Effects of Lime on the Chemistry of Sugarbeet Tissue

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INTRODUCTION

Pretreatment of sugarbeet tissue with lime has been known to the industry for many years. In 1905 Weinrich proposed processing ground beets (21), and in 1908 and 1910 he patented processes involving the pressing of brei or chips which had been limed and then neutralized (22, 23). In 1956 Borghi described the Bonelli process for pressing juice from ground beets as an alternative to diffusion (4), and results of extensive tests on the process were later published (2, 3). In 1956 Loof and Pohl suggested the diffusion of cossettes in dilute lime water (11). In 1959 Susic proposed diffusion of cossettes which had been treated with a mixture of lime and sugar (16). In 1965 Goodban and McCready proposed that cossettes be treated with powdered lime followed by normal diffusion (10), and Bobrovnik et al. studied this method further (1).

Degtyar (7) reported that the mechanical properties of cossettes cut from stale beets could be improved by addition of lime to diffusion water, whereas in Hungary 20^{Be} lime solution is occasionally added to the cutting machine drum for this purpose (18).

To the authors knowledge there has been no sustained commerical application of any of the above techniques, aside from the occasional lime treatment of rotten and stale beets.

Recent renewed interest in liming before extraction stems from the desire to reduce energy consumption in this industry. It has been estimated that the energy consumed per dollar

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value of product (87,000 Btu, 1973 prices) is greater than for any other food product industry (17). Of the over 2.3 X 10^6 Btu required to process one ton of beets approximately 25% is for pulp drying, 50% for thin juice concentration, 5% for lime production and 5% for heating the juices. Liming of fresh beet tissue holds the promise of reducing energy consumption in several of these operations.

Potential advantages of beet liming are mostly a consequence of the reactions of calcium hydroxide with the pectic substances that hold the cells together and make up as much as 30% of the water insoluble portion of the beet. In the standard extraction process, pectin polymer degrades and peptizes, entering the sugar juice along with other colloidal material from the cells. Subsequently, these impurities must be removed from the diffusion juice in liming, carbonation, settling and filtratation operations. When calcium hydroxide is added directly to the fresh beet tissue at 40°C or lower, deesterification of the pectin predominates over degradation; calcium crosslinks carboxyl groups to form a firm insoluble calcium pectate (10). Calcium crosslinked pectin produces a pulp that is firmer than conventional pulp. As a consequence, the pulp may dewater mechanically to a greater degree than conventional pulp, reducing the energy required to fully dry the pulp in rotary kiln dryers. The pulp solids could be significantly increased since pectin crosslinking may prevent pectin losses to the sugar juice. Also, extraction temperatures may be lowered, since the beet cells will be denatured, and the high pH prevents fermentation at lower temperatures.

In sugarbeet pectin, about 50% of the carboxyl groups and about 30% of the hydroxyl groups in positions 2 and 3 are acetylated. Four reactions may occur when pectin is treated with calcium hydroxide: deacetylation producing acetate as a by-product; ester hydrolysis or demethylation producing methanol; calcium crosslinking of the free carboxyl groups and polymer degradation by glycosidic bond cleavage (Figure 1). At low temperatures the predominant reactions are the demethylation, deacetylation and crosslinking reactions.

At high temperatures glycosidic bonds adjacent to esterified carboxyl groups are also broken (Rx No. 4), greatly reducing the mechanical strength of the beet tissue. Since the glycosidic bond is broken only when adjacent to the esterified carboxyl group, cold demethylation protects the pectin from subsequent hot alkaline degradation. Deacetylation, on the other hand, may be disadvantageous. Schweiger (15) has shown that solutions of acetyl pectates do not form gels or precipitates with calcium ion when the acetylation of hydroxyl groups (positions 2 and 3) is above 55%; however, gels and precipitates will readily form when the degree of acetylation is below this amount. Schweiger suggests that hydroxyl groups are involved in calcium bonding along with the carboxyl groups, and he further suggests that they have to be in vicinal pairs belonging to the same unit (note that vicinal pairs occur only when less than 50% of the hydroxyl groups of the polygalacturonic acid are acetylated). Since sugarbeet pectin has no more than 30% acetylation, leaving sufficient vicinal pairs for gel formation, further deacetylation may have little advantge in terms of pulp handling characteristics and only add an impurity, calcium acetate, to the subsequently pressed and/or extracted sugar juice. Some deacetylation will be unavoidable during the cold demethylation, but fortunately, calcium acetate is not a particu-

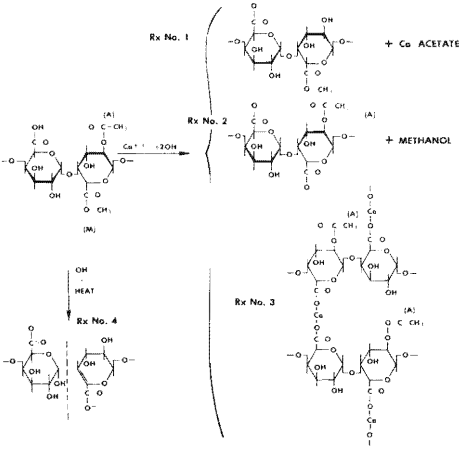

Figure 1. The reactions of pectin with calcium hydroxide. De-esterification: reaction No.1 deacetylation, reaction no.2 demethylation. Reaction no.3 is calcium crosslinking of pectin carboxyl groups. Reaction no.4 is pectin degradation. M indicates a methylated carboxyl group, A indicates an acetylated hydroxyl group. Dashed line indicates a broken glycosidic bond.

larly deleterious impurity, having a negative melassigenic coefficient of -0.55 (13).

This paper presents the results of experiments to determine the effect of variations in the conditions of liming sugarbeet tissue on the chemistry of the pectin-lime reactions, the yield of extraction pulp, and the extraction rates. Subsequent papers will be concerned with the effects of liming of sugarbeet tissue on diffusion juice, on thin juice purity and composition, and on pulp processing characteristics.

MATERIALS AND METHODS

Saponification Rates

The relative rates of demethylation and deacetylation of limed beet tissue were obtained by mesuring the residual ester and acetyl content of pulp after reaction with lime. Beets were washed in a rotary washer, trimmed, and dipped for about 3 minutes in a cold solution of chlorine (1000 ppm). The beets were then dried by brief contact with 50°C dry air and stored at 1°C for no more than 4 days before cutting and liming. Cossettes were cut in a pilot plant cossette cutter designed and constructed at this laboratory. Julienne strips were produced with special attachments to an Urschel dicer. These strips had an 1/8" square cross section. Cossettes and julienne strips were limed by mixing with dry reagent grade $Ca(OH)_2$ in a double cone mixer after thermal equilibrium had been reached. The lime level corresponded to 1% CaO, and at timed intervals 200 gram samples were removed from the mixer and placed immediately into acidified acetone (750 ml. acetone, 200 ml. H_2O, 50 ml. Con. HCl). These cossette slurries were then frozen at -34°C, and the acetyl and methoxyl contents of the marc were later measured by the method of McComb and McCready (12), as revised by Gee et al. (9). Fresh unlimed control samples were also frozen in the acidified acetone mixture, and some were set aside for determination of cossette factor and Silin number.

Yield of Pulp Solids

Cossettes that had been treated either with dry $Ca(OH)_2$ (at 0.5% and 1.0% as CaO on beets) or in thin juice lime

slurry (2.0 and 4.0%, calculated as CaO) were carefully weighed, placed in 20-mesh wire baskets, and suspended in 70° and 75° running water. After extraction for a given time period, pulp was removed from the running water, dried in an oven at 100°C for 16 hours and weighed. the 20-mesh wire baskets were fine enough so that virtually no beet tissue could escape. The dry pulp sugar content was determined by extracting the sugar in ethanol by the standard AOAC method followed by colorimetric analysis of the total sugar as recommended by Dubois et al. (8). Calcium analysis was carried out on the dry pulp by atomic absorption using a Perkin Elmer 303 AA spectrophotometer. Sample preparation was by a modified dry ashing method of Chapman and Pratt (6). Final determination of the solids was accomplished by subtracting the sugar and calcium content from the total dry solids to determine the weight of the insoluble solids not influenced by unextracted sugar or the calcium added in the liming process. Ratios of corrected solids to corrected control solids were then calculated.

Sugar Extraction Rates

Dry lime treated cossettes, slurry treated cossettes and control cossettes were extracted in 20-mesh wire baskets in 75°C and 80°C running water. Sample baskets were removed from the water at 1, 2, 4, 6, 8, and 10 minute intervals. Dry lime treatment was by mixing of $Ca(OH)_2$ (at 0.5% or 1.0% as CaO) with the cossettes for 5 minutes in a double cone mixer, followed by 10 minutes of standing before extraction at 80°C.

Slurry treatment was achieved by dipping cossettes into 2% and 4% lime slurrys (as CaO on wt/wt basis) of thin juice (14^{Bx}) for five minutes and draining for 10 minutes. These slurry treated cossettes were extracted in the same fashion as the dry lime treated cossettes in 75°C running water. Extracted cossettes were dried and sugar determined by the same methods used in the pulp yield experiments.

Lime Consumption

To determine the lime consumption for slurry treatment,

1 liter $Ca(OH)_2$ per liter of thin juice were used. Three successive 200 gm batches of cossettes were dipped for 10 minutes each. Total calcium and total alkalinity were measured titrimetrically using 1/28 N HCl and 1/28 N EDTA both before and after cossette treatment.

RESULTS AND DISCUSSION

The results of the demethylation and deacetylation studies on beet strips limed at 1% for various time periods and temperatures are shown in Figures 2 through 9. All duplicate analyses were repeatable with 4%. Cossettes had a Silin No. of about 12 and a cossette factor of 25. Julienne strips had a Silin No. of 6.4 and a cossette factor of 290.

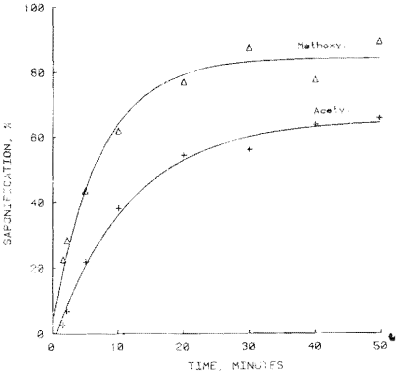

Figure 2. Saponification of beet pectin. Degree of demethylation and deacetylation v.s. time. Cossettes treated at 5°C with dry Ca $(OH)_2$ 1.3% on the beets (1% as CaO).

Saponification of Cossettes

For cossettes, demethylation and deacetylation rates

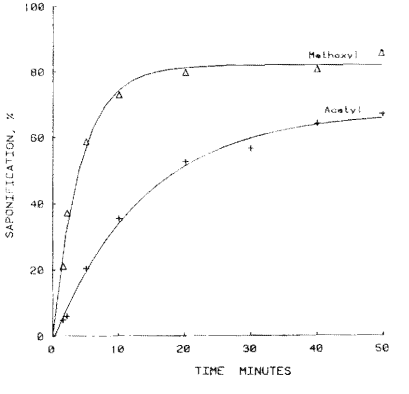

Figure 3. Saponification of beet pectin. Degree of demethlation and deacethlation v.s. time. Cossettes treated at 18°C with dry $Ca(OH)_2$ 1.3% on beets (1% as CaO).

were similar at 5° and 18°C, over the first 50 minutes, although demethylation progressed somewhat more rapidly at 18°C than at 5°C. Figure 4 shows much more rapid deacetylation at 37°C than at the lower temperatures. At 5°C and 18°, deacetylation never became more than about 60% complete, but at 37°C deacetylation rose to almost 80% completion.

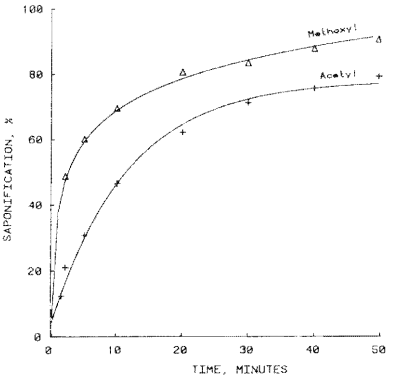

Figure 4. Saponification of beet pectin. Degree of demethylation and deacetylation v.s. time. Cossettes treated at 36°C with dry $Ca(OH)_2$ 1.3% on beets (1% as CaO).

Saponification of Julienne Strips

From Figures 5 and 6 it can been seen that lime did not penetrate into the julienne strips nearly as well as it did into the cossettes. Even after 50 minutes reaction time total demethylation was less than 50%. A comparison of the surface of cossettes with julienne strips would suggest that the smaller degree of penetration of lime into the julienne strips is due not only to their greater thickness but also to the "cleaner cut" obtained in the Ursnel compared to the feathered and cracked surfaces obtained in a cossette cutter. The much lower demethylation rates for julienne strips would be in agreement with the observation made by Goodban and McCready that lime penetration into a cossette is more rapid than would be predicted from results with microtome-cut pieces (10). Use of julienne strips was discontinued as soon as cossettes were available, for much of the advantages of liming beet tissue is lost if the lime or sugar cannot diffuse through the strip in a reasonable time.

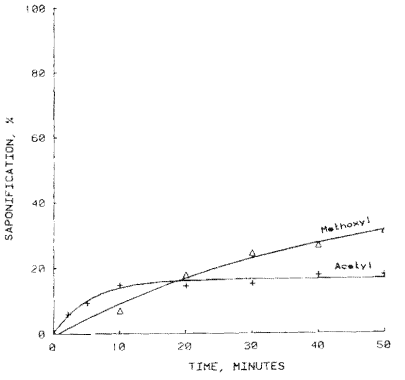

Figure 5. Saponification of beet pectin. Degree of demethylation and deacetylation v.s. time. Julienne cuts treated at 6°C with dry $Ca(OH)_2$ 1.3% on beets (1.0% as CaO).

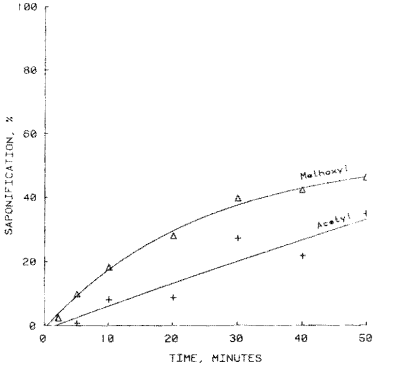

Figure 6. Saponification of beet pectin. Degree of demethylation and deacetylation v.s. time. Julienne cuts treated at 35°C with dry $Ca(OH)_2$ 1.3% on beets (1% as CaO).

Rate of Demethylation vs. Deacetylation

Since demethylation is a positive reaction promoting Ca^{+2} crosslinking and inhibiting pectin degradation while deacetylation is probably disadvantageous, consuming lime and producing acetate ion impurity, the ratio between deacetylation and demethylation could provide valuable insight into optimum processing conditions. In Figure 7, the deacetylation to demethylation ratios are plotted for the cossette treatment at 1% lime addition (CaO) for 5, 18, and 37°C. At 18°C and equilibration times under 20 minutes this ratio is significantly lower than at 5° or 37°. Figure 3 shows that about 90% of maximum demethylation was achieved in about 10 minutes. It might be concluded, then, that optimum temperature for the addition of dry lime would be around 20° with a 10 to 15 minute reaction time before diffusion.

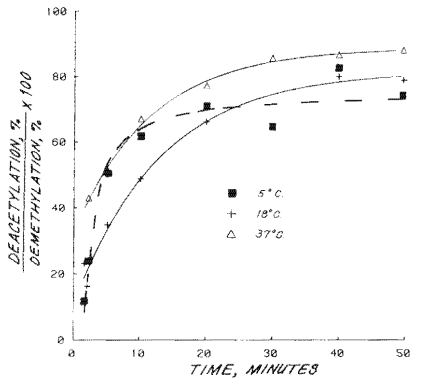

Figure 7. Deacetylation to demethylation ratios for sugar beet cossettes limed at 1.3% $Ca(OH)_2$ on beets (1% as CaO) at 5°C, 18°C and 37°C.

Effects of Temperature on Saponification of Cossettes

In Figure 8 the curves of Figures 2, 3 and 4 are superimposed onto one graph without the data points. This shows that the demethylation and deacetylation curves are not stacked according to increasing temperature as one might expect; there is much crossover in the curves. However, looking at total deesterification (i.e. demethylation and deacetylation) for these three temperatures the curves are stacked according to temperature (Figure 9). Thus, after 10 minutes equilibration the % demethylation is greater at 18° than at 37°, yet total deesterification is always greater the higher the temperature. All this would seem to indicate that demethylation and deacetylation are not independent of one another, and it would not seem unreasonable to expect Ca^{+2} crosslinking of carboxyl groups to inhibit both demethylation and deacetylation through steric hindrance or simply retardation of the rates of diffusion of calcium hydroxide into the cossette tissue.

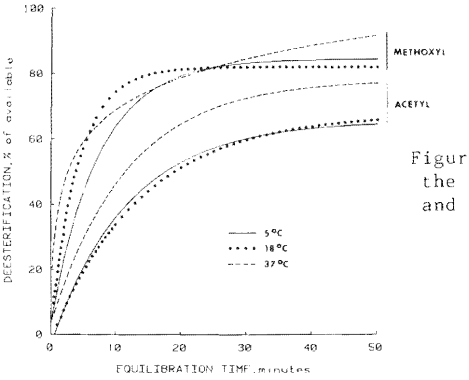

Figure 8. Superimposition of the curves of figures 2, 3, and 4 without data points.

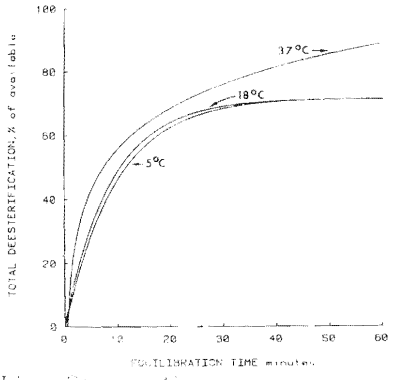

Figure 9. Total deesterification of beet pectin in 5°C, 18°C and 37°C cossette runs, where methoxyl and acetyl groups are added together to determine degree of total esterification.

Lime Consumption

Pectin has been reported by Vukov to comprise 16.3 ± 5.9% of sugarbeet marc for normal European beets (19). However, the beets used in these experiments contained around 25% pectin in the marc, with about 0.44 methyl groups per pectin unit and about 0.8 acetyl groups per pectin unit on the untreated pulp. If it is assumed that the marc comprises about 5% of the beet then the pectin comprises about 1.25% of the beet. The average unit molecular weight of sugarbeet pectin in these beets was 176.12 + 0.8 X 42 + 0.44 X 14, or 215.88, where 176.12 is the formula weight of the anhydrogalacturonic acid unit. Only one calcium equivalent per pectin unit is required to totally demethylate and cross-link the pectin. If total deacetylation is included, then 1.8 equivalents of CaO is required per pectin unit. If it is assumed that the original beet is 1.25% pectin, then full demethylation and deacetylation will require 0.29% CaO on the cossettes.

Total acid content of sugarbeet press juice for a normal year, as reported by Wallenstein (20), is 60 meq/kg of pulp. Since the press juice does not contain much petinic acid, Wallenstein's value corresponds to an additional lime demand of 0.168% for a total lime consumption of 0.460% on the cossettes.

When cossettes are limed by treatment in a thin juice lime slurry the lime consumed is the sum of that lime which reacts with the cossettes and that which is carried over on

removal of the cossettes from lime slurry reaction vessel. The average results for these experiments are shown in Table 1.

Table 1. Calcium and alkalinity changes of one liter of thin juice-lime slurry on treatment of 200 gms. of cossettes (Expressed as % CaO).

	Alkalinity[a]	Calcium[a]
Initial slurry	1.88	1.90
Final slurry	1.50	1.58
Consumed* (% on Cossettes)	0.63	0.53

[a]Average of three experiments.

The consumption of alkalinity at 0.63% Ca (CaO) was 37% greater than theoretical. In addition, lime slurry was lost from the treatment vessel because of carryover of slurry with the cossettes. The average carryover volume was about 40 ml. per 200 gram batch. This represented about 0.75 grams of CaO per batch, or 0.38% on the cossettes, for a total lime use of about 1.0% on the cossettes. Although this is about the same lime consumption as with dry liming, it could probably be reduced by using a less concentrated lime slurry or a series of progressively less concentrated thin juice lime slurries.

Cossettes treatment with a thin juice lime slurry would be favored over dry liming because of the relative ease of operation, minimized cossette damage with cossette slurry mixing compared to dry lime mixing, potential for using available equipment. For example, some cells of an Oliver Morton or Robert battery could be easily converted to this use.

Yields of pulp solids

Results presented in Tables 2 and 3 show that solids yields were increased by as much as 30%, although generally the increase was on the order of 10 to 20% in the dry lime experiments and around 27% in the slurry liming experiments. Lime reaction times of up to 90 minutes did not seem to appreciably change the value of the limed to unlimed solids ratio. Only treatment of cossettes at 37°C with 0.5% dry

lime did not appreciably increase the solids yield in the pulp.

Table 2. Effect of dry liming on residual pulp weight after extraction at 70°C for one hour.

Beet Temp., °C	Lime Level %	Equilibration Times (min.)	Limed Solids* Control Solids
4	0.5	40	1.16
4	1.0	20	1.30
4	1.0	45	1.15
20	1.0	20	1.11
20	1.0	40	1.11
37	0.5	20	1.04
37	0.5	40	1.06
37	1.0	15	1.17
37	1.0	30	1.12

* Dried at 110°C for 16 hours; sugar and calcium weights subtracted from total pulp weight.

Table 3. Effect of slurry liming* on residual pulp weight after extraction at 75°C for fifty minutes.

Slurry Lime Conc. %CaO	Dip Time Minutes	Total Equilibration Time Before Extraction (Min)	Limed Solids Control Solids Ratio
4	3	15	1.27
4	10	15	1.27
4	3	30	1.29
2	3	30	1.28
2	3	15	1.26
2	10	15	1.24

* Slurries used were both 2 and 4 percent lime (as CaO) in 15 Brix dilluted thick juice, slurry and cossette temp. were 20°C.

All samples run in duplicate.

Sugar Extraction Rates

Results shown in Figures 10 and 11 reveal a 25 to 50% increase in residual sugar in the pulp of the limed cossettes after 10 minutes of extraction, a result that was not unexpected since calcium pectate membranes have been used in the past to retard sugar diffusion (5). Although this result would seem to indicate the need for more prolonged diffusion for limed cossettes, the greatly improved dewatering obtainable with limed pulp may serve to eliminate the disadvantage. Calculations made from data on the solids content of limed

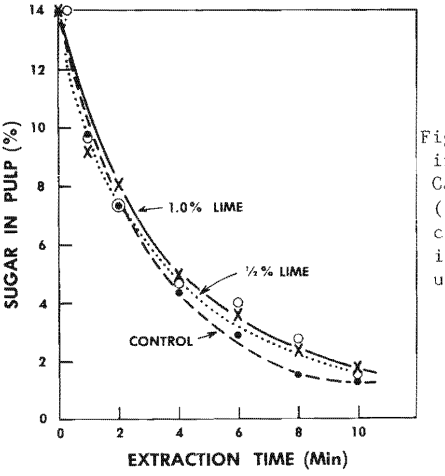

Figure 10. Residual sugar in cossettes limed with dry $Ca(OH)_2$ at 0.5% and 1.0% (calculated as CaO) plus control after extracting in 75° running water for up to 10 minutes.

press pulp and control press pulp (14), combined with the known increase in pulp solids brought about by liming, indicate that more sugar could be removed from limed cossettes than from unlimed cossettes for the same extraction and pressing conditions, since more sugar-bearing press water could be removed and returned to the process. Thus the slight increase in residual sugar in limed pulp would not produce less favorable extraction economics for this process.

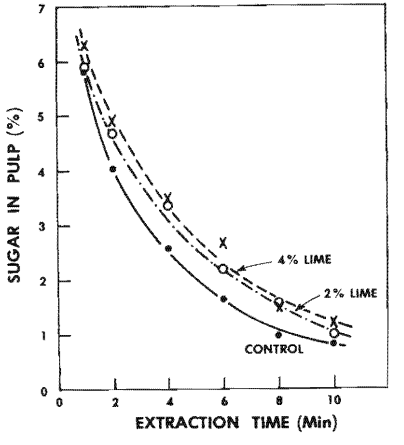

Figure 11. Residual sugar in cossettes limed with 2% and 4% thin juice (14Bx) lime slurries [(added as $Ca(OH)_2$, calculated as (CaO)] for five minutes and drained for 10 minutes, compared to untreated control. Extraction was in 80°C running water for up to 10 minutes.

SUMMARY

The addition of lime to sugarbeet tissue at lower temperatures causes demethylation of the pectin in the cell walls of the beet tissue, allowing Ca^{2+} to crosslink the pectin as

a stable insoluble matrix. This permits alkaline diffusion with less disintergration of the pulp. High deacetylation rates and pectin degradation above 37°C could limit process to lower temperatures.

The retention of pectin in the pulp after lime treatment of beet tissue was improved, as was indicated by a 10 to 30% increase in solids in the pulp. Cossettes dipped in lime slurry gave the best overall pulp weight increase of about 27%. In a factory operation, the magnitude of the ratio of pulp solids per ton of beets should be an indicator of the releative amount of calcium pectate formation versus the amount of degradation, and should be a useful parameter of process control. Since beet pulp is worth about $100/ton as cattle feed, a 10 to 30% increase could represent a substantial economic advantage.

Although extraction rates were significantly reduced by cossette liming, total sugar yield from cossettes should be improved over conventional processing due to the increase in press water yield for the same pressing conditions (14). A thinner cossette might also be advantageous. Sugar extraction would be improved, and since hydrodynamic resistance would be less than for unlimed cossettes of the same size, the objections to smaller cossettes would not be applicable. Other forms of beet tissue could be used with various extraction systems, but the cossette has a number of processing advantages.

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LITERATURE CITED

(1) Bobrovnik, L. D., G. P. Voloshanenko and A. R. Sapronov. 1977. Effect of the liming of beet chips on juice quality. Sakh. Prom. (Moscow) 1:11-13.

(2) Bonelli, A. 1955. Process of obtaining sugar by means of defecation with CaO carried out on beets after crushing and rolling them, thereby avioiding the hot diffusion process. Italian Patent No. 573,733.

(3) Bonelli, A. 1959. Estrazione dello zucchero per defaccasione operate direttamente sulle barbabietole. L'Industria Saccarifera Italiani 52:399-411.

(4) Borghi, M. 1946. Il nuovo processo del dott. Bonelli per l'estrazione dello zucchero dalle bietole. La Chimica e l'Industria 28(11-12):177-184.

(5) Camirand, W. M. et. al. 1968. Dehydration of Membrane Coated Foods by Osmosis. J. Sci. Food Agric. 19, 472-474, August.

(6) Chapman, H. D. and P. F. Pratt. 1961. Methods of analysis for soils, plants, and waters. University of California.

(7) Degtyar, M. Y. 1948. Diffusion of long-stored beets. Sakhar. Prom. 4:28-29.

(8) Dubois, M., K. A. Gilles, J. K. Hamilton, P. A. Rebers and F. Smith. 1956. Colorimetric method for determination of sugars and related substances. Anal. Chem. 28(3):350.

(9) Gee, M., E. A. McComb and R. M. McCready. 1958. A method for the characterization of pectic substances in some fruit and sugarbeet juices. Food Research 23:72-75.

(10) Goodban, A. E. and R. M. McCready. 1965. Liming of sugarbeet cossettes. J. Am. Sugar Beet Technol. 13:564-572.

(11) Loof, H. G. and W. Phol. 1956. Process for extracting sugarbeets, using weakly alkaline water. French Patent No. 1,129,771.

(12) McComb, E. A. and R. M. McCready. 1957. Determination of acetyl in pectin and in acetylated carbohydrate polymers. Anal. Chem. 29:819.

(13) McGinnis, R. A. 1971. Beet-sugar technology. Beet Sugar Development Foundation, Fort Collins, Colorado, Second Edition. Pg. 585, pg. 125.

(14) Randall, J. M., W. Camirand, and E. M. Zaragosa. 1981. Effect of cossette liming on dewatering of beet pulp. J. Am. Soc. Sugar Beet Technol. (In press).

(15) Schweiger, R. G. 1946. Acetyl pectates and their reactivity with polyvalent metal ions. J. Organic Chem. 29(10):2973-2978.

(16) Susic, S. K. Studija o problemu alkine difuzije u industriji secera. 1959. Prehranbena Industrija 13:1409-1414.

(17) Unger, S. G. 1975. Engery utilization in the leading energy-consuming food processing industries. Food Technol. 29(12):33-43.

(18) Vukov, K. and M. Tegze, 1953. A meszezes hatasa a repaszeletra, (The Effect of Liming on Sugar-Beet Cossettes). Cukoripar 6:213-215.

(19) Vukov, K. Physics and Chemistry of Sugar-Beet in Sugar Manufacture. 1977. Page 49.

(20) Wallenstein, H. D., and K. Bohn, Sauren in Ruben and Saften (Acid in Beets and Juice) Z. Zuckerind., 13, 125 (1963).

(21) Weinrich, M. 1905. Process of treating sugarbeets. U.S. Patent No. 803,945.

(22) Weinrich, M. 1908. Process of treating sugarbeets. U.S. Patent No. 881,641.

(23) Weinrich, M. 1910. Process of treating sugarbeets. U.S. Patent No. 950,035.