

Full Paper

Simultaneous production of α -cellulose and furfural from bagasse by steam explosion pretreatment

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Abstract: Sugar cane bagasse was pretreated by steam explosion for the simultaneous production of furfural and α -cellulose pulp. The components of bagasse were fractionated after steam explosion. The details of the process are as follows. Bagasse was soaked in water for one night and steamed at temperatures varying between 206 and 223 °C for 4 minutes. The steam exploded pulp was strained and washed with hot water to yield a liquor rich in hemicellulose-derived mono- and oligosaccharides. The remaining pulp was delignified by alkali for 120 minutes at 170°C using, separately, NaOH load of 15, 20 and 25% of weight of the pulp. The delignified pulp was further bleached twice with 4% H₂O₂ charge of weight of the pulp to produce high α -cellulose pulp. The water liquor was evaporated and further hydrolysed and dehydrated with diluted H₂SO₄ in a stainless steel reactor to produce furfural. The result shows that the optimal pretreatment of steam explosion for 4 min at 218°C leads to the yield of α -cellulose pulp at 193-201 g·kg⁻¹ of the original bagasse, and that furfural can be produced from xylose present in the liquor with a maximum conversion factor of 0.16.

Keywords: steam explosion, sugar cane bagasse, furfural, α -cellulose pulp, delignification

Introduction

Bagasse is a waste product from the sugar industry, which is usually used as energy source in factory at present. However, the amount of bagasse left is still high enough for more value-added products. In Thailand, bagasse is used as forage and raw material for production of pulp for paper making and particle board. It has been reported that bagasse contains pentosan with concentration of 250-270 g·kg⁻¹ of the original bagasse, which mainly consists of arabinoxylan [1]. Pentosan can be hydrolysed into xylose by acid treatment, then subsequently modified into more value-added chemical substances such as furfural and xylitol [2]. In addition, the residue after production of furfural or xylitol can be used as energy source or raw material for production of high α -cellulose pulp.

Furfural is a basic chemical which can be utilised in a variety of industries such as chemical industry, refining oil industry, food industry and agricultural industry. It is usually produced from agricultural wastes containing pentosan as the main component, notably corn cob, rice straw, bagasse and rice hull [3]. Usually, furfural can be produced by 2 processes. One is through a one-stage process in which pentosan is hydrolysed into xylose after which it is immediately dehydrated to furfural. In this one-stage process, both reactions simultaneously occur in same reactor. On the other hand, the two-stage process starts with hydrolysis of pentosan into xylose in one reactor. After that, the second stage of dehydration reaction is carried out in another reactor to obtain furfural. The advantage of the two-stage process is that the residue from the process can be further utilised for production of cellulose, glucose or ethanol while that from the one-stage process can be used only as fuel. Figure 1 shows the two-stage process for furfural production. Mansilla and coworkers [3] compared the efficiency of furfural production from rice hull between the one-stage and the two-stage process. The first process is conventional, but the yield of furfural is low. Another process is the two-stage process developed more recently and gives higher yield of furfural [2]. Furthermore, the residue arising from two-stage process can be either used as fuel or raw material for α -cellulose pulp production. Furfural is a colourless viscous liquid which becomes dark brown and more viscous in the presence of oxygen. Its boiling point is approximately 160°C. The process for preparing furfural from pentosan from agricultural residues is shown in Figure 1.

The α -cellulose pulp can be substituted for cotton as raw material for producing cellulose derivatives such as carboxymethylcellulose (CMC), cellulose acetate and rayon [4]. Among a variety of processes aiming at fractionation of biomass, steam explosion has been proposed and investigated [5]. Hydrolytic treatment of biomass by pressurised steam alone or with addition of small amount of an inorganic acid, followed by sudden decompression has been studied as a method of depolymerisation of macromolecules in the biomass [6]. Steam pretreatment is an effective way of hydrolysis of hemicellulose and partial decrystallisation of cellulose to facilitate enzymatic attack. The steam explosion process is run at high pressure and high temperature (usually between 180 and 230°C) in a short period of time. As a result, steam explosion technique is truly useful for the separation of cellulose, hemicellulose and lignin from raw materials. This is indicated by the study of the technique for production of α -cellulose from wheat straw [5], production of ethanol from bagasse [7], enzymatic hydrolysis of eucalyptus pulp after steam explosion pretreatment [8], simultaneous production of ethanol and kraft pulp from aspen [9], and treatment of olive stone to improve hemicellulose solubility and enzymatic cellulose hydrolysis [6].

The aim of this work is to evaluate the fractionation of bagasse by the process sequence based on controlled auto-hydrolysis at high temperature followed by hemicellulose extraction and alkali delignification. The work was carried out at the laboratory bench scale, and discusses the yield, chemical composition and recovery potential of cellulose and hemicellulose products.

Materials and Methods

Raw material and chemicals

The sugarcane bagasse with moisture content of 10.78% on receiving from Mitra Phol Sugar Co. Ltd. in Suphanburi Province, Thailand, was used in this study. Glucose, xylose, furfural, and limonene were purchased from Aldrich Chemical Co. Ltd.

The pulp to be used for rayon production was supplied from Thai Rayon Company, Angtong Province, Thailand.

Analytical methods

A part of the bagasse sample was ground with a Wiley mill (Kinematica AG Co. Ltd., Tokyo, Japan) to pass a 420 μ m sieve for chemical analyses. The content of the ethanol-benzene extractive, lignin, α -cellulose, pentosan and ash were determined using the Tappi Test Method [10]. Holocellulose content was determined by sodium chlorite method according to Browning [11]. The viscosity and brightness of α -cellulose pulp were determined following the Tappi Test Method [10].

Steam explosion fractionation

Fractionation of bagasse was performed by the procedure shown in Figure 1. The bagasse sample (150 g oven dry weight) was soaked in water, and placed in a stainless steel batch reactor of 2.5 L capacity (Nitto Kouatsu Co. Ltd., Tokyo, Japan). Heating was accomplished by direct steam injection into the reactor. The sample was treated for 4 min at the desired temperature from 206 to 223 °C. Explosive discharge of the digester content into a collecting tank was actuated by rapidly opening a pressure release valve. The pulp slurry was collected and extracted with hot water (80°C) with a ratio of fibre to water of 1:10 (w/v) for 15 min (Figure 1). The pulp was filtered, air-dried at room temperature and pulp yield was determined after overnight oven drying at 105°C. The chemical composition of the pulp was analysed as described for the original bagasse. A part of the hot water extract was stored at 4°C for determination of glucose and xylose content by LC10A High Performance Liquid Chromatography (Shimadzu Co. Ltd., Kyoto, Japan) with RI detector and Aminex HPX-87C column, according to the method of Montane et al. [5].

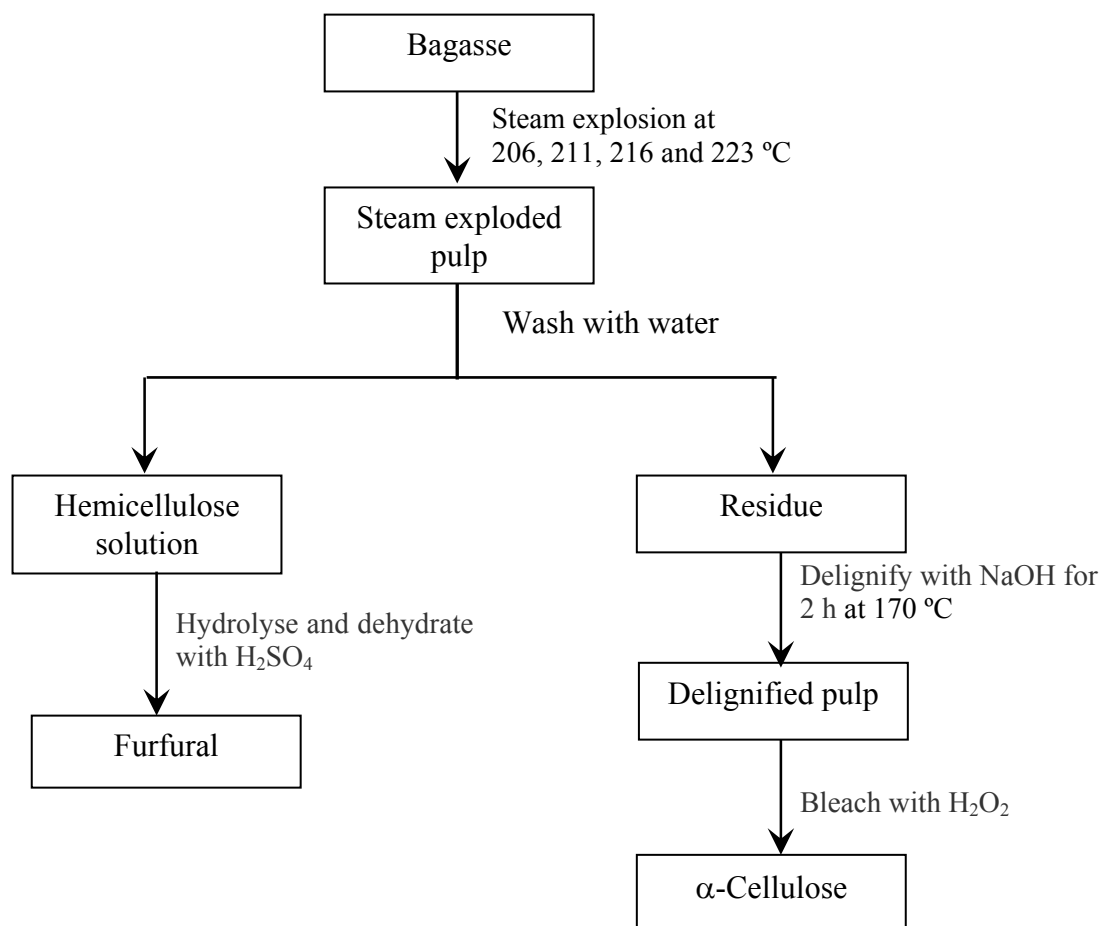


Figure 1. Steam explosion for two-stage production process of α -cellulose pulp and furfural from bagasse

Dehydration of authentic xylose and hot water extract of steam exploded pulp

Prior to the production of furfural from the hot water extract of the steam exploded pulp, authentic xylose was used as a substrate to assess the optimum dehydration condition. Xylose solution ($60 \text{ g}\cdot\text{l}^{-1}$, 800ml) was placed in a stainless steel reactor (1 L capacity) and separately treated for 2 hr at 50, 170, 190 and 210°C. The reaction was catalysed by a series of H₂SO₄ concentrations of 0.05, 0.08, 0.10 and 0.125 mole/litre of the reaction mixture. The vapour evaporated from the reactor after 30, 60, 90 and 120 min was condensed with a condenser cooled by tap water. The optimum condition was then employed for the dehydration of the hot water extract after steam explosion to afford furfural. The hot water extract (8 litres) of the steam exploded pulp was concentrated 4-, 6-, 8- and 10-fold and then used as substrates to optimise the dehydration condition. The reaction was performed in a stainless steel reactor (1 L capacity) and catalysed by an appropriate H₂SO₄ solution to obtain furfural.

Furfural content was subsequently determined as follows. A part of the condensed liquid (5 ml) was extracted with toluene (2 x 5 ml). An aliquot of the toluene solution containing 10% limonene (Aldrich Co. Ltd.) as an internal standard was analysed by a gas chromatograph (Agilent Technologies A 6890N, USA.) with a FID detector. A capillary column, DB-WAX (30 m x 0.32 mm ID, 0.25 μm film thickness) (J&W Scientific, Folsom, California, USA) was used. Carrier gas was He at a flow rate of

1.4 ml·min⁻¹ and split ratio of 50:1. Column temperature was kept at 45°C for 2 min and then programmed at 6°C·min⁻¹ to 200°C. Temperature of injector and detector was maintained at 200 °C.

Production of α -cellulose pulp

After steam explosion process, the pulp remaining after washing with hot water was delignified by digestion with NaOH (15, 20 and 25% w/w of oven-dried pulp) for 2 hr at 170°C using a ratio of pulp to liquid of 1:10 (w/v) to determine the optimum NaOH concentration for the delignification process. The delignified pulp was collected by filtration and washed with water several times until a colourless solution was obtained. A part of the delignified pulp was air-dried, and the yield was determined after oven drying at 105 °C overnight. The chemical composition was determined as described for the original bagasse. The pulp was further subjected to a two-stage alkaline H₂O₂ bleaching starting with bleaching for 3 hr at 80°C using a ratio of pulp to liquor of 1:10 (w/v). The chemical load on the bleaching liquor was 4% H₂O₂, 3% NaOH and 0.5% MgSO₄ based on weight of oven-dried pulp. The pulp was filtered and thoroughly washed with distilled water before a second bleaching using the same condition as above. Following the two-stage bleaching, the brightness of resulting pulp fell in the same level as that of the commercially available Rayon. The bleached pulp was subsequently analysed for brightness using Technibrite™ Micro TB-1C (Technidyne Co. Ltd., Indiana, USA), viscosity using a capillary viscometer (Tappi T230om-94) and 0.5 M cupriethylenediamine as a solvent, and chemical composition using the method as described for the original bagasse.

Results and Discussion

Results of the determination of the extractives, lignin, pentosan, holocellulose, α -cellulose and ash content of the original bagasse used in this investigation are 37, 199, 251, 664, 456, and 18 g·kg⁻¹ respectively of the oven-dried bagasse. The content of α -cellulose is high enough to be applied to the α -cellulose pulp production process.

It is found that the pentosan content is significantly decreased by the steam explosion treatment from 251 g·kg⁻¹ of raw material to 18-65 g·kg⁻¹ of the steam exploded pulp (Table 1). This is in contrast with the contents of holocellulose (638-694 g·kg⁻¹), α -cellulose (459-501 g·kg⁻¹), and lignin (162-201 g·kg⁻¹), which are not truly affected by the steam explosion condition. It is concluded that the pentosan content in the pulp decreases significantly during the steam explosion process with removal efficiency from 84 to 96% of the original bagasse sample (Table 1). This is also consistent with the results by Ibrahim and his coworkers [4] that the pentosan in bagasse is hydrolysed during the prehydrolysis stage with 1.5% H₂SO₄ for 90 min at 140°C, which is the optimum condition. However, it should be noted that the disadvantages of the acid hydrolysis are a lower % removal of pentosan and the requirement of a longer reaction period (90 min at 140°C with 1.5% H₂SO₄) compared with the steam explosion. In addition, the use of H₂SO₄ causes corrosion of the reaction vessel. The yield of pulp is 600 g·kg⁻¹ of the original bagasse and the removal efficiency of pentosan is 71.4%, which is significantly lower than that obtained by the steam explosion pretreatment (84-96%). These results suggest clearly that the acid prehydrolysis of lignocellulose should be substituted by steam explosion to obtain pentosan effectively.

Table 1. Pulp yield and chemical components in bagasse pulp after steam explosion

Steam temperature °C	Time min	Pulp yield ¹ g·kg ⁻¹	Pentosan ² g·kg ⁻¹	Lignin ² g·kg ⁻¹	Holocellulose ² g·kg ⁻¹	α-Cellulose ² g·kg ⁻¹
206	4	606	65 (84.3)	162 (50.7)	682 (37.8)	501 (33.4)
211	4	594	58 (86.3)	186 (44.5)	694 (37.9)	499 (35.0)
218	4	571	32 (92.7)	201 (42.3)	693 (40.4)	479 (40.0)
223	4	568	18 (95.9)	192 (45.2)	638 (45.4)	459 (42.8)

¹ Based on bagasse; ² Based on steam exploded pulp

Figure in bracket = % removal from the original bagasse by steam explosion treatment

It is found that the pulp yield decreases with rising temperature of the steam explosion process, from 606 to 568 g·kg⁻¹ of the original bagasse sample. The condition at 223°C for 4 min seems to be the best due to highest pentosan removal of 96% and pulp yield of 568 g·kg⁻¹. However, this condition was not selected for the next step, because it was too severe and was not appropriate for α-cellulose pulp production. Thus the explosion condition of 4 minutes at 218°C was selected based on the pentosan removal (>92% of pentosan from the raw material) and pulp yield (571 g·kg⁻¹) for producing furfural and α-cellulose pulp.

Results from chemical analysis of α-cellulose pulp after delignification and bleaching are shown in Tables 2 and 3. It is apparent that the contents of holocellulose and α-cellulose increase while delignified pulp yield and contents of pentosan, lignin and ash decrease with increase of NaOH dosage. This trends are good agreement with the results of Ibrahim et al.[4], although higher dosage (25%) of NaOH is required compared to this investigation (NaOH dosage of 15-20%) to obtain the same quality of the resulting pulp. Thus, it can be inferred that the pretreatment of lignocellulose such as bagasse with steam explosion can lead to a more effective removal of lignin than the acid hydrolysis pretreatment, probably because of an acid condensation of lignin during H₂SO₄ treatment being avoided.

Ibrahim et al. [4] used four successive chemicals for pulp bleaching, viz. chlorine, sodium hydroxide, sodium hypochlorite and sodium chlorite. Two-stage bleaching with 4% aqueous solution of H₂O₂ used in this experiment gave a pulp of similar quality. These data therefore seem to indicate that steam explosion is a more effective and environmentally friendly pretreatment of bagasse for α-cellulose pulp production.

The α-cellulose and pentosan contents of the resulting α-cellulose pulp from bagasse in this investigation are similar to those of the rayon pulp (Table 3), which is produced from cotton linter. However, brightness and viscosity of the bagasse α-cellulose pulp are lower, and residual lignin and ash contents are also higher than those of the rayon pulp. Low brightness and viscosity would probably be due to the presence of higher content of residual lignin in bagasse α-cellulose pulp. These

disadvantages can be improved by additional bleaching step using ClO_2 or NaClO_2 . This improvement has also been reported for α -cellulose production from rice straw by Montane et al. [5]. In the report, the rice straw was preliminarily treated by steam explosion and two-stage H_2O_2 bleaching. Then the pulp was bleached again with NaClO_2 . The α -cellulose pulp obtained was demonstrated to be equivalent to the rayon grade pulp used in industry [5].

Table 2. Chemical components of pulp after delignification at different concentrations of NaOH

NaOH concentration % of SE pulp (w/w)	Pulp yield ¹ g·kg ⁻¹	Holocellulose ² g·kg ⁻¹	α -Cellulose ² g·kg ⁻¹	Pentosan ² g·kg ⁻¹	Lignin ² g·kg ⁻¹	Ash ² g·kg ⁻¹
15	227	944 (67.7)	932 (53.6)	18 (98.4)	51 (94.2)	10.1
20	220	959 (68.2)	948 (54.3)	16 (98.6)	37 (95.9)	6.5
25	199	971 (70.9)	961 (58.1)	16 (98.7)	22 (97.8)	6.1

¹ Based on the original bagasse; ² Based on delignified pulp

Figure in bracket = % removal from the original bagasse by steam explosion treatment

Table 3. Chemical components of pulp after bleaching with 4% H_2O_2 at different concentrations of NaOH

NaOH concentration g·l ⁻¹	Pulp Yield ¹ g·kg ⁻¹	Holo-Cellulose ² g·kg ⁻¹	α -Cellulose ² g·kg ⁻¹	Pentosan ² g·kg ⁻¹	Lignin ² g·kg ⁻¹	Ash ² g·kg ⁻¹	Viscosity cp	Brightness %ISO
150	214	956 (69.2)	939 (55.9)	16 (98.6)	18 (98.1)	5.6	152.6	36.2
200	201	971 (70.6)	956 (57.9)	15 (98.8)	7.4 (99.3)	4.6	104.3	65.6
250	193	975 (71.7)	961 (59.3)	14 (98.9)	6.3 (99.4)	4.4	85.5	70.5
Rayon pulp	-	986	970	16	7.7	2.0	141.2	80.0

¹ Based on bagasse; ² Based on bleached pulp

Figure in bracket = % removal from the original bagasse by steam explosion treatment

Prior to furfural production from the hot water extract of the steam exploded pulp, the monosaccharide composition was analysed by HPLC. It was found that the hot water extract of the steam exploded pulp was composed of xylose and glucose at the concentrations of $2.9 \text{ g}\cdot\text{l}^{-1}$ and $0.5 \text{ g}\cdot\text{l}^{-1}$, respectively (Table 4). The hot water extract was concentrated under reduced pressure to 1/4, 1/6, 1/8 and 1/10 volume to increase the concentration of xylose. These concentrated solutions were subsequently hydrolysed with 3% H_2SO_4 for 1 hr at 121°C according to Montane et al. [5] to determine the total glucose and xylose content in the hot water extract. The content of oligosaccharides containing glucosyl and xylosyl residues was calculated by subtraction of monomeric residues from those after hydrolysis of the hemicellulose solution. The result suggests that the hot water extract was composed mainly of xylosyl residues with a minor content of glucosyl residues. This result is similar to the amounts of pentosan and hexosan in the hot water extract from steam explosion treatment of eucalyptus wood [8].

Table 4. Total glucose and xylose in hemicellulose solution after hydrolysis with 3% H_2SO_4

Hemicellulose solution	Monosaccharide in hemicellulose solution		Oligosaccharide in hemicellulose solution		Total sugar in hemicellulose solution	
	Glucose $\text{g}\cdot\text{l}^{-1}$	Xylose $\text{g}\cdot\text{l}^{-1}$	Glucose $\text{g}\cdot\text{l}^{-1}$	Xylose $\text{g}\cdot\text{l}^{-1}$	Glucose $\text{g}\cdot\text{l}^{-1}$	Xylose $\text{g}\cdot\text{l}^{-1}$
Unconcentrated	0.5	2.9	0.6	3.2	1.1	6.1
Concentrated 4-fold	1.8	11.9	2.5	13.2	4.3	25.0
Concentrated 6-fold	2.2	19.6	1.9	14.4	4.1	34.1
Concentrated 8-fold	2.7	25.5	2.6	23.6	5.3	49.0
Concentrated 10-fold	5.1	28.9	4.6	29.3	9.7	58.2

The hot water extract was concentrated prior to furfural production. The concentrated solution was reacted for 2 hr at 190°C with H_2SO_4 (0.08 mole/litre of solution) in a stainless steel reactor. Furfural produced by the dehydration reaction was quantified by gas chromatography. The molar conversion factor from the xylosyl residue to furfural was 0.16 for the 6-fold concentrated solution, which surprisingly was somewhat higher than that for the treatment of authentic xylose solution (0.12, Table 5). Also, it can be observed from Table 5 that there seems to be an optimum concentration for the hemicellulose solution which gives the highest conversion factor. As the hemicellulose solution is progressively concentrated, the conversion factor seems to increase to a maximum and then decrease. Since there were in the hemicellulose solution both xylosyl and glucosyl oligosaccharides as well as other extractives such as lignin decomposition products, this might have an effect of suppressing further modification of the furfural formed by consuming some excess acid catalyst. Also, the ratio of the substrate (hemicellulose) to the acid catalyst also progressively changes (increases) as the solution is increasingly concentrated. These may therefore be the causes of the conversion factor variation observed. A similar observation and assumption has been made by Currasco and Roy [1].

It has been demonstrated that the activation energy (E_a) for the first step from oligosaccharides to xylose is higher than for the second step from xylose to furfural [1,12], indicating that xylose can be converted to furfural faster than the hydrolysis of oligosaccharides to xylose. Therefore, separation of xylose from the mixture of xylose and xylooligosaccharides is not required prior to dehydration.

Table 5. Amount of furfural from hemicellulose solution at different concentrations of xylose

Solution	Xylose $\text{mmol}\cdot\text{l}^{-1}$	Furfural mmol	Conversion factor from xylosyl residue to furfural
Hemicellulose solution, concentrated 4- fold	167	25.3	0.152
Hemicellulose solution, concentrated 6- fold	227	36.5	0.160
Hemicellulose solution, concentrated 8- fold	327	40.2	0.123
Hemicellulose solution, concentrated 10- fold	388	29.5	0.076
Pure xylose solution	400	47.1	0.118

Conclusions

Bagasse was converted to high value added materials, viz. furfural and α -cellulose pulp by steam explosion pretreatment followed by fractionation of cell wall components. The yields of furfural and α -cellulose pulp depend on the temperature and the time period of steaming. The major components of the water-soluble fraction of the steam exploded pulp were xylooligosaccharides together with xylose. After concentration of the water-soluble fraction, the xylooligosaccharides could be directly converted into furfural without prehydrolysis to the xylose monomer. The highest conversion factor for the conversion of the xylosyl residue to furfural in the concentrated water-soluble fraction was 0.16.

In the other part of the work, the steam exploded bagasse pulp was delignified with alkali, and bleached with aqueous H_2O_2 to afford α -cellulose pulp, the quality of which is comparable to the rayon grade pulp. Production of α -cellulose pulp was performed by steam explosion pretreatment with less consumption of chemicals in the delignification and bleaching stages than that in the acid hydrolysis pretreatment. However, pulp brightness and viscosity was lower than that of rayon grade α -cellulose, probably because of higher residual lignin content in the bagasse α -cellulose. The ash content in the bagasse α -cellulose was also higher than that in the rayon grade α -cellulose. Further improvement such as additional bleaching stages using chlorine-containing agents would be required to produce better quality α -cellulose pulp from steam exploded pulp.

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