

EXHAUSTION OF SOUTH AFRICAN FINAL MOLASSES

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Abstract

A relationship between true purity, reducing sugar and ash was developed for South African molasses. This relationship was established by equilibrating molasses with sucrose at 40°C and a viscosity of approximately 1 000 poises. The formula proposed is $p = 51,02 - 10,89 r/a$ in which

p = true purity

r = reducing sugars

a = sulphated ash

Introduction

Many investigations have been carried out attempting to correlate the composition of final molasses with its purity after obtaining equilibrium, under certain pre-defined conditions, in the system sucrose - cane molasses.

The aim of these relationships has been to provide a value, derived from a few simple analyses, by which the final obtainable purity of the molasses which could have been achieved in the factory could be judged. These correlations generally had no strong physical or theoretical basis and were merely statistical averages from which, in some cases, considerable deviations were possible¹³.

Some formulae have been in use for a considerable time in a number of cane-sugar producing countries³. As it is doubtful whether one relationship will be valid for the wide variety of molasses compositions, most sugar producing areas have developed their own individual relationships between the target purity and some impurities which can be easily determined. Examples of individual formulae are those in use in Hawaii⁹, Australia⁵, Taiwan², Mauritius¹² and India⁶.

To derive their relationships, some investigators^{2 3 12} have used selected samples of factory molasses which were believed to have been exhausted and determined the various analytical parameters, after which a regression analysis was carried out.

Other relationships have been derived from laboratory exhaustion experiments^{5 9}. In Australia the relationship between true purity, reducing sugar and ash was calculated from results using a laboratory scale crystalliser. The samples were equilibrated at a viscosity of 1 000 poises and a temperature between 40° and 50°C. In a later stage of the investigation, equilibrium was obtained in copper vessels vibrating at 50 cycles⁴.

The viscosity was found to be the most important parameter and Foster⁵ stated that it should be sufficient to measure the viscosity of a molasses sample under controlled conditions to be able to judge the exhaustion of the sample. He however considered this to be too difficult for

most sugar factory laboratories and preferred for this reason the determination of reducing sugars and ash content.

Payne⁹ also considered it necessary to obtain saturated molasses at a constant viscosity before using the analytical data for a relationship between purity, reducing sugar and ash. The viscosity to which the data were corrected was 600 poises at 50°C.

A number of investigators have tried to base these relationships on theoretical considerations. Ramaiah and Vishnu¹⁰ postulated the existence of salt-sucrose complexes and were able to establish from a number of optical rotation measurements of sucrose in salt solutions of various concentration, the specific rotation and the nature of Na, K and Ca complexes with sucrose¹¹.

Assuming the existence of these salt-sucrose complexes, Gupta⁷ found, from a kinetic analysis, that an exhaustion relationship between molasses purity, reducing sugars and ash should have the form

$$p = A - B r/a$$

in which p = true purity of the molasses

r = reducing sugar concentration

a = ash concentration

The fact that a number of the published relationships show this form^{5 6 9 12} tends to add support to his arguments.

In some cases, the correlation coefficient of these relationships does not show a high value, as for example for the Mauritian formula¹² where the correlation coefficient is 0,453. Others show much higher values: Australia 0,897⁵, Hawaii 0,83⁹.

The correlation coefficient should however be considered with reservation, as in a number of these exhaustion relationships, the independent variable (true purity) is not completely independent of the dependent variables^{3 6}. This is illustrated by the fact that for randomly generated values for the variables, a rather high value for the correlation coefficient can be obtained. This may be of the order of 0,5¹⁵.

Development of an Experimental Exhaustion Technique:

In the initial experiments, C massecuites from factories were equilibrated in laboratory crystallisers. The design of these crystallisers was similar to those used in Australia⁵, differing only in length, being 275 mm long. The factory massecuites however were often found to be unsuitable, being either not "tight" enough, having insufficient crystal surface, or containing false grain.

In a later stage, final molasses were used, which were boiled in a stirred laboratory vacuum

pan having a strike volume of 13 l.¹

It was soon found that unless the concentration of the molasses could be carried out to a defined viscosity suitable data were not obtained. For this reason, the laboratory pan was equipped with a viscosity measuring device.

A current measurement of the stirrer motor on the pan proved to be too insensitive. An electronic viscometer (Bendix Ultrason) was tried; this has a probe consisting of a reed vibrating longitudinally at 30 kc, with a small amplitude. It was found however that the ultrasonic vibrations induced false grain formation and the measurements showed a poor reproducibility.

Finally, a torque measuring device on the main stirrer shaft was constructed. This device was similar in design to the one described by Nicklin and Beale⁸. The motor was constructed in a fixed position in line with the stirrer shaft. The stirrer shaft was driven by a counter shaft fitted in a cage which could rotate freely around the stirrer shaft. The force which counter-balanced the torque on the cage was a weak spring at the end of a non-elastic cord. As the viscosity of the massecuite increased, the spring stretched and a pointer attached to the spring moved along an arbitrary scale. The latter was calibrated at various points on the scale by measuring the viscosity of the molasses by means of a Hoeppler viscometer. The reproducibility of this device was found to be of the order of 100 poises.

In an attempt to reduce the time necessary for obtaining equilibrium in the system sucrose-molasses, crystallisation in an ultrasonic bath was tried. However, the massecuite remained supersaturated and no crystallisation took place. Similar results were obtained using Foster's⁴ vibrating method

Experimental Method

Approximately 14 kg of the molasses under

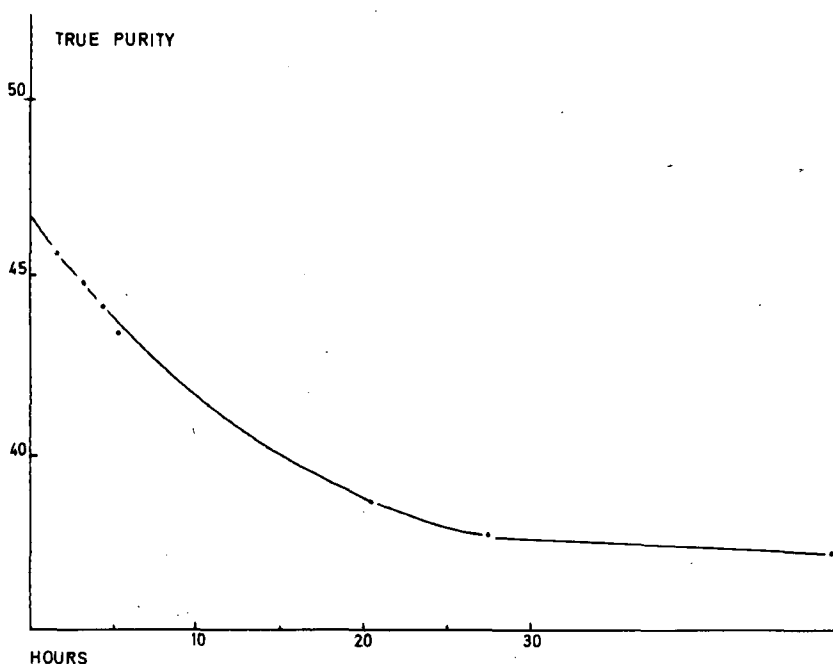


Fig. 1. True purity versus time of a C-massecuite cooled at 40°C

investigation was diluted to 65° Bx and pumped into the electrically heated vacuum pan described above. The diluted molasses was heated slowly at a vacuum of 80 mbar absolute ($T = 45-50^{\circ}\text{C}$). By this means, trapped air was released.

As soon as the boiling point was reached, the temperature of the calandria was adjusted to 90°C by regulating the energy to one of the calandria heating elements.

Concentration of the massecuite was then continued until the torque viscometer showed a reading of approximately 100-200 poises. In order to allow further concentration with the object of reaching the super saturation zone, the boiling-point temperature was increased to 65-70°C. This was achieved by lowering the vacuum to 133 mbar absolute.

Concentration was continued until a viscosity at 60°C of 500-600 poises was obtained, when a sample was withdrawn from the pan and the viscosity checked by a Brookfield viscometer.

At this point about 4.5 kg of baking sugar were introduced into the pan and the molasses was boiled for a further two minutes to thoroughly mix the introduced crystals and the molasses.

Boiling was then stopped and the massecuite obtained was drawn into the thermostatically controlled crystalliser described previously. The massecuite was cooled down to 40°C and allowed to equilibrate for 24 hours at this temperature. This brought the viscosity up to approximately 1 000 poises.

In separate tests, the cooling curves of C-massecuites were investigated. A typical example is given in Fig. 1. Although the figure shows that complete saturation was not obtained in 24 hours, this time was considered to be sufficient for practical purposes and was therefore chosen for these experiments.

Separation of the crystals and molasses was carried out by pressure filtration (7 bar) and the molasses obtained was analysed for dry solids, sucrose, reducing sugar and ash.

Dry solids were determined according to the Laboratory Manual for South African Sugar Factories 1962 (page 67).

Reducing sugars were determined by diluting 4 g of molasses to 250 ml. After heating to 40°C 1 g of anhydrous potassium oxalate was added and the solution was filtered after the addition of 4 g of kieselguhr. This filtrate was titrated according to Lane and Eynon.

Sucrose was determined by titrating the above filtrate according to Lane and Eynon after inversion by hydrochloric acid at 65°C for 30 minutes followed by neutralizing. The sucrose was subsequently calculated by subtracting the amount of reducing sugars from the amount of total sugars found after inversion and multiplying this difference by 0,95.

Sulphated ash was determined by taking 10 g of molasses, evaporating to dryness and following the procedure described in the above mentioned Manual, (page 56).

Results

According to the method described above, 29 different samples of molasses were equilibrated with sucrose at 40°C and approximately 1 000 poises.

The analytical data of these molasses are listed in Table I.

TABLE I

Sample No.	True Purity	% NON SUGARS	
		Reducing Sugars	Sulph. ash
1	39,64	29,68	36,22
2	42,44	29,00	32,08
3	41,27	33,54	34,04
4	44,62	28,92	37,25
5	41,33	30,69	32,45
6	39,31	30,09	28,21
7	42,84	29,02	35,58
8	44,52	22,07	37,24
9	41,80	27,66	34,03
10	40,73	29,17	33,62
11	40,31	28,95	33,39
12	40,61	29,94	33,55
13	33,45	40,92	28,53
14	37,13	39,35	31,73
15	36,93	38,46	32,12
16	39,52	37,16	32,05
17	39,71	36,45	31,73
18	39,42	35,96	30,38
19	40,40	33,47	32,40
20	41,46	34,25	31,34
21	39,53	35,81	29,47
22	38,02	34,43	27,87
23	39,02	33,62	29,45
24	38,37	33,51	29,87
25	39,11	33,37	31,66
26	36,83	37,44	29,66
28	35,49	34,65	29,55
29	38,31	34,38	36,13

The results were regressed on an ICL 1901A computer using a multi-linear regression program MULT*

The following relationships were considered:

- $p = k_1 + k_2 r/a$
- $p = k_3 + k_4 \log k_6 r/a$
- $p = k_5 + 100 k_6 r/ns$
- $p = k_7 + 100 k_8 a/ns$
- $p = k_9 + 100k_{10} r/ns + k_{11} a/ns$
- $p = k_{12} + 100 k_{13} r/ns^1$
- $p = k_{14} + 100 k_{15} a/ns^1$
- $p = k_{16} + 100 k_{17} r/ns^1 + 100 k_{18} a/ns^1$

p = true purity

k = constant

a = ash

r = reducing sugars

ns = non sucrose = dry solids - sucrose

ns¹ = non sugars = dry solids - sucrose - red sugars

*Program supplied by Hulsmith (Pty) Ltd.

The choice of functional forms was limited to those in general use at present while the coefficients were restricted to first-order for ease of application.

The coefficients and statistics obtained for the above regressions are shown in Table II.

TABLE II

Relationship	Correlation coefficient	Standard dev. of residuals	F Statistic	Significance level
1. $p = 51,02-10,89 r/a$	0,842	1,356	65,67	0,005
2. $p = 39,93-24,32 \log r/a$	0,828	1,408	58,89	0,005
3. $p = 55,25-47 r/ns$	0,802	1,498	48,84	0,005
4. $p = 19,4 + 63 a/ns$	0,680	1,841	23,24	0,005
5. $p = 42,85 - 36 r/ns + 27 a/ns$	0,836	1,406	30,07	0,005
6. $p = 49,84-21 r/ns^1$	0,765	1,620	39,58	0,005
7. $p = 24,20 + 53 a/ ns^1$	0,192	0,141	1,07	0,250
8. $p = 42,34-22 r/ ns^1 + 17 a/ ns^1$	0,797	1,550	23,43	0,005

A consideration of the statistics obtained indicates that relationships 1,2 and 5 show the best correlation, the latter formula having the form of the well-known Douwes-Dekker formula. From the theoretical considerations discussed in the introduction, however, relationships 1 and 2 are to be preferred.

The formula therefore proposed for the judging of the degree of exhaustion of South African cane molasses is (c.f. Fig. 2):
 $p = 51,02 - 10,89 r/a$

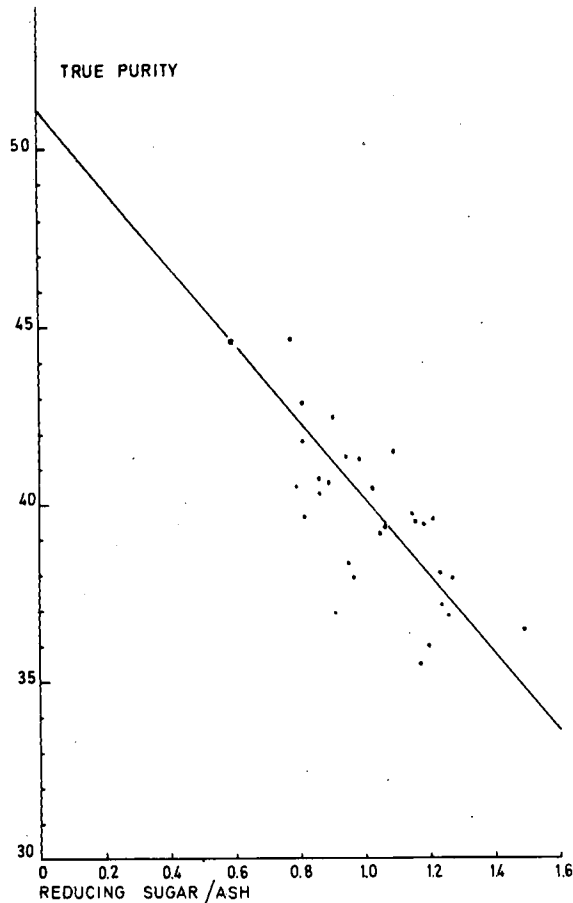


Fig. 2. Regression line of true purity versus reducing sugar/ash ratio of final molasses for 29 observations.

Influence of Specific Ash Components and Nitrogen:

For beet molasses, in which the amount of reducing sugars is small and the inorganic components represent the major part of non-sucrose components, good correlations have been found between purity and sodium and potassium. It has also been established that postassium is more melassigenic than sodium¹⁴.

The molasses samples used in this investigation were therefore analysed for Ca, Mg, K and Na by atomic absorption. Nitrogen was determined by Kjeldahl analysis.

The various relationships which were tried are shown in Tables III and IV.

The results do not indicate any strong correlation with respect to ash components % dry solids. While reducing sugars/ash-components

statistics are slightly better they do not match those obtained for reducing sugars/ash for the same data.

Application to Factory Data

In Figs. 3 and 4, the difference between the actual purities and the Douwes-Dekker and the Sugar Milling Research Institute target purities are shown for 4 factories. EM and DL are equipped with continuous centrifuges, which are able to handle massecurites of higher viscosities than batch machines. It can be expected therefore that these two factories will show smaller deviations from the target purities than AK and FX which are equipped with batch centrifuges. This fact is better illustrated by the Sugar Milling Research Institute's formula than by the Douwes-Dekker formula. Empangeni molasses show in general a low reducing sugars/ash ratio, while Felixton molasses have normally a high ratio.

It is evident from the figures that larger deviations between actual and target purity occur if the reducing sugar/ash ratio is high. The Douwes-Dekker target purity in this range often is higher than the actual factory purity. The same was concluded by Foster in Australia⁵. However, a larger deviation occurs in the other direction if the new Sugar Milling Research Institute formula is applied. The same difference, but to a lesser extent, occurs if the Australian relationship $p = 40,67 - 17,8 \log r/a$ is applied to South African factory results. The effect of varying reducing sugar/ash ratio on the purity for the various formulae is shown in Figure 5.

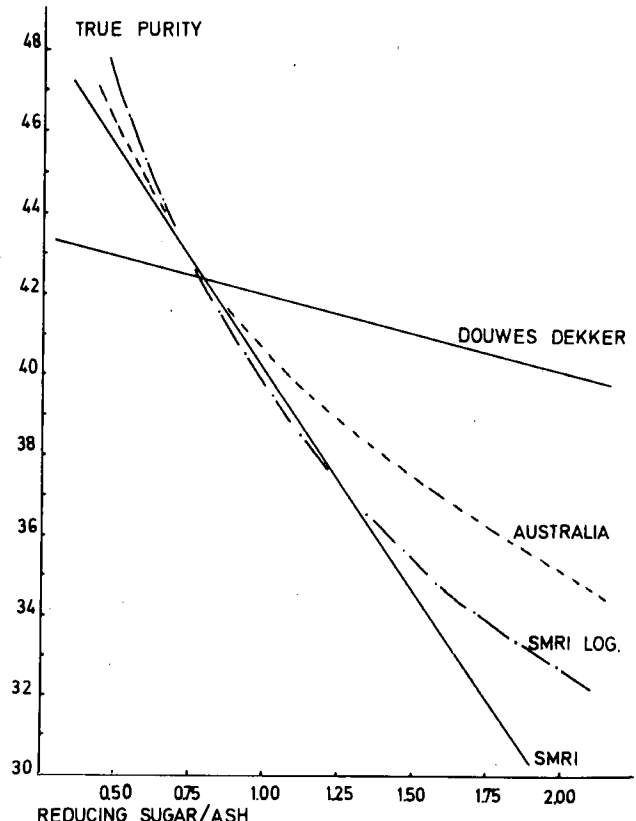


Fig. 5. Various regression lines of true purity versus reducing sugar/ash ratio

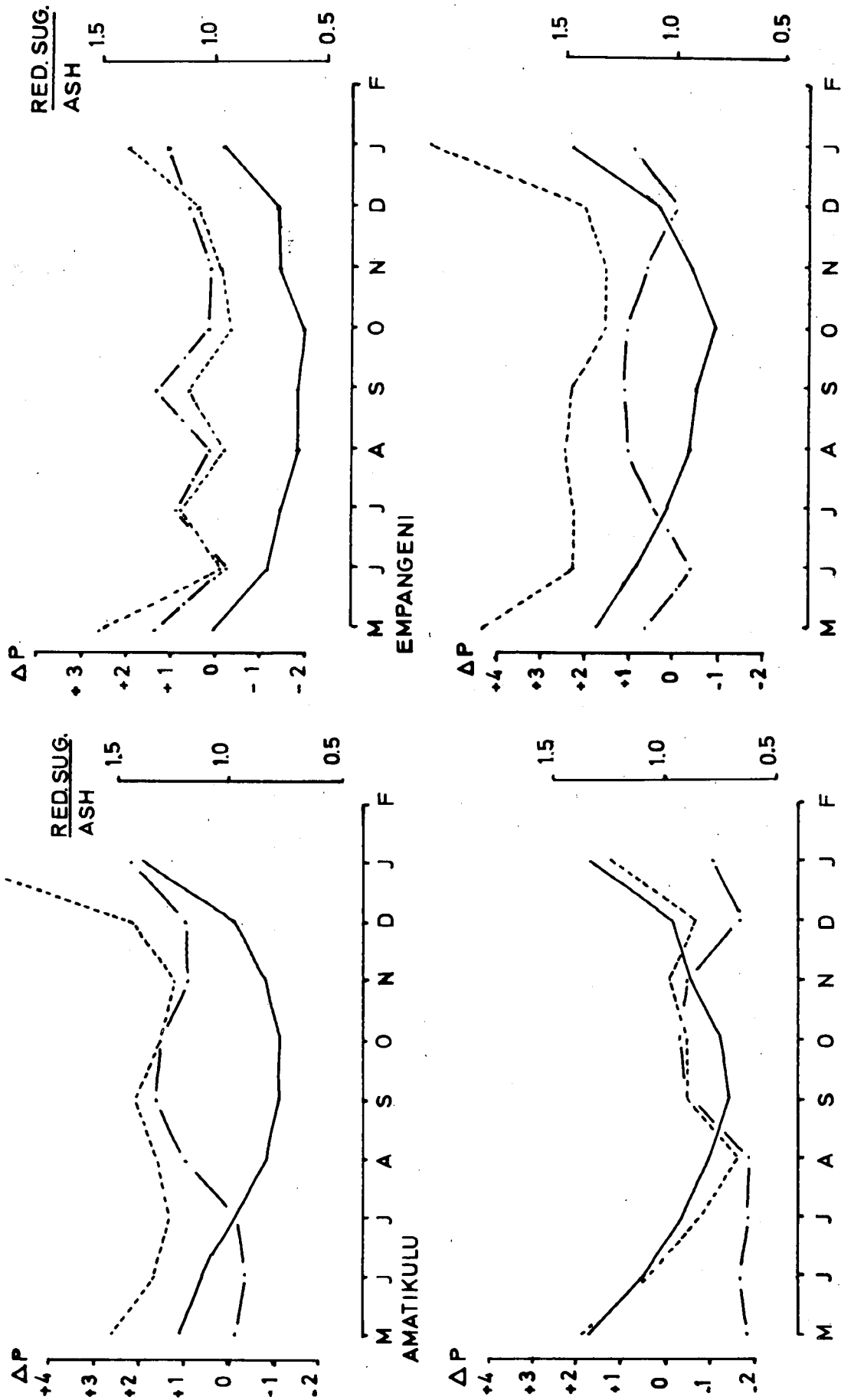


Fig. 3. Actual purities and target purities for DL and AK during 1971/1972 season

· · · True purity - Douwes Dekker target purity
 - · - · True purity - SMRI target purity
 — Reducing sugars/ash ratio

Fig. 4. Actual purities and target purities for EM and FX during 1971/1972 season.

· · · True purity - Douwes Dekker target purity
 - · - · True purity - SMRI target purity
 — Reducing sugars/ash ratio

TABLE III

Ash Components % Dry Solids (DS) True Purity = Const + $k_1x_1 + k_2x_2$ etc. No. of observations 28

CONST.	Ca % DS	Mg % DS	Na % DS	K % DS	N ₂ % DS	Metal Ions % DS (Ca+Mg) % DS	Alk Ions % DS (Na+K) % DS	Multiple Correlation r	Std Dev of Residuals	F-Statistic
1	33,19	6,15	—	—	—	—	—	0,513	1,948	9,32
2	38,47	—	1,89	—	—	—	—	0,202	2,224	1,11
3	39,28	—	—	22,12	—	—	—	0,114	2,256	0,34
4	36,43	—	—	—	0,73	—	—	0,361	2,117	3,90
5	40,57	—	—	—	—	-0,57	—	0,087	2,262	0,20
6	33,05	5,97	0,49	—	—	—	—	0,516	1,983	4,54
7	34,99	—	—	—	—	2,71	—	0,418	2,002	5,51
8	36,41	—	—	2,31	0,72	—	—	0,361	2,159	1,88
9	36,42	—	—	—	—	—	0,73	0,361	2,117	3,91
10	32,21	5,35	-0,07	-6,28	0,44	—	—	0,551	2,015	2,50
11	34,10	—	—	—	—	2,08	0,43	0,461	2,055	3,37
12	32,05	5,35	-0,02	-5,02	0,44	0,09	—	0,551	2,060	1,92
13	32,79	—	—	—	—	0,63	2,35	0,469	2,087	2,25
14	33,52	—	—	—	—	0,70	3,00	0,429	2,091	2,82
15	36,78	—	—	—	—	-0,23	—	0,363	2,157	1,90

TABLE IV

Reducing sugars (r) /ash components True purity = Const + $k_1x_1 + k_2x_2$ etc. No. of observations 28

Const	r/Ca	r/Mg	r/Na	r/K	r/N ₂	r/Metal ions	r/Alk ions	Multiple Correlation r	Std. Dev. of residuals	F-statistic
1	45,15	-0,28	—	—	—	—	—	0,703	1,614	25,43
2	42,94	—	-0,10	—	—	—	—	0,496	1,972	8,47
3	40,20	—	—	-0,3E-3*	—	—	—	0,232	2,208	1,48
4	42,56	—	—	—	-0,60	—	—	0,474	1,999	7,54
5	42,52	—	—	—	—	-0,18	—	0,317	2,153	2,90
6	45,16	-0,27	-0,004	—	—	—	—	0,703	1,645	12,23
7	44,73	—	—	—	—	-0,42	—	0,660	1,705	20,08
8	42,79	—	—	-0,3E-3	-0,57	—	—	0,509	1,993	4,38
9	42,60	—	—	—	—	—	-0,61	0,477	1,995	7,67
10	45,44	-0,25	-0,004	-0,6E-4	-0,21	—	—	0,718	1,680	6,13
11	45,05	—	—	—	—	-0,36	-0,22	0,676	1,707	10,51
12	46,47	-0,20	-0,01	-0,1E-3	-0,19	-0,09	—	0,723	1,689	5,00
13	46,47	—	—	—	—	-0,11	-0,35	0,703	1,679	7,84
14	46,32	—	—	—	—	-0,12	-0,40	0,693	1,668	11,58
15	44,35	—	—	—	—	-0,13	—	0,529	1,964	4,87

NOTE: For comparison purposes, the following relationships using r/a was obtained for the same samples.

$tp = 49,69 - 9,62 r/a$

$r = 0,777$; $tp = 39,79 - 21,25 \log r/a$
 std dev = 1,428;
 F-stat = 39,69:

$r = 0,779$
 std dev = 1,422
 F-stat = 40,22

*E = exponential, -0.3E-3 = -0,0003

TABLE V

Exhaustion of FX Molasses

	solids	sucrose	r.s./ash	Actual purity	Target purity	difference
original sample	88,15	34,54	1,37	39,18	36,11	3,07
analysis after saturation	87,24	31,64	1,40	36,27	35,78	0,49

It is the intention to further investigate the reason for these excessive deviations between actual and target purity for high reducing sugar/ash. A controlled experiment was carried out on a FX molasses sample with high reducing sugar/ash ratio. The molasses was equilibrated under the standard laboratory conditions described previously and the results are shown in Table V.

From these data it is evident that in laboratory experiments little deviation from the target value was found. The value of 0,49 is within the experimental error.

Conclusion

The developed exhaustion relationship allows a better judgement on the actual molasses exhaustion than the Douwes-Dekker formula at present in general use in South Africa.

Although at present a straight line relationship is proposed, the possibility of a logarithmic one will be further investigated. Figure 5 shows that for a r/a below 1,35 there is little difference between the two formulae. Above this value they deviate and more investigations are required in this range. The formula also has to be checked for its validity in different periods of the crushing season. No special influence of individual ash components on the exhaustability of final molasses have been found but further investigations on individual organic components and their influence on molasses viscosity will have to be carried out.

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