an effective papermaking additive, as well as for pigment coating and paper surface sizing, in the paper and packaging sectors. Similarly, the cellulose fibres derived from these plentiful agricultural leftovers may be appropriate for the production of additional cellulose derivatives and composites. With the exception of peeled maize cobs, these agricultural leftovers can also be used as alternate sources of high quality cellulose fibres in papermaking.

REFERENCES

1. Ambjörnsson, H. A., Schenzel, K., Germgård, U. (2013) Carboxymethyl Cellulose Produced at Different Mercerization Conditions and Characterized by NIR FT Raman Spectroscopy in Combination with Multivariate Analytical Methods. *BioResources*, 8(2), pp. 1918-1932.
2. Eyler, R. W., Klug, E. D., Diephuis, F. (1947) Determination of Degree of Substitution of Sodium Carboxymethylcellulose. *Analytical chemistry*, 1, pp. 24- 27.
3. Hon, D. N.-S., Shiraishi, N. (2001) *Wood and cellulosic chemistry*. 2nd ed. New York, Basel: Marcel Dekker, Inc.
4. Iglič, B. (1988). *Kratka tehnologija pridobivanja vlaknin iz proizvodnje papirja ter kartona za slušatelje lesarstva na Biotehnični fakulteti Univerze Edvarda Kardelja v Ljubljani*. Ljubljana: Biotehniška fakulteta VTOZD za lesarstvo.
5. Karlsson, H. (2006). *Fibre Guide (Fibre analysis and process applications in the pulp and paper industry*. 1st ed. Kista: AB Lorentzen & Wettre.
6. Klemm, D., Wagenknecht, W., Heinze, T., Heinze, U., Philipp, B. (1998) *Comprehensive Cellulose Chemistry*. Weinheim: Wiley-VCH.

7. Kürschner, K., Hoffer, A. (1931).
Eine neue quantitative
Cellulosebestimmung. Chemiker
Zeitung, 17, pp. 161-168.
8. Singh, R. K., Singh, A. K. (2013)
Optimization of Reaction
Conditions for Preparing
Carboxymethyl Cellulose from
Corn Cob Agricultural Waste.
Waste and Biomass Valorization, 4,
pp. 129-137.
9. Wise, L. E., Murphy, M.,
D'Addieco, A. A. (1946) Chlorite
Holocellulose, its Fractionation and
Bearing on Summative Wood
Analysis and Studies on the
Hemicelluloses. Paper Trade
Journal, 122 (2), pp. 35-43.
10. Yáñez-S, M., Matsuhiro, B.,
Maldonado, S., Gonzalez, R.,
Luengo, J., Uyarte, O., Serafine, D.,
Moya, S., Romero, J., Torres, R.,
Kogan, M. J. (2018)
Carboxymethylcellulose form
bleached organosolv fibers of
Eucalyptus nitens: synthesis and
physicochemical characterization.
Cellulose, 25, pp. 2901-2914.