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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.

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:

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

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 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

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