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Carboxymethylation of α-cellulose isolated from *Lantana camara* with respect to degree of substitution and rheological behavior

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Abstract

Lantana camara is a noxious weed posing a serious threat to the ecology and demands concerted efforts for its management. Utilization of its abundantly available cellulosic biomass as chemical feedstock could be a practical proposition for the management of this weed. α-cellulose (Av DP 430) was, therefore, isolated from this weed and its carboxymethylation was studied under varying reaction conditions with respect to maximum DS. The influence of reaction conditions on apparent viscosity of the prepared derivatives was also studied. The conditions optimized were concentration of aqueous NaOH 3.24 mol/AGU, 20% (w/v); concentration of MCA 2.05 mol/AGU; carboxymethylation time 3.5 h and temperature 55 °C with isopropyl alcohol as the solvent medium to yield CMC of DS 1.22. Rheological studies of 1 and 2% solutions of the optimized product showed their non-Newtonian pseudoplastic behavior.

Keywords: Lantana camara; Cellulose; Carboxymethyl cellulose; Apparent viscosity

1. Introduction

Lantana camara L. (Verbenaceae) is a noxious weed which has imposed a great threat to land productivity, grazing livestock, biodiversity and consequently to the overall ecology (Pass, 1991; Sharma, Makkar, & Dawra, 1988). It is widely acknowledged that attempts to manage this weed using mechanical, chemical and biological means have met with limited success (Sharma, 2004). Alternatively, luxuriant growth and vigorous survival make this weed of potential economic value for utilization of its abundantly available biomass into value added products offering thereby an efficient and effective method for its management. During the last few years, research has been conducted to utilize the lantana biomass for development of furniture products, baskets, mulch, compost, drugs and other biologically active agents (Inada, Nakanishi, Tokuda, & Sharma, 1997; Sharma, 2004; Sharma & Sharma, 1989).

There has been an increasing importance of cellulose—rich biomass from various sources as chemical feed stock, since these materials consist of cellulose, hemicellulose and lignin containing many functional groups susceptible for chemical derivatization reactions (Barkalow & Young, 1985; Ghosh & Ganguly, 1994; Patnaik, Sarangi, Mohanty, & Singh, 1989; Patra & Singh, 1994; Samal & Bhuyan, 1994). Etherification of cellulose is one of the most important routes of cellulose derivatization. Patents disclosing the preparation of cellulose ethers date back to the early 1900s (Lilienfeld, 1912; Lilienfeld, 1916). Carboxymethylation of cellulose is a versatile transformation because it provides access to water-swellable or water soluble polymers and intermediates with various valuable features (Feddersen & Thorp, 1993; Sandford & Baird, 1983). Preparation of carboxymethyl cellulose (CMC) was first patented in 1918 (Jansen, 1918). Since then reactants have not changed significantly although the processes have. CMC has got ample scientific attention, especially due to its polyelectrolyte character, and its practical utility in food, cosmetic and pharmaceutical applications. A survey of the literature reveals that besides the cotton linters and wood pulp, a number of cellulose biomass from various other sources such as agricultural wastes e.g. rice straw, sugarcane bagasse, saw dust and cotton stables (Hebeish et al., 1994),

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orange mesocarp (Akaranta & Osuzi, 1997), weed, *Eichoria crassipes* (Barai, Singhal, & Kulkarni, 1997) and agave (Ramos, Frollini, & Heinze, 2005; Vieira, Heinze, Antonio-Cruz, & Mendoza-Martinez, 2002) have been used as a base material for production of CMC differing in their DS and properties using different set of reaction conditions depending upon the DP and composition of the cellulosic material. The goal of these modifications is to increase the utilization of this abundantly available cellulose biomass as a feedstock as an alternative to expensive cotton linters, and wood pulp which now-a-days are discouraged due to environment conservative regulations.

Prompted by the aforesaid facts, the possibility of using *L. camara* weed as a feedstock for production of α-cellulose and its subsequent derivatization into CMC was examined and findings are reported herein.

2. Experimental

2.1. Materials

Lantana camara used in the study were collected from the field of the institute's campus. All the chemicals used were of laboratory grade.

2.2. Methods

2.2.1. Proximate chemical analysis of Lantana camara

Moisture content and bulk density of the material were determined and found to be 65.88% and 210.76 kg/m^3, respectively. Plant material was reduced to chips of 1–2″ size and air dried. Chips were reduced to dust, and the dust passing through 40 mesh and retained on 60 mesh were taken for studies. Proximate chemical composition of the plant material was studied using the standard methods to assess the quality and solubility of raw material for further processing and results of the analysis are presented in Table 1.

2.2.2. Isolation of alpha cellulose

The air dried chips were subjected to following treatments. The conditions at each stage were optimized and 1 kg production of alpha cellulose (yield 38.76%; Brightness 81.0% ISO) was carried out under optimized conditions.

Table 1
Proximate chemical composition of *Lantana camara*

Sl. No.	Parameters	Value%	Method used
1.	Hot water solubility	7.0	APPITA P 4 M-61
2.	1% NaOH solubility	18.0	APPITA P 5 M-61
3.	Alcohol–benzene solubility	4.45	APPITA P 7 M-70
4.	Holocellulose	71.34	TAPPI 9 M-54
5.	Alpha cellulose	64.91	TAPPI T-203 OM 88
6.	Pentosans	13.0	TAPPI T-203 OM 84
7.	Lignin	27.25	TAPPI T-222 OM 88
8.	Ash	1.8	APPITA P3 M-69

2.2.2.1. Water prehydrolysis. The chips were prehydrolysed in autoclave keeping bath ratio 1:4 at 100 °C for 30.0 min. The yield after prehydrolysis was 95.5%.

2.2.2.2. Alkali hydrolysis. Water prehydrolysed chips were treated with 2% alkali as NaOH. The bath ratio was maintained 1:4 and heated in autoclave to 120 °C for 60 min. The yield was 85.9%.

2.2.2.3. Pulping. The pulping of alkali hydrolysed chips was carried out with 20% alkali as NaOH at 160 °C for 90.0 min. The kappa number of the pulp was 26 and pulp yield was 48% with 3.8% screen rejects.

2.2.2.4. Bleaching. Bleaching was carried out using hypochlorite (2.0%) / chlorine dioxide (2.0%)/hydrogen peroxide (1.0%) bleaching sequence.

2.2.3. Characterization of the cellulose

Cellulose obtained as above was characterized for its DP and composition and are presented in Table 2. DP was determined by CED viscosity method using following formula:

$$\mathrm{DP}^{0.905} = 0.75(\eta)$$

where η is intrinsic viscosity.

2.2.4. Carboxymethylation of α-cellulose

Synthesis of CMC was carried out in two steps—alkalization and etherification of α-cellulose under heterogeneous conditions. Alkalization was conducted at 25 °C in which aqueous NaOH (3.24 mol/AGU; 10–40% w/v) was added to vigorously stirred slurry of α-cellulose (3 g) in iso-propanol (80 ml) over a period of 30 min. Stirring was continued for another 60 min. Then monochloro acetic acid (1.55–2.30 mol/AGU) dissolved in 10 ml iso-propanol was added under continuous stirring and the reaction mixture was heated up to the desired temperature (35–65 °C) and stirred at that temperature for fixed duration (1.5–4.5 h). After neutralizing the excess alkali with acetic acid, the CMC samples were filtered, washed with 70% aq. methanol, followed by absolute methanol, and dried at 60 °C in oven.

Table 2
Characteristics of the cellulose isolated from *Lantana camara*

Characteristics of cellulose	Value (%)	Method used
α-cellulose	94.80	TAPPI T2003 OM-88
β-cellulose	2.50	
γ-cellulose (by difference)	1.42	
Lignin	0.80	TAPPI T-222
Ash	0.48	APPITA P3 M-69
Viscosity	576 cm^3 gm	SCAN 15
Av. DP	430	SCAN 15

Yield: 110–133%. IR (KBr): 1605 cm^{-1} ν_{as} (COO^-); 1421 cm^{-1} ν_s (COO^-).

2.2.5. Determination of degree of substitution (DS)

The DS of the prepared CMC samples was determined by the standard method (Green, 1963).

2.2.6. Determination of apparent viscosity (η)

The apparent viscosity (η) of all the samples (1.0% solution in water), wherever possible was determined at the shear rate of 3.4 s^{-1} using a Brookfield Digital Viscometer model 'RVTD', Stoughton, USA. Apparent viscosity of the optimized product was also determined at different shear rates ranging from 3.4–34 s^{-1}. All measurements were made at 25 ± 1 °C.

2.2.7. IR spectra

FT-IR spectra were recorded on a JASCO FT-IR 5300 using KBr pallets.

3. Results and discussion

Carboxymethylation of α-cellulose isolated from *L. camara* was optimized with respect to DS by varying the process parameters as shown in Table 3. Each of these parameters was varied one by one keeping the remaining parameters constant in the reaction. Apparent viscosity (η) of the products obtained under varied reaction conditions was determined and its dependence on each of the variables was investigated. The viscosity of 1 and 2% aq. solutions of the optimized CMC was also determined and the values so obtained were used to characterize the optimized product.

The effect of alkali concentration on DS and η was studied.As shown in Fig. 1, it was observed that the DS increased with increasing the concentration of aqueous NaOH from 10 to 20% and thereafter decreased considerably. The carboxymethylation process involves following two competitive reactions which take place simultaneously (Barai, Singhal, & Kulkarni, 1997).

$$\underset{\text{Cellulose}}{\text{Cell}-\text{OH}} + \underset{\text{Chloroacetic acid}}{ClCH_2COOH} + NaOH$$

$$\rightarrow \underset{\text{Sodium Carboxymethyl Cellulose}}{\text{Cell}-OCH_2COONa} + NaCl + H_2O \qquad (1)$$

$$ClCH_2COOH + NaOH \rightarrow \underset{\text{Sodium Glycolate}}{HOCH_2COONa} + NaCl \qquad (2)$$

Table 3
Reaction parameters for carboxymethylation

Aq. NaOH concentration (mol/AGU; w/v%)	3.24; 10–40
MCA (mol/AGU)	1.55–2.30
Temperature of carboxymethylation (°C)	35–65
Duration of carboxymethylation (h)	1.5–4.5

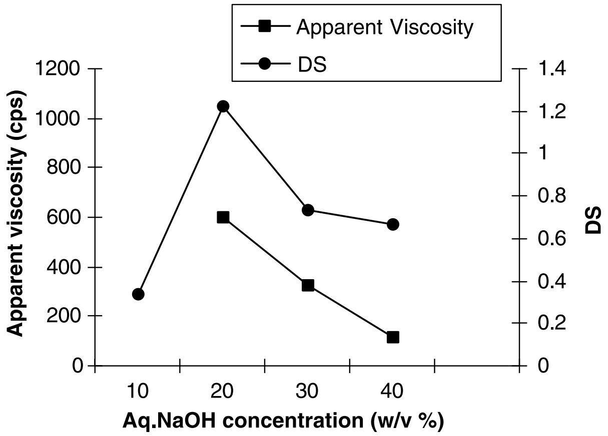

Fig. 1. Effect of aq. NaOH concentration (3.24 mol/AGU) on DS and apparent viscosity (MCA 2.05 mol/AGU; temp. 55 °C; time 3.5 h).

The increase in DS (1.22) up to 20% is due to the predominance of reaction (Eq. (1)) over its competitive reaction (Eq. (2)). Above this concentration the side reaction [Eq. (2)] between NaOH and MCA becomes more significant consuming NaOH to form sodium glycolate lowering thereby the DS. These findings are in accordance to those reported in literature (Barai, Singhal, & Kulkarni, 1997). The η of the sample resulted from the reaction carried out with 10% NaOH could not be determined owing to its insolubility in water. The value of η was found to be 600 cps on increasing the concentration of aqueous NaOH from 10 to 20%. This increase in apparent viscosity can be attributed to the increase in hydrodynamic volume because of introduction of carboxyl groups as evident by increasing value of DS. However, further increase in the concentration of aqueous NaOH beyond 20% led to a sharp decline in the value of η from 325 to 112.6 cps. These results suggest that, during carboxymethylation, with further increase in the concentration of NaOH, a significant degradation of cellulose molecules occur causing a decline in the molar mass and consequently a drop in the viscosity.

With concentration of aq. alkali 20%, the effect of MCA concentration on DS and η was examined. The results are plotted in Fig. 2. It was observed that the DS increased from 0.79 to 0.98 with increasing MCA concentration and reached to a maximum (1.22) at molar ratio of MCA to AGU of 2.05. Increase in the concentration of monochloroacetic acid seems to enhance the availability of the acid molecules in the proximity of the cellulose hydroxyls, facilitating thereby the carboxymethylation (Barai, Singhal, & Kulkarni, 1997). No significant increase in DS occurred on further increase in MCA concentration to 2.30 mol/AGU. This may probably be attributed to the non-availability of enough cellulose-alkoxide for reaction with MCA (Hebeish & Khalil, 1988). With increasing concentration of MCA (2.05–2.05 mol/AGU) values of η also changed in a parallel fashion from 225 to 600 cps and remained almost constant (590 cps) with the MCA content increased up to 2.30 mol/AGU. This may be due to the

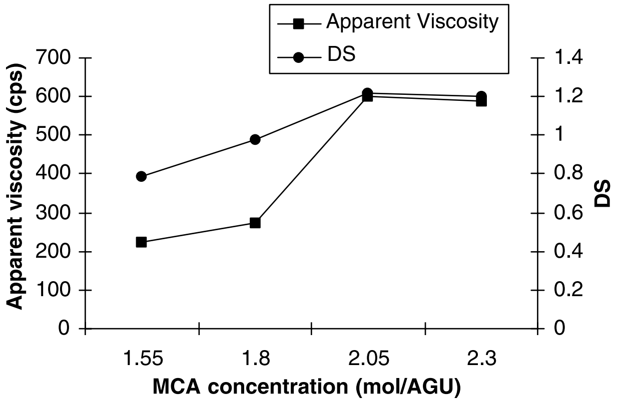

Fig. 2. Effect of MCA concentration on DS and apparent viscosity (Aq. NaOH 3.24 mol/AGU, 20%; temp. 55 °C; time 3.5 h).

hydrodynamic volume enhanced by the increased number of carboxyl groups introduced.

Using concentration of alkali of 20% NaOH and of MCA of 2.05 mol/AGU, the effect of temperature of carboxymethylation was studied on DS and η. As shown in Fig. 3, an increase in DS from 0.59–1.22 was observed with the increase in temperature from 35 to 55 °C followed by a fall in DS at 65 °C (0.69). The increase in DS up to 55 °C could be linked with the advantageous effect of temperature on swellability of cellulose fibers as well as diffusion and adsorption of MCA facilitating thereby the reaction between MCA and the cellulose molecules. Lowering of the DS beyond 55 °C could be attributed to the degradation of carboxymethylated celluose under the influence of atmospheric oxygen. Similar observations have been reported for the carboxymethylation of cellulose (Hebeish, Abou-Zied, Waly, & Higazy, 1984; Tijsen, Kolk, Stamhuis, & Beenackers, 2001; Youssef, Nada, & Ibrahem, 1989). With increasing temperature of carboxymethylation (35–55 °C), values of η (350–600 cps) changed in a parallel fashion, which could be attributed to the hydrodynamic volume enhanced by the increased carboxymethyl contents.

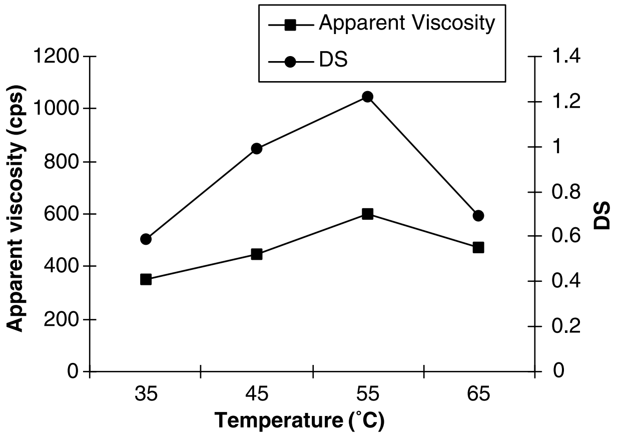

Fig. 3. Effect of temperature of carboxymethylation on DS and apparent viscosity (Aq. NaOH 3.24 mol/AGU, 20%; MCA 2.05 mol/AGU; time 3.5 h).

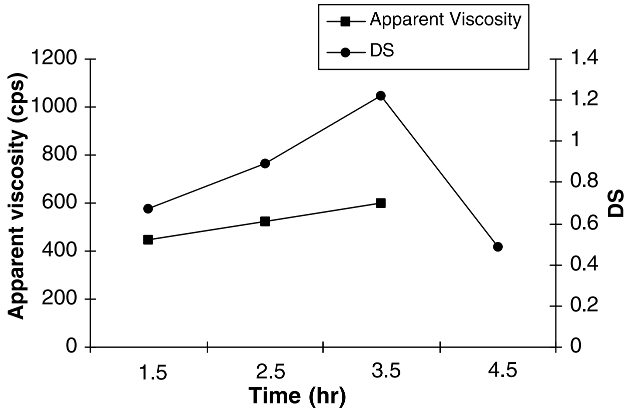

Fig. 4. Effect of time of carboxymethylation on DS and apparent viscosity (Aq. NaOH 3.24 mol/AGU, 20%; MCA 2.05 mol/AGU; temp. 55 °C).

A decreased value of η (475 cps) was observed on further increasing the temperature to 65 °C. This lowering in apparent viscosity could be interpreted as a consequence of corresponding decline in the molar mass due to the atmospheric oxidative degradation of the CMC (Hebeish et al., 1984).

Performing the reaction at 55 °C with concentration of alkali of 20% NaOH and of MCA of 2.05 mol/AGU, effect of duration on DS and η was investigated and its results are illustrated in Fig. 4. On increasing the carboxymethylation time from 1.5 to 3.5 h DS was found to increase from 0.67 to 1.22. However, further increase in the time resulted in a lowering of DS (0.49). The increment in DS on prolonging the duration of carboxymethylation up to 3.5 h is due to the direct consequence of the favorable effect of time on diffusion and adsorption of the reactants with the ultimate effect of inducing better contacts between MCA and the immobile cellulose hydroxyls. The lowering of DS on prolonging the carboxymethylation time may be attributed to the atmospheric oxidative degradation of CMC. Similar influence of duration of reaction on DS of carboxymethylated flax cellulose has been reported by Hebeish et al., 1984.

The values of η when carboxymethylation was performed for a period from 1.5–3.5 h showed increase from 450–600 cps. The η of the sample resulted from the reaction carried for 4.5 h could not be determined owing to its insolubility in water. The increase in apparent viscosity with increasing carboxymethylation time may be due to the increase in hydrodynamic volume because of introduction of carboxyl groups as evident by increasing value of DS.

The single most important property of CMC utilized in its wide range of practical applications is to modify the properties of aqueous environment and control the rheology of hydrated systems. In aqueous solution, it represents a complex rheological system as it forms aggregates and associations, and hence higher-level structures (Kulicke, Reinhardt Fuller, & Arendt, 1999). Consideration of the end uses for CMC makes it immediately apparent that

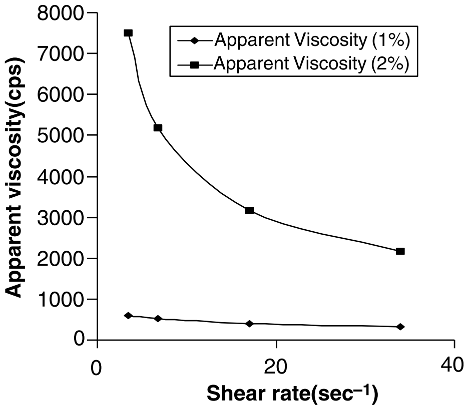

Fig. 5. Effect of shear rates on the apparent viscosities of the aqueous solutions (1%, 2%) of the optimized CMC.

the rheological properties of the CMC solutions are of prime importance.

Rheological studies of the optimized CMC were, therefore, carried out by measuring apparent viscosity of its 1 and 2% aqueous solutions. A plot of η values of the aqueous solutions (1 and 2%) of the optimized CMC verses shear rates (Fig. 5), shows that values of η of both the solutions of the optimized product are dependent upon shear rate and decrease with increasing shear rate. No time effects was detected and the viscosity obtained with decreasing rate was identical with that obtained with increasing shear rate. Thus, both the solutions of the optimized product exhibit non-Newtonian pseudoplastic behavior.

4. Conclusions

The results show that α-cellulose can be isolated from *L. camara* and can subsequently be modified to carboxymethyl cellulose by typical carboxymethylation reaction. Using optimized set of conditions viz: concentration of aqueous NaOH 3.24 mol/AGU, 20% (w/v); concentration of MCA 2.05 mol/AGU; carboxymethylation time 3.5 h and temperature 55 °C with isopropyl alcohol as the solvent medium, Na-CMC of viscosity 600 cps (1% solution) and 7500 cps (2% solution) having a DS of 1.22 could be prepared. *L. camara*, therefore, seems to be a potential feedstock for production of α-cellulose which can subsequently be converted into a water soluble Na-CMC for a variety of applications paving thereby a way for management of this noxious weed by its utilization into products of commercial importance.

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