甘蔗バガスの加圧・ NaOH 処理による化学組成・消化率への影響：III. セルロース結晶度及びその溶解度への影響(畜産学科)

The Effects of Treatment of Bagasse with Sodium Hydroxide under Steam Pressure on Chemical Changes and Digestibility

III. Effect on Degree of Cellulose Crystallinity and Solubility

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I INTRODUCTION

The susceptibility of fiberous materials to enzymatic degradation have been suggested[6] to be affceted by (1) the degree of cellulose crystallinity (DCC) as well as (2) moisture content of the fiber, (3) the size and diffusibility of the enzyme molecules involved in relation to the size and surface properties of the gross capillaries, the interstices between microfibrils, and the space between cellulose molecules in the amorphous regions, (4) the nature of the substances with which cellulose is associated, and (5) the degree of polymerization of anhydro-glucose -units.

Influence of DCC on the enzymatic degradation of cellulose have been studied by many workers[21, 24, 37]. Cellulosic fiber consists of crystalline regions where the intermolecular action between the hydroxyl groups of the cellulose molecules is very strong and amorphous regions where no such action or weakened interaction is present. The former regions are more resistant to enzymatic attack due to the lower water regain value or packed nature, while the latter regions are high in the value, more susceptible and easily digested. Nikitin[21], suggested that any type of chemical or physical treatment of cellulosic materials which causes changes in the physico-chemical structure of the materials, alters the ratio of crystalline regions to amorphous regions, and strengthen or weaken the intermolecular forces in the fiber system. Thus, any treatments which reduce DCC increase the susceptibijity or digestibility of fiberous materials to or by enzymatic decomposition.

This research was conducted, using the same bagasse materials treated under the same conditions as those in the previous works[27, 28], to evaluate the effect of pressure (atmospheric, 150 and 300 PSI), NaOH (0, 5 and 10%) and time (5, 15 and 25 minutes) on DCC and cellulose solubility (CS). Also using the previously reported data[27, 28], correlations of CS with sample recovery, proximate nutrients, and criteria involved in the process of cellulose preparation as well as with DCC to elucidate the mechanisms in relation to the improved nutritive value of bagasse materials were examined.

II MATERIALS AND METHODS

Cellulose solubility was determined applying the methods of Dehority and Johnson[9] and

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Crampton and Maynard[7]. Thirty ml of 0.5 M cupriethylenediamine (CED) were added to the centrifuge tubes containing residues from dry mater solubility (DMS) determination. The residues were broken up, flushed with N_2 gas and placed on a mechanical shaker for 2 hrs. The mixtures were centrifuged and the residues were washed with 0.5 M CED solution. This step was repeated. To the residues, acetic nitric acid solution (5 parts acetic, 1 part nitric acid) was added and boiled gently in a water bath for 20 minutes. Twenty five ml of 95% ethanol was added, mixed well, centrifuged and another 25 ml of ethanol was added. The mixtures were transfered to gooch crucibles and washed with hot water, hot benzene, hot ethanol, and ether. The gooch crucibles were dried, weighed, ashed and weighed again. The cellulose was determined as difference after treatment with CED solution. Also, the amount of cellulose in the original ground materials for each treamment combination was measured and CS was calculated using the following equation:

$$CS=\frac{\text{Original cellulose}-\text{CED cellulose}}{\text{Original cellulose}}\times 100$$

Degree of crystallinity of cellulose, prepared by the method of Tu[35], was estimated using the procedure described by Whistler and Walfrom[38]. Five bagasse cellulose samples of 0.2 g were dried at 65 C over night, cooled and weighed for dry weight determination. The cellulose samples were transfered into glass test tubes containing 35 ml potions of 6 M HCI solution which had been previously heated to 99 $\pm$ 1 C in a water bath. To keep the temperature and water level constant boiled water was added to the bath as needed. The tubes were removed at 1 hr intervals and filtered through medium porosity fritted glass crucible under suction. The residue was washed several times with hot distilled water. The weight of residue at each interval was plotted and an extrapolation was made to zero time and the intercept was used to give an estimate of crystallinity.

All data were subjected to the analysis of variance procedures for $3\times 3\times 3$ randomized factorial design[30]. When differences were observed, Duncan's Multiple Range Test was applied to determine the significance of differences among treatment means.

III RESULTS AND DISCUSSION

The analysis of variance for DCC, CS and summarized effects of NaOH and pressure on these criteria are shown in Tables 1 and 2.

DCC was increased by pressure ($P< .01$), while NaOH and time did not. No interactions were observed. Pressures of 150 PSI (77.40%) and 300 PSI (79.26%) had higher ($P<.05$)DCC than atomospheric PSI (73.95%). Pressure of 300 PSI, however, was not different from 150 PSI. The increased DCC with increased pressure level is probably caused by decreased sample recovery or decreased dry matter (DM) loss, that is, amorphous portion of the cellulose was lost in the solution during pressure treatment due to the use of a large amount of water in this experiment and cosequently the cellulose became higher in crystalline portion. The significant

Table 1. Analysis of variance for degree of cellulose crystallinity and cellulose solubility in CED

Source of variance	Degree of freedom	Degree of crystallinity	Cellulose Solubility in CED
Replication (2)	1		
NaOH (3), N	2	17.5044	146.9784 **
Pressure (3), P	2	130.7543 **	2309.2945 **
Time (3), T	2	1.1227	22.5797
N×P	4	13.3677	90.8971 **
N×T	4	1.8873	4.3606
P×T	4	7.0716	11.5903
N×P×T	8	1.0724	6.4433
Error	26	8.4862	12.7670

*CED : Cupriethylenediamine.
** P<.01.

Table 2. Summarized effects of pressure and NaOH on degree of cellulose crystallinity (DCC) and cellulose solubility (CS)

NaOH %	Item	Pressure (PSI)			Mean
		0	150	300	
0	DCC	72.71 *	77.32	80.23	76.76
	CS	65.44	85.28	93.44	81,39[a]
5	DCC	76.04	78.31	79.38	77,91
	CS	65.13	75.95	89.35	76.81[b]
10	DCC	73.09	76.58	78.17	75.95
	CS	73.47	84.04	88.65	82.07[a]
Mean	DCC	73.95[b]	77.40[a]	79.26	
	CS	68.02[c]	81.77[b]	90.09[ab]	

[a, b, c] Means with same superscript in same row and line are not significantly (P> .05) different.
* Average of 6 samples.

negative regression of DCC on sample recovery (P<.01, r = − 0.7733, Y = 89.9690−0.1465X) well explains this possibility. This result is similar to the fact that as enzymatic hydrolysis of

cellulose advances the amorphous regions are digested and the residue becomes higher in crystalline content[37].

No significant effect of NaOH on DCC is in contrast to the results reported by Walseth[37], Hermans and Weidinger[18], Sperlin et al.[31] and Assaf et al.[2] who have observed that treatment of cellulosic materials with NaOH decreased DCC.

It is also very interesting to mention that regression of CS on DCC was possitive and significant ($P < .01$, $r = 0.7237$, $Y = 2.7723X - 133.0270$); that is, as DCC increased CS increased. These results do not agree with those of Walseth[37], Hermans and Weidinger[18], Sperlin et al.[31] and Assaf et al.[2] who found increased susceptibility of cellulose to enzymatic or chemical degradation with decreased DCC or increased amorphous regions. This result indicates the involvement of some other mechanisms than DCC. Baker et al.[3] studied, by using the x-ray diffraction method, the relationship of DCC of cotton linters and four different wood celluloses to their cellulose digestibilities, and found no correlation. However, these workers reported that cellulose digestibility was related to the hight-width ratio of the main peaks of x-ray curves; the higher the ratio the lower the digestibility. Cotton linter and wood celluloses (SW 40 B, BW 40, raybond and SW 40 A) with cellulose digestibilities of 48.4%, 60.5%, 65.2%, 69.0% and 73.8% showed 11.5, 7.8, 7.4, 5.9 and 5.7 hight-width ratios, respectively. Sundaram[33], and Cowling and Brown[6] suggested that in addition to degree of crystallinity rigidity of crystallites or degree of orientation of crystallites with respect to fiber axis affects the tensile strength or susceptibility of cellulose to enzymatic hydrolysis. Stroll[32], and Marchessault and Howsino, cited from Baker et al.[3], have suggested that order distribution or packing perfection in cellulose crystallites may be in closer agreement with accessibility of cellulose than degree of crystallinity.

The means for DCC, CS, and their comparisons are presented in Table 3. The highest DCC was in treatment NO. 7 (81.83%) which was not significantly different from treatments 5, 8, 9, 14, 15, 16, 18, 25 and 27 where pressure was applied, whereas treatment NO. 7 was different ($P < .05$) from treatments 1, 2, 3, 4, 6, 10, 11, 12, 13, 17, 19, 20, 22, 23, 24 and 26 where no pressure was applied except for 6, 13, 17, 22, 23, 24 and 26. The controls had DCC of about 73% or 27% amorphous regions. This result, using hydrochloric acid, is similar to that of Tomlin and Davis[34] who obtained 31.5% amorphous regions in bagasse cellulose using x-ray diffraction method. Hermans and Weidinger[18], Assaf[2] and Brenner et al.[5] suggested that HCl acid method results in higher crystalline value than x-ray method due to (1) the fact that hydrolized amorphous portion may be converted to crystalline material and/or (2) the assumption that hydrolysis of crystallites proceeds at the same rate even during the early stages of hydrolysis when the amorphous material is still present, is probably incorrect. Some workers believe that the degradation occurs from the ends and consequently does not start untill the amorphous regions have removed. However, Hermans and Weidinger[18] have suggested that although the absolute scale of figures obtained by chemical method are not the same there is a parallel sequence between chemical and x-ray methods.

Table 3. Effects of NaOH, pressure and time on degree of cellulose crystallinity (DCC) and solubility (CS)

NaOH %	PSI	Time(min.)	NO.*	DCC	CS
		5	1	72.25^{g}	65.74^{ij}
	0	15	2	72.67^{g}	66.21^{ij}
		25	3	73.23^{f}	64.38^{j}
		5	4	76.67^{bcdef}	80.84^{def}
0	150	15	5	78.11^{abcd}	87.02^{abcde}
		25	6	77.23^{bcde}	87.99^{abcde}
		5	7	81.83^{a}	92.31^{ab}
	300	15	8	71.79^{abcd}	94.45^{a}
		25	9	80.09^{ab}	93.56^{a}
		5	10	76.39^{bcdef}	65.38^{j}
	0	15	11	75.18^{defg}	65.15^{j}
		25	12	76.57^{bcdef}	64.88^{j}
		5	13	77.25^{bcde}	72.12^{hij}
5	150	15	14	78.85^{abcd}	75.48^{fgh}
		25	15	78.83^{abcd}	80.25^{efg}
		5	16	81.79^{a}	87.41^{abcde}
	300	15	17	81.83^{bcde}	91.56^{abc}
		25	18	79.29^{abc}	89.10^{abcd}
		5	19	72.35^{g}	73.50^{fghi}
	0	15	20	74.06^{efg}	72.64^{ghij}
		25	21	72.88^{g}	74.28^{fghi}
		5	22	75.68^{cdefg}	84.26^{bcde}
10	150	15	23	76.07^{bcdef}	84.44^{bcd}
		25	24	77.37^{bcde}	83.53^{cde}
		5	25	78.38^{abcd}	87.69^{abcde}
	300	15	26	77.93^{bcd}	88.50^{abcde}
		25	27	78.83^{abcd}	89.73^{abc}

^{a,b,c}...Means with same superscript are not significantly($P > .05$) different.

* Treatment combination number.

Application of cupriethylenediamine (CED) for the determination of cellulose solubility (CS) of grasses or mixed forages has been well established by Dehority and Johnson[8, 9]. They observed significant correlation of CS in CED with cellulose digestibility in vitro ($r = 0.901$), DM digestibility in vitro ($r = 0.807$), nutritive value index ($r = 0.842$), and energy digestibility ($r = 0.880$). However, these workers reported that such correlations were not found for legumes and suggested that some components of legumes, readily digested by rumen microorganisms, but relatively insoluble in CED, mask the cellulose and thus decrease CS in CED.

CS was changed ($P < .01$) by NaOH and pressure, but not by time. Level of 10% NaOH showed the highest CS (82.07%) which was higher ($P < .05$) than 5% NaOH (76.81%) but not different from 0% NaOH (81.39%). The 0% treatment was higher ($P < .05$) than the 5%

NaOH. CS was increased ($P<.05$) from 68.02% to 81.77% and 90.48% as the pressure level was increased from atomospheric to 150 and 300 PSI, respectively. The insignificance of time suggests that onece high pressure of either 150 or 300 PSI is established less than 5 minutes is long enough to increase CS. This obsevation confirms the result of Guggolz et al.[17]. They found that treatment of bagasse with 3% NaOH (w/w) at 400 PSI for 45 seconds significantly increased the total soluble after enzyme (TSAE) from 15% to 76%.

Two way interaction between NaOH and pressure was found. At each NaOH level, CS increased consistently with increased pressure, while CS at each level of pressure was not consistent with increased NaOH level. At atomospheric pressure the addition of 10% NaOH (73.47%) increased CS compared to those of 0% NaOH (65.44%) and 5% NaOH (65.13%). At 150 PSI, CS decreased from 85.28% to 75.95% and then increased to 84.04% as NaOH was increased from 0% to 5% and 10%, respectively. At 300 PSI, CS decreased from 93.44% to 89.35% and 88.65% with increased NaOH level. These decreased CS values caused by the addition of NaOH at both 150 and 300 PSI seem to be partly related to increased sample recovery or decreased DM loss, or more specifically, to decreased fiber destruction.

Treatment of bagasse with water alone at 300 PSI caused the highest CS. This result is in agreement with that of Guggolz et al. (unpublished data). They found higher TSAE values for treatment using water alone at 400 PSI than combination of NaOH and pressure. However, the same workers in other study reported that a combination of 3% NaOH (w/w) with 400 PSI obtained 76% TSAE, while water alone at the same level of pressure showed 46% TSAE.

Treatment with 5% NaOH alone (NO. 10, 11 and 12) did not increase CS, whereas 10% NaOH (NO. 19, 20 and 21) increased or approached the significant level. Using the Beckman method[4], it is considered that at least 1 to 2 hrs of treatment is required to improve the digestibility of cellulosic material. Many workers have demonstrated that soaking of cellulosic materials with 1 to 1.5% NaOH solution for 1 to 24 hrs significantly increased their digestibilities. William and Godden reported that treatment of chopped straw with 1.5% solution of NaOH for 24 hrs and treating 1 hr with steam increased digestibility of organic matter, crude fiber and NFE from 47.3%, 60.1% and 39.6% to 73.7%, 87.4% and 62.9%, respectively. However, digestibility of ether extract (EE) was reported to have been reduced from 43.6% to 24.7%. Nordfeldt[22] treated bagasse with NaOH using Beckman method and reported that digestibility of DM, OM, CF, NFE, and TDN were all increased from 14.8%, 19.45%, 28.56%, 17.13% and 19.36% to 34.82%, 38.15%, 46.24%, 26.56% and 34.26%, respectively. Kehar[20], treating rice and wheat straw with 1% NaOH solution for 24 hrs, reported an increase in digestibility of total carbohydrates from 57% to 76% for rice straw and from 51% to 72% for wheat straw. Feist et al.[11] reported that treatment of hardwoods with 0.5% NaOH solution for 2 hrs increased in vitro digestibility from 35% to 50%, and that treatment with 1% NaOH for 1 hr showed similar results. From these results they concluded that treatment time is inversely proportional to NaOH concentration. Their data also demonstrated that if the concentration of the solution is the same the amount of NaOH per unit of material (w/w) does not change in vitro digest-

ibility of this material. Donerfer et al.[10] observed that the higher water dillution caused slight increase in cellulose digestibility in vitro even if the amount of NaOH per unit of the material (w/w) was the same.

In Table 3, treatment with 0% NaOH at 300 PSI for 15 minutes (NO. 8)yielded the highest CS (94.45%) which was different ($P<.05$) from those of controls, 4, 10, 11, 12, 13, 14, 15, 19, 20, 21, 22, 23, and 24, but not significantly different from 5, 6, 7, 16, 17, 25, 26 and 27. These observations suggest that the best treatment combination in this design for improving the nutritive value of bagasse from standpoint of CS and economy probably would be the treatment with water alone at either 150 or 300 PSI.

In order to examine the mechanisms involved in the increased or decreased CS, correlations of CS with sample recovery, ADF, ADL, proximate nutrients[27] and criteria during cellulose preparation[28] were studied. The results are presented in Table 4. CS was significantly

Table 4. Correlation of cellulose solubility (Y) with sample recoverry, ADF[a], ADL[b], DCC[c], proximate nutrients and criteria for cellulose preparation

Correlation with	Equations	Coeffcients
Sample recovery	$Y = 140.5705 - 0.6758X$	$r = -0.9279$ **
ADL	$Y = 84.6642 - 0.4214X$	$r = -0.1315$
ADF	$Y = 1.8120X - 35.1045$	$r = 0.8694$ **
DCC	$Y = 2.7723X - 133.0270$	$r = 0.7237$ **
Dry matter[d]	$Y = 6.9724X - 538.4919$	$r = 0.5768$ **
Crude protein	$Y = 96.4793 - 13.5796X$	$r = -0.4741$ *
Ash	$Y = 80.5396 - 0.0820X$	$r = -0.0173$
Ether extract	$Y = 73.8425 + 5.9449X$	$r = 0.5652$ **
Crude fiber	$Y = 17.0118 + 1.2700X$	$r = 0.7029$ **
NFE	$Y = 125.8956 - 1.0743X$	$r = -0.6721$ **
Alcohol extraction (AE)	$Y = 60.8047 + 1.3326X$	$r = 0.8425$ **
Delignification (DL)	$Y = 65.2056 - 1.6235X$	$r = -0.5982$ **
Holocellulose (HLCE)	$Y = 162.9620 - 1.0867X$	$r = -0.9025$ **
Cellulose (CE)	$Y = 3.4970 + 1.6869X$	$r = 0.7957$ **
Hemicellulose (HECE)[e]	$Y = 100.4619 - 0.7578X$	$r = -0.9332$ **

[a] Acid detergent fiber. [b] Acid detergent lignin.
[c] Degree of cellulose crystallinity. [d] Equilibrated DM.
[e] Loss in KOH solution. * $P<.05$. ** $P<.01$.

($P<.01$, $r=-0.9279$) increased as sample recovery decreased or DM loss increased. There was no significant ($P>.05$, $r=-0.1315$) correlation between CS and ADL (unpublished data). This may indicate participations of other factors than lignin in CS increase; probably (1) reduced orientation or rigidity of crystallites[3, 6, 33], (2) decreased degree of polymerization[3, 13, 25],

(3) decreased silica content[1, 16, 26, 29, 36] and decreased DCC. Also it is possible that lignin -cellulose bond was considerably destroyed and free lignin as well as easily soluble other nutrients was lost in the solution leaving highly conjugated portion. DCC at this NaOH level (0 %), however, was increased from 72.11% to 77.32% and 80.23% with increased pressure levels. This is in contradiction to most of the literature. In this study, rigidity of crystallites, degree of polymerization and silica content were not determined. Ferguson[12] found increase in digestibility of NaOH treated wheat straw with decreased lignin content from 15.4% to 13.64%. Archibald[1] reported increase in lignin content of rice hulls, oat hulls and barley when treated with 1% or 3% NaOH solution, but found decrease when oat hulls and cottenseed hulls were treated with 1.5% NaOH solution. Correlation of CS with ADF was significant ($P < .01$, $r = 0.8694$); CS increased as ADF increased. However, it appears that ADF content decreased in view of absolute level since DM loss was higher than the relative increase of ADF. Goering et al.[15] observed that DM solubility of feces from cows fed alfalfa hay was increased due to decreased amount of ADF and cell wall constituents. These workers' results were confirmed by Guggolz et al.[16] whose data showed the same relation. However, Saxena et al.[26] found increase in ADF content with increased digestible DM. Ololade[23] and Kamstra[19] detected no difference in ADF, though digestibilities of barley straw and corn stover were increased. Correlation of CS with DCC was significant ($P < .01$, $r = 0.723$). There was significant ($P < .01$) positive correlations between CS with DCC and equilibrated DM content ($r = 0.7029$), EE ($P < .01$, $r = 0.5652$) and CF ($P < .01$, $r = 0.7029$). As well as ADF, absolute CF content seems to be reduced because of the same reasons as for ADF. CS was negatively correlated with CP ($P < .05$, $r = -0.4741$) and NFE ($P < .01$, $r = -0.6721$). Correlation with ash content was negative but not significant ($P > .05$, $r = -0.0173$). Godden[14] reported NaOH treatment increased contents of CF and ash of straw and decreased CP, EE and NFE with increased digestibility of total EE. Archibald[1] found NaOH treatment of seed hulls decreased EE, NFE, CP and total ash, and increased CF with increased digestibilities of these nutrients. Ferguson[12] reported similar results except EE.

The relationships of CS with alcohol extraction (AE), holocellulose (HLCE) content, delignification (DL), cellulose (CE) content and loss (hemicellulose, HCE) in KOH solution during cellulose preparation were also examined. Significantly positive correlations of CS with AE ($P < .01$, $r = 0.8425$) and CE ($P < .01$, $r = 0.7957$) were observed. Here, again, relative CE content was increased, whereas absolute content seems to be reduced due to the same reasons for ADF and CF contents. CS was negatively correlated with DL ($P < .01$, $r = -0.5982$), HLCE ($P < .01$, $r = -0.9025$) and HCE ($P < .01$, $r = -0.9332$).

IV SUMMARY

This study was conducted, using Hawaiian bagasse obtained from variety 50-7209, to determine the effects of sodium hydroxide treatment of this ligno-cellulosic material under steam

pressure on the degree of cellulose crystallinity (DCC) and cellulose solubility (CS). Under the conditions of this experiment, the results are summarized as follows:

DCC was increased by pressure treatment. This result seems to be due to the loss of more soluble amorphous regions of cellulose in the decanted solution. As a result, negative correlation between CS and DCC was not observed. No significant correlation of CS with ADL was found either. This also suggests loss of free lignin liberated from lignin-cellulose conjugation. These are well confirmed by significantly positive correlations of CS with ADF, DCC, CF and cellulose, and by significantly negative correlations with sample recovery, NFE, delignification, holocellulose and hemicellulose.

Data of CS indicated that treatment of bagasse with steam pressure alone was more effective and seemed to be more economical than the combination of pressure and NaOH. It was also suggested that as easily soluble substances were lost in the solution under present treatment conditions steam treatment which do not lose such substances must be employed.

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甘蔗バガスの加圧・NaOH処理による化学組成・消化率への影響

Ⅲ. セルロース結晶度及びその溶解度への影響

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要 約

前報同様，ハワイで最も多く(54%)栽培されている品種，50－7209より得たバガスを材料とし圧力（大気圧，150 PSI，300PSI），NaOH濃度（乾物に対し0%，5%，10%）及び処理時間（5分，15分，25分）の三要因のバガスセルロースの結晶度及びその溶解度に対する効果を検討した。その結果は概略次の通りであった。

期待に反し，加圧処理により結晶度は増加した。処理廃液中に可溶度の高い非結晶部が溶出したのが原因と思われる。このため，結晶度とセルロース溶解量間に有意な負の相関は認められなかった。また，セルロース溶解量とリグニン量の負の相関も有意ではなく，リグニン－セルロース結合より遊離したリグニンの廃液中への流失も示唆された。これらの関係はセルロース溶解度と酸性データーゼント繊維，結晶度，粗繊維量及びセルロース量などとの有意な正の相関や，セルロース溶解量と回収量，可溶無窒素物，脱リグニン量，ホロセルロース及びヘミセルロースなどとの有意な負の相関からも理解できる。

セルロース溶解度に関する結果より，バガス処理には圧力のみの処理がNaOHとの組合せ処理より効果的で経済的と思われる。家畜飼料を目的とする実際の処理に当っては，処理液の出ない可溶物質を処理材料内に保持可能な条件を検討すべきであろう。

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