THE SELECTIVE REMOVAL OF FINAL MOLASSES COMPONENTS BY ETHANOLIC PRECIPITATION

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Abstract

The technical feasibility of increasing sucrose recovery by means of selective removal of final molasses components after liming and ethanolic precipitation is investigated. It is possible to increase the purity of 65% of the molasses solids by 8 - 9 units. The reducing substance/ash ratio is increased by 75%. The method is technically feasible but the economic factors are unclear.

Introduction

The aim of a sugar milling operation is to maximise the extraction and recovery of sucrose. At present, 9% or more of available sucrose is lost in the final molasses. This loss can be reduced either by improving exhaustion or by treatment of the molasses to recover extra sucrose.

Various chemical and physical treatments have been tried on cane molasses with minimal success.

The calcium or barium saccharate process is widely used in the beet industry. Sucrose is converted into an insoluble calcium or barium saccharate and recovered after filtration by carbonatation. The high level of reducing sugars normally found in cane molasses precludes the use of this process.

Olivarius[1] sought to overcome this difficulty by selective fermentation of the reducing sugars followed by saccharate recovery. He achieved considerable success in pilot scale trials, however, in full scale production, problems such as bacterial action and yeast mutation arise.

Various trials carried out at Empangeni on desludging B molasses have given negative results. Electrodialysis, electrolysis and electrophoresis perform similarly disappointingly.[2] Ultrafiltration[2] has produced some promising results but the attendant technology will have to make significant advances especially with respect to throughput rates and membrane temperature sensitivity before it can be considered as a viable means of sucrose recovery.

The addition of a miscible solvent to aqueous solutions causes precipitation of various components of that solution according to the nature and quantity of solvent used. Reich[3] applied this principle to recovering non-sugars from molasses. The method of Ruff and Withrow[4] for determining gums in molasses and the subsequent modification thereof by Jennings[5] also employs this principle. In both cases the solvent is ethanol. The possibility of a substantial purity rise, due to precipitation of ash components with the gums, prompted an investigation of the method as a means of increasing sucrose recovery.

The advantages of such a process were seen to be twofold.

(1) Reduction in ash leading to an increase in both purity and reducing substance/ash ratios.

(2) Reduction in viscosity due to removal of gums and insoluble suspended matter.

Experimental

Method of treatment

Samples of molasses of known solids contents were weighed out to contain a known quantity of solids. Varying amounts of water were added and predetermined quantities of commercial non-coloured methylated spirits were added slowly with stirring over 5 minutes. As the addition of ethanol proceeds the formation of floc is observable when the ethanol/water mass ratio is about 1 : 1. Further addition causes the precipitant phase to become more viscous causing agglomerates to form at first a fluid mass and then a sticky black substance. The final physical properties of the precipitant phase are dependent on the solids/water/ethanol mass ratio in the system. The higher the level of ethanol, the more viscous and easily separable is the precipitate phase.

The stirring was maintained for about 30 minutes until the supernatant phase was observed to be clear. The supernatant was then decanted and weighed. In samples containing less ethanol, separation was aided by centrifuging. Analyses of the supernatant for purity and, in some experiments, ash components was then carried out using the standard methods of analyses according to the Huletts Laboratory Operations Manual.

Identification of important factors

A Plackett-Burman screening test[6] was used to identify the important variables affecting purity rise. It was found that the solids/water/ethanol ratio was the only significant factor of the ones tested. The effect of temperature and the presence of settling aids such as bagacillo was found to be insignificant. A later series of tests showed that the purity rise attainable at the optimum solids/water/ethanol ratio could be increased by liming the molasses to pH 8.

A number of molasses samples were subsequently treated with various combinations of ethanol and water during the season. The results obtained are summarised as follows:

Purity rise profiles.

The purity rise profile for a typical limed molasses sample is shown in Fig. 1. As can be seen there is an optimum water/ethanol ratio at which the purity rise in the supernatant is at a maximum. The value of this maximum is dependent on the solids/ethanol ratio. The mass of solids in the supernatant phase

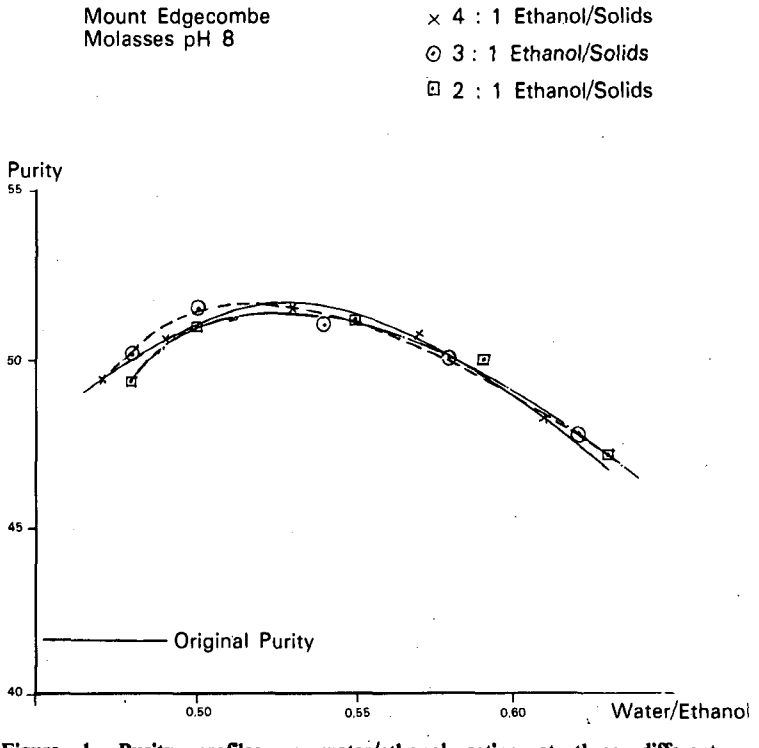

Figure 1: Purity profiles vs water/ethanol ratios at three different ethanol/solids ratios.

was found to be linearly dependent on the water/ethanol ratio at a given solids/ethanol ratio; this is shown in Fig. 2. The more total solvent present, the more solids will be found in the supernatant phase. In terms of purity rise, any ethanol/solids ratio in excess of 2 : 1 brings diminishing returns although the total mass of material separated at that purity increases. It can be expected that, at the point of maximum purity rise, the percentage of the solids to be found in the supernatant phase will increase from 50% to 80% of the total solids treated as the ethanol/solids ratio increases from 2 : 1 to 8 : 1. The average purity rise maximum is 8 - 9 units for final molasses.

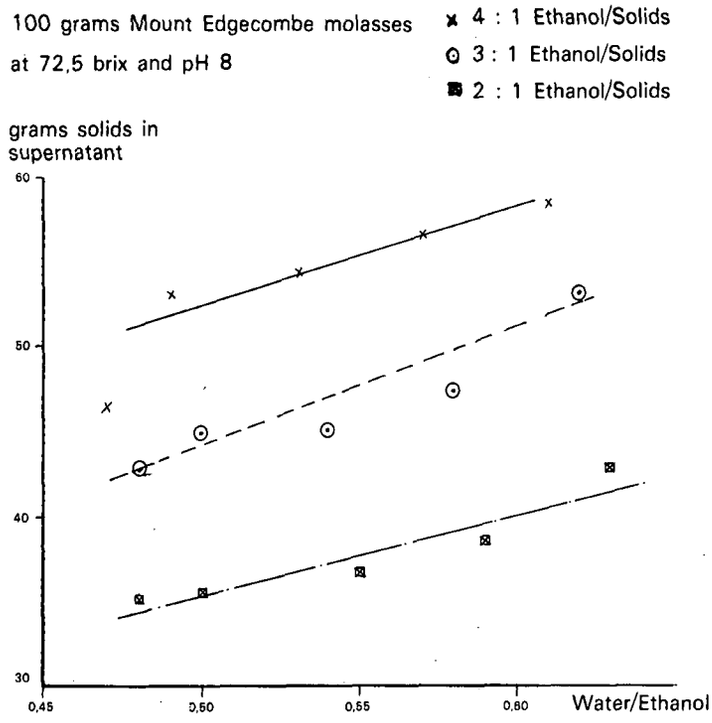

Figure 2: Grams solids in supernatant vs water/ethanol ratio.

Ash Components.

Ash components are differently affected by the water/ethanol ratio according to their relative solubilities. Supernatant components analysed were reducing sugars, sucrose, Na, Mg, K, Ca and insolubles. The percentages of these components to be found in the supernatant depends on the water/ethanol ratio in the manner depicted in Fig. 3, which shows a typical component solubility profile at a low ethanol/solids ratio. The purity rise profile in nominal units is also shown for comparison. Differing values are found for each molasses but the form of the curves remains similar. The curves for sucrose, Na and K are linear, whereas the remainder are exponential. At larger ethanol/solids ratios the percentages increase since more water is present at a given water/ethanol ratio. Although the form of the curves depicted in Fig. 3 remains the same, at ethanol/solids ratios greater than 2 : 1, the sucrose values are greater than the reducing sugars values leading to a larger maximum purity rise than at ethanol/solids ratios of less than 2 : 1.

Reducing sugars/ash ratio in supernatant.

The log reducing sugars/ash ratio in the supernatant phase was found to be linearly related to the ethanol/water ratio, with a significance better than 1%, the form ethanol/water = a + b log reducing sugars/ash being analogous to the SMRI target purity formula[7]. The values of constants a and b depend on the original value of the log reducing sugars/ash and on the ethanol/solids ratio. Two examples are shown in Figs. 4 & 5.

The point of maximum purity rise unfortunately does not coincide with high values of reducing sugars/ash ratio but the reducing sugars/ash is still higher than in the untreated molasses. The reducing sugars/ash ratio value at the point of maximum purity rise tends to be lower if the original molasses has a low reducing sugar/ash ratio and diminishes with increasing ethanol/solids ratio. Typically, the reducing sugars/ash ratio lies in the region of 2,0 - 2,7 at the point of maximum purity rise representing an increase of about 75% on the untreated molasses reducing sugars/ash ratio.

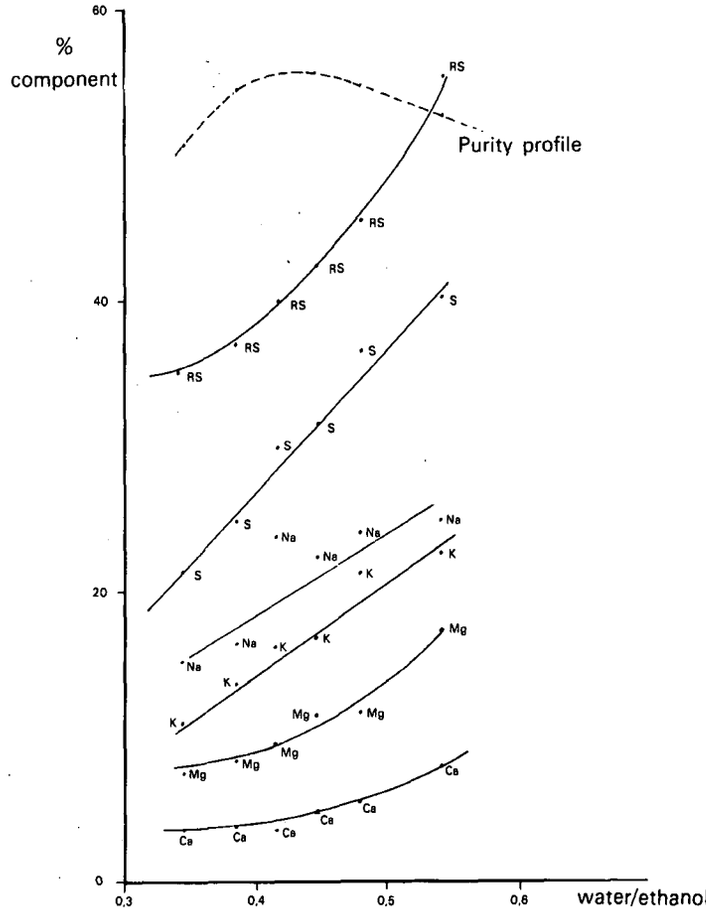

Figure 3: Mass percent of individual components in treated molasses found in supernatant phase at various water/ethanol ratios. Amatikulu molasses, 3 : 2 ethanol/solids ratio.

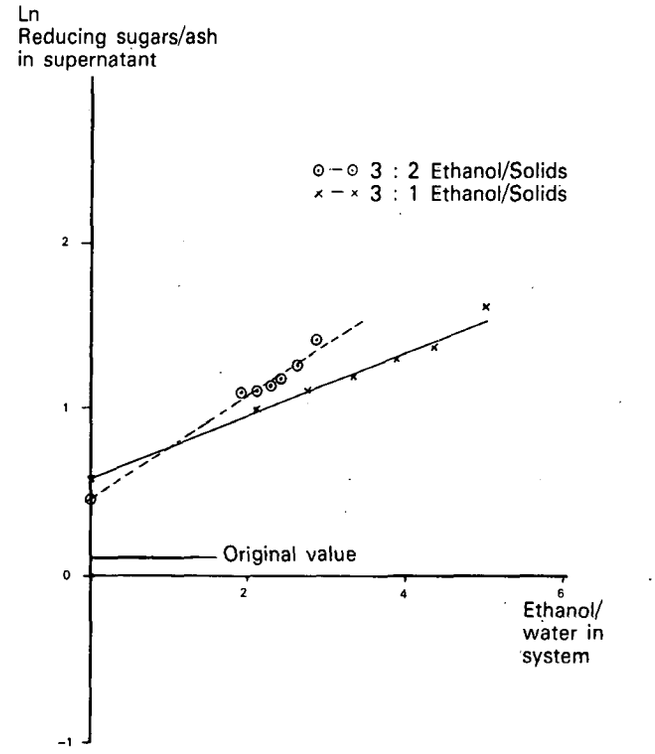

Figure 4: Ln reducing sugars/ash ratio in supernatant vs ethanol/water ratio in system. Amatikulu molasses at two different ethanol/solids ratios.

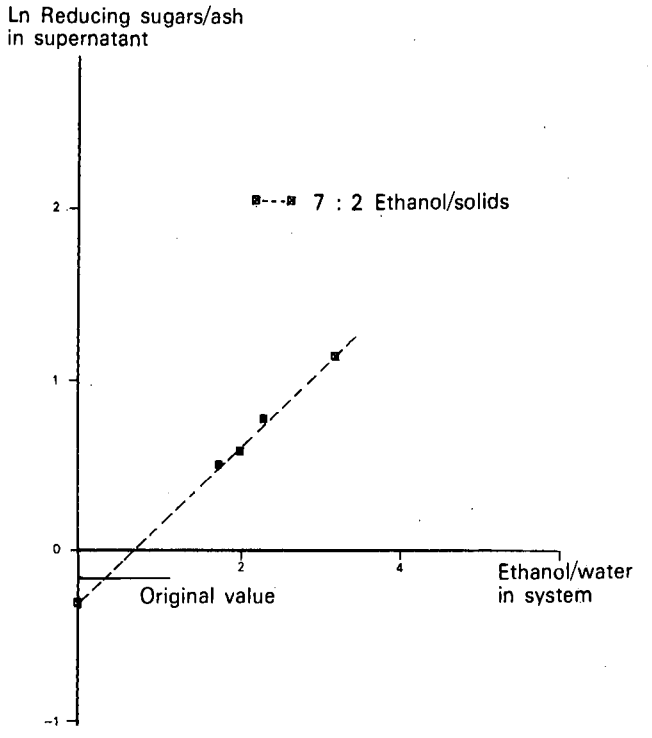

Figure 5: Ln reducing sugars/ash ratio in supernatant vs ethanol/water ratio in system. Mount Edgecombe molasses at 7 : 2 ethanol/solids ratio.

Note that although the SMRI target purity is very low at these values of reducing sugars/ash the nature of the ash in the supernatant phase is more melassigenic due to the high proportions of Na and K and thus target purity difference for boiled down supernatant tends to be greater than for the original molasses.

Exhaustion tests –

The SMRI kindly conducted three boiling down tests on brixed up supernatant solutions. The Amatikulu sample was not limed neither was it at the maximum purity rise point. Results are shown in Table 1.

Table 1

Results of SMRI Boiling down tests

Molasses	Purity units	Reducing sugars/ ash ratio	SMRI Target Purity[7]	TPD	Purity rise(R) and drop unit (D)
AK control	39,6	1,16	38,5	1,1	8,1 (R)
AK purified	47,7	2,1	33,7	14,1	7,9 (D)
AK boiled down	39,8	2,0	34,1	5,8	
ME control	37,7	1,56	36,1	1,6	6,3 (R)
ME purified	44,0	2,63	31,7	12,3	10,3 (D)
ME boiled down	33,7	2,64	31,6	2,1	
NB control	34,9	1,5	36,5	-1,6	9,7 (R)
NB purified	44,6	2,6	31,9	12,7	9,9 (D)
NB boiled down	34,7	2,4	32,3	2,4	

Both the Mount Edgecombe and Noodsberg samples which were close to the maximum purity rise point were exhaustible to purities less than the original molasses purity. In both cases the TPD increased slightly. Even though the Amatikulu sample was not at optimum purity rise point, exhaustion to very close to the original purity was possible.

A practical example of a treatment –

For most molasses tested, the maximum purity rise occurs at a solids/water/ethanol ratio of 100 : 180 : 350 for a limed molasses.

This ratio is not critical as the purity rise profile is fairly flat in the region of the maximum. (Refer to Fig. 1)

Molasses would thus be diluted until, for every 100 parts of solids, there were 165 parts by mass of water in the system. 365 parts by mass of 96% commercial alcohol would be added slowly whilst stirring and a separation would take place. After centrifuging – 500 gravities for 10 minutes was found to be adequate – a liquor of higher purity containing 65 parts of solids can be separated from a precipitate phase of low purity. The way the components are split between the phases in a typical separation is tabulated below.

TABLE 2

Typical precipitation of Amatikulu molasses components

	Molasses		Supernatant		Precipitate	
	100 g solids →		64,7 g solids		+ 35,3 g solids	
Reducing Sugars	25,0		19,3		5,7	
Sucrose	38,0		30,5		7,5	
Ash	17,0		7,4		9,6	
Others (gums etc).	20,0		7,5		12,5	
Reducing sugars/ ash	1,47		2,6		0,59	
Purity	38,0		46,9		21,4	
Ash components:	%	gms	%	gms	%	gms
Na	4	0,68	6	0,44	3	0,24
K	55	9,35	75	5,61	39	3,74
Mg	6	1,02	7	0,51	5	0,51
Ca	12	2,04	2	0,12	2	1,92
Insolubles	12	2,04	Nil	Nil	21	2,04
Undetermined	11	1,87	10	0,75	12	1,12
Total	100	17,0	100	7,43	100	9,57
Water	180		162,5		17,5	
Ethanol	350		345		5	
% Solids	15,9		11,3		61,1	

Prospects for further development –

The method of sucrose recovery is technically feasible giving a good separation both of the viscous molasses components and a proportion of the ash. As a consequence, losses of sucrose in final molasses could be decreased by one third which would represent a substantial revenue increase.

Economically however, the picture is not clear. There are three problems.

(1) Ethanol recovery from the supernatant and precipitate. It appears that a substantial capital investment in rectification columns, steam stripping apparatus etc. would be required at a time when the industry is experiencing a low rate of return on capital.

(2) Loss of solids in the precipitate phase. The loss of revenue amounts to 35% of the present income from molasses processors.

(3) Loss of ethanol. At minimum a 1% loss of ethanol on solids treated could be expected even with sophisticated recovery plant. At R450 per ton this represents a substantial loss.

Unless economic factors improve, this method of molasses treatment remains a laboratory method for gaining a greater understanding of the physical chemistry of molasses component interactions.

Summary and Conclusions

The selective precipitation of molasses components by liming to pH 8 and adding ethanol has been investigated. Treatment of a limed molasses to a solids : water : ethanol ratio of 100 : 180 : 350 results in a purity rise of 8 - 9 units accompanied by a 75% increase in reducing sugars/ash ratio. Losses of sucrose in final molasses can thereby be decreased by up to one third.

Technically the method is feasible however economic factors do not appear to be very encouraging.

Acknowledgments

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