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Optimization of sugarcane bagasse cellulose acetylation

Daniel Alves Cerqueira, Guimes Rodrigues Filho *, Carla da Silva Meireles

Instituto de Química da Universidade Federal de Uberlândia, Av. João Naves de Ávila, 2121 Cx.P. 593 CEP: 38400-902 Uberlândia, Minas Gerais, Brazil

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Abstract

In this work we performed an optimization process of the acetylation reaction of sugarcane bagasse cellulose. The optimization was carried out varying acetic acid, acetic anhydride and catalyst volume, as well as reaction and activation times. Intrinsic viscosity was used as parameter for determining the quality of the produced material. Cellulose acetate viscosity-average molecular weight increased from 5.5×10^3 to 55.5×10^3 g mol^{-1}.

Keywords: Sugarcane bagasse; Cellulose acetate; Acetylation; Optimization; Viscosity-average molecular weight

1. Introduction

Nowadays, with the rise of oil price, many countries are considering the use of ethanol as an alternative fuel. Consequently, many countries are increasing their sugarcane production to feed this growing market. Brazil, for example, is the world's largest producer of sugarcane, with an expected production of 470 million metric tons in the 2006/2007 harvest. Due to federal incentive, this production tends to increase since many new sugarcane mills will be assembled. Only in the region known as Triângulo Mineiro, where our group is situated, 13 new sugarcane mills will be installed until 2010.

In spite of being good for business, this increasing in sugarcane production brings some environmental inconvenience, such as the generation of a huge amount of residues. For example, every metric ton of sugarcane generates about 280 kg of bagasse. Some of this bagasse is burned to produce energy, but a huge amount is still not used. Since bagasse is composed mainly by cellulose (30–50%) and lignin (20–24%), many papers have been produced aiming at the utilization of bagasse cellulose for production of several cellulose derivatives (Liu, Sun, Zhang, & Ren, 2007; Pasquini, Belgacem, Gandini, & Curvelo, 2006; Vieira et al., 2007; Rodrigues Filho et al., 2000) and bagasse lignin for production of phenolic resins (Khan, Ashraf, & Malhotra, 2004; Pandey, Soccol, Nigam, & Soccol, 2000; Tita, de Paiva, & Frollini, 2002).

One of the most important cellulose derivatives is cellulose acetate, which is extensively used in several activities (coatings, membranes, cigar filters, etc.). One of its main applications nowadays is the production of membranes for separation processes such as hemodialysis, reverse osmosis and gas separation. Cellulose acetate is produced by cellulose acetylation, in which cellulose reacts in the presence of acetic anhydride that is used as acetylating agent, acetic acid used as a solvent, and sulfuric acid or perchloric acid used as catalyst (Steinmeier, 2004; Sassi & Chanzy, 1995; Edgar et al., 2001).

Our group has been working for a long time with sugarcane bagasse for producing cellulose acetate, and membranes of this material (Rodrigues Filho et al., 2000). However, membranes made of this material were difficult to work with due to their brittle character, which was probably due to a low molecular weight of the produced material. An attempt to improve the workability of these membranes was to produce blends with polystyrene (Rodrigues Filho, Silva, & Meireles, 2005), which indeed

* Corresponding author. Tel.: +55 34 3239 4174; fax: +55 34 3239 4208.
E-mail address: guimes@ufu.br (G.R. Filho).

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resulted more resistant. Yet, cellulose acetate produced from sugarcane bagasse cellulose still had a low molecular weight, which was probably due to the acetylation methodology. Thus, the aim of this paper is to improve the experimental conditions of the acetylation reaction in order to increase the molecular weight of cellulose acetate produced from sugar cane bagasse.

In order to improve the acetylation procedure, a simplex optimization was performed (Barton & Ivey, 1991; Deming, 1986). In this optimization methodology, it is necessary a set of $n+1$ experiments to define the simplex of n dimensions, where n is the number of variables to be optimized. After performing each of the $n+1$ experiments, the simplex moves toward the optimum by reflecting the point with the worst value through the centroid (P_c) of the remaining n points.

For example, in a system in which two variables need to be optimized (X and Y) a two dimension simplex would be established. Since $n=2$ (two variables), it is necessary to use three points: P1, P2 and P3. This set is shown in Fig. 1.

Considering that P1 was considered as the worst point regarding any measurable property of the produced material, the centroid point is calculated as the average of the remaining points P2 and P3. Thus

$$P_c = \frac{P2 + P3}{2}.$$

The next point (P4), also called reflection, is obtained by reflecting the worst point through the centroid, which is expressed by

$$P4 = P_c + (P_c - P1).$$

To assure progress, two additional rules apply: (i) if any point of the simplex is retained for $n+1$ reflections, a new observation will be taken at that point to replace the current observation. This rule ensures that the simplex does not remain at a point whose value is unusually low due to experimental error; (ii) if a reflected point is still the worst of the simplex, this point will not be accepted. Instead, the next-to-worst point is reflected through the other points. This rule causes the simplex to continually cycle around the region containing the optimum.

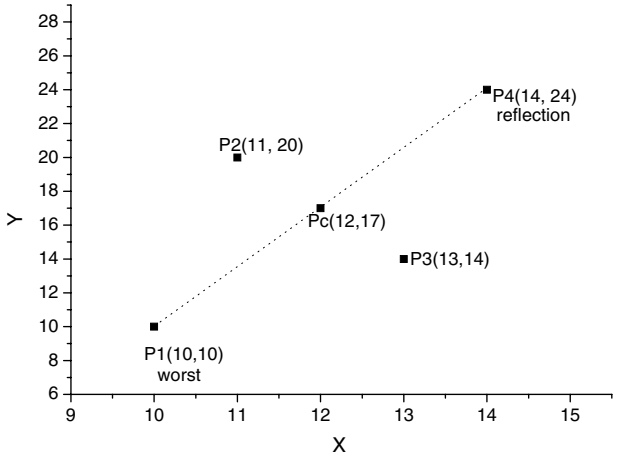

Fig. 1. Example of reflection in simplex optimization.

In this paper, simplex optimization was carried out using five variables, and intrinsic viscosity was used as comparison parameter.

2. Experimental

2.1. Sugarcane bagasse purification

Bagasse was purified using the method develop by Rodrigues Filho et al. (2000), described below:

A mixture of 76 mL NaOH (0.25 M) and 4 g of dry, ground bagasse was kept at room temperature for 18 h. Then, this mixture was filtered and washed with distilled water in order to remove the soluble impurities. Next, the bagasse was refluxed with a HNO_3/ethanol solution (20% v/v) for 3 h, with the alcoholic solution being changed at 1 h intervals. After the reflux, the bagasse was washed with distilled water and oven dried at 105 °C for 3 h.

Klason lignin and α-cellulose content determination of raw and purified sugarcane bagasse has been described in a previous paper (Vieira et al., 2007).

2.2. Optimization of the acetylation process

Acetylation methodology was performed based on the methodology described by Sassi and Chanzy (1995).

The following variables were optimized: VHAc – acetic acid volume; CV – catalyst (sulfuric acid) volume; AT – activation time; VAA acetic anhydride volume; RT – reaction time.

A mixture composed by 1 g purified bagasse and VHAc mL acetic acid was stirred for 30 min. Then, a solution composed by CV mL H_2SO_4 and 9 mL acetic acid was added to the system, which was stirred for AT minutes. The mixture was filtered and VAA mL acetic anhydride was added to the filtrate. This solution was returned to the recipient containing bagasse and stirred for 30 min. After this time, the mixture stood for RT hours at 28 °C. The mixture was filtered to remove undissolved particles. Water was added to the filtrate to stop the reaction and precipitate cellulose acetate. The produced cellulose acetate was then washed with distilled water to remove acetic acid, and then dried at room temperature overnight.

The initial steps are shown in Table 1.

2.3. Determination of the intrinsic viscosity using the single point method

For each cellulose acetate sample, a 2 g/L solution was prepared using an 8:2 dichloromethane/ethanol solution as solvent system (Knaus & Bauer-Heim, 2003). Experimental determination was carried out by counting the efflux time of the solvent system and samples solutions in an Ostwald viscometer, which was immersed in a thermo-

Table 1
Initial experimental conditions used for the optimization of cellulose acetylation

	RT (h)	AT (min)	CT (mL)	VHAc (mL)	VAA (mL)
P1	48	15	0.25	20	20
P2	48	15	0.25	20	10
P3	48	15	0.15	20	20
P4	28	15	0.25	20	20
P5	24	15	0.15	20	20
P6	2	25	0.10	25	20
P7	3	30	0.05	25	25

stated bath at 25 °C for a few minutes in order to stabilize the temperature before the measurements were carried out.

Intrinsic viscosity was determined using the single point method, developed by Solomon and Ciută (1962). According to this method, the intrinsic viscosity is calculated using the following relationships:

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - \ln(\eta_{rel}))}}{c},$$

$$\eta_{rel} = \frac{t}{t_0}, \quad \eta_{sp} = \eta_{rel} - 1,$$

where $[\eta]$ is the intrinsic viscosity, η_{rel} is the relative viscosity, η_{sp} is the specific viscosity and c is the concentration of the solution, t and t_0 are the solution and solvent efflux times, respectively.

The viscosity-average molecular weight ($\overline{M}_v$) was determined using the Mark–Houwink–Sakurada equation

$$[\eta] = k(\overline{M}_v)^a,$$

where k and a are constants related to the type of polymer, solvent and temperature.

2.4. FTIR

FTIR spectra were recorded in a FTIR Perkin-Elmer Spectrum 1000. Thirty-two scans were recorded at 4 cm^{-1} resolution in the region from 4400 to 400 cm^{-1}, using KBr pellets. The FTIR spectra were used to determine the degree of substitution (DS) of the samples, as described by Hurtubise (1962), where the ratio between the absorbance values of the C=O stretching (1750 cm^{-1}) and O–H stretching (3400 cm^{-1}) is related to the DS of cellulose acetate samples (Hurtubise, 1962).

3. Results and discussion

The sugarcane bagasse was chemically characterized, and its α-cellulose and lignin content were, respectively, 44.9% and 23.8%. After sugarcane bagasse purification, α-cellulose and lignin content were, respectively, 75% and 3.84%.

Before starting to discuss the simplex optimization developed in this paper, it must be said that the original process utilizes $N + 1$ experiments for each step, where N is the number of variables. However, in this paper $N + 2$ experiments were used in each step and the optimization was still valid since it led to produce a material with higher intrinsic viscosity than the original process.

Table 2 shows the set of experiments used for the simplex system, as well as the intrinsic viscosity values for these experiments.

As it may be seen in Table 2, experiment P1 presented the lowest value of intrinsic viscosity among the starting experiments. The first reflection, P8, resulted in a material that did not dissolve in the solvent system; thus, a new reflection was performed using the second worst experiment, leading to experiment P9. The optimization process

Table 2
Optimization sequence of cellulose acetylation

	RT (h)	AT (min)	CT (mL)	VHAc (mL)	VAA (mL)	$[\eta]$ (mL/g)
P1	48	15	0.25	20	20	17.0
P2	48	15	0.25	20	10	34.5
P3	48	15	0.15	20	20	54.2
P4	28	15	0.25	20	20	47.0
P5	24	15	0.15	20	20	55.9
P6	2	25	0.10	25	20	75.3
P7	3	30	0.05	25	25	136.4
P_c 1=	26	19	0.16	22	19	
np(P8)=	3	25	0.07	23	18	Insoluble
P1	48	15	0.25	20	20	17.0
P2	48	15	0.25	20	10	34.5
P3	48	15	0.15	20	20	54.2
P4	28	15	0.25	20	20	47.0
P5	24	15	0.15	20	20	55.9
P6	2	25	0.10	25	20	75.3
P7	3	30	0.05	25	25	136.4
P_c 2=	26	19	0.16	22	21	
np(p9)=	6	23	0.07	23	32	47.5
P1	48	15	0.25	20	20	17.0
P3	48	15	0.15	20	20	54.2
P4	28	15	0.25	20	20	47.0
P5	24	15	0.15	20	20	55.9
P6	2	25	0.10	25	20	75.3
P7	3	30	0.05	25	25	136.4
P_c 3=	19	21	0.13	22	23	
np(P10)=	9	26	0.01	24	26	74
P3	48	15	0.15	20	20	54.2
P4	28	15	0.25	20	20	47.0
P5	24	15	0.15	20	20	55.9
P6	2	25	0.10	25	20	75.3
P7	3	30	0.05	25	25	136.4
P9	6	23	0.07	23	32	47.5
P_c 4=	16	22	0.10	23	24	
np(p11)=	8	29	0.06	25	27	57.6
P5	24	15	0.15	20	20	55.9
P6	2	25	0.10	25	20	75.3
P7	3	25	0.05	25	25	136.4
P8	3	23	0.07	23	18	Insoluble
P9	6	23	0.07	23	32	47.5
P10	9	26	0.01	24	26	74
P11	8	30	0.06	26	28	57.6
P_c 5=	9	24	0.07	24	25	
np(P12)=	14	25	0.08	25	32	125.9

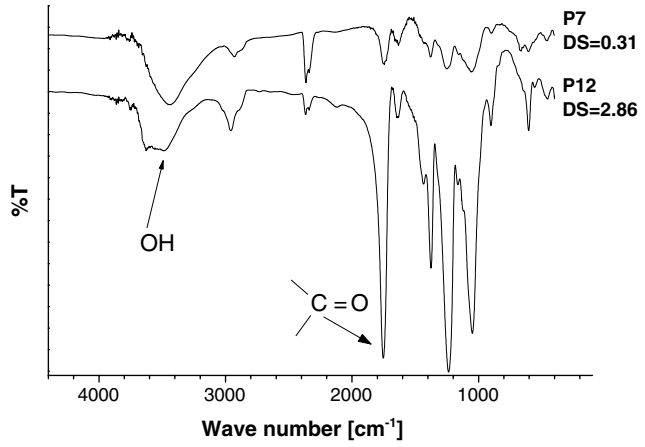

Fig. 2. FTIR of cellulose acetates produced according to P7 and P12.

was carried out normally on the following experiments, P10 and P11. However, in an attempt to eliminate the 48 h procedures of the optimization set for reducing the reaction time, another set of experiments with points P5 to P11 was created, which resulted in step P12. At this point, P12 produced a material with high intrinsic viscosity value. Thus it was decided to end the simplex optimization. Fig. 2 shows FTIR scan of these procedures.

As expected, all the samples present a broad band for OH group around 3400 cm^{-1}, as well as a band around 1750 cm^{-1} for C=O group from acetate. A high ratio between these two bands (1750 cm^{-1}/3400 cm^{-1}) indicates a high DS sample, since during the acetylation reaction the cellulose OH group is replaced by an acetate group (Hurtubise, 1962). Thus, although P7 presents high intrinsic viscosity value, it presents low DS. On the other hand, P12 presents both high DS and intrinsic viscosity, being considered the best acetylation procedure to obtain a cellulose triacetate.

For the used solvent system, dichloromethane/ethanol (8:2), the Mark-Houwink-Sakurada constants are $K = 13.9 \times 10^{-3}$ and $a = 0.834$ (Knaus & Bauer-Heim, 2003). The viscosity-average molecular weight, $\overline{M}_v$, of the material produced according to P1 and P12 were $\overline{M}_v = 5031$ g mol^{-1} and $\overline{M}_v = 55,541$ g mol^{-1}, respectively. This represents an increase of about 1100% in $\overline{M}_v$ of cellulose acetate produced from cellulose of sugarcane bagasse.

4. Conclusion

After the optimization process, cellulose acetate from cellulose of sugarcane bagasse reached $\overline{M}_v = 55,541$ g mol^{-1}.

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