THE EFFECT OF SOME IMPURITIES ON MOLASSES EXHAUSTION

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Abstract

Molasses exhaustion has been investigated in South Africa since 1949, and Bruijn *et al.* (1972) applied a laboratory exhaustion procedure which has since been used extensively (Rein and Smith, 1981). The same approach and equipment have been used to investigate the effect of selected impurities on molasses exhaustion. These impurities include fructose, glucose, inorganic ash constituents, such as potassium, sodium and calcium, and organic impurities, for example starch and dextran. All the impurities, except the monosaccharides, are shown to increase the equilibrium purity of molasses and thus to reduce the exhaustion. It has also been possible to rank the order of the melassigenic effects of the ash constituents studied. This is of practical importance when alternate technologies are considered, for example juice softening.

Introduction

The South African sugar industry uses as its criterion of exhaustion a 'target purity' which is expressed as a function of the reducing sugars (glucose and fructose) and sulphated ash ratio. It is well known that the solubility of sucrose is decreased in the presence of reducing sugars and that most inorganic salts tend to increase its solubility.

The analysis of the individual constituents of ash and their effect on exhaustion, especially for South African cane molasses, is not clear as few studies in this area have been done. A literature survey conducted on molasses exhaustion (Day-Lewis, 1993) has shown that in the beet industry (Quentin, 1954, 1957), sucrose solubility in molasses increases with the presence of cations and the relative solubility of sucrose is as follows:

$$\begin{array}{ccccccc} K^{+} & > & Na^{+} & > & Ca^{2+} & > & Mg^{2+} \\ 1,0 & & 0,94 & & 0,66 & & 0,61. \end{array}$$

This indicates that potassium is the most melassigenic cation present in beet molasses. These data were obtained for beet molasses which undergoes a totally different process to that in the South African sugar industry.

The literature survey also shows that when the molasses exhaustion formula was derived for the cane sugar industry (Bruijn *et al.*, 1972), several ash components were investigated (sodium, potassium, calcium and magnesium). The results obtained were inconclusive as far as the relative melassigenic powers of these ions is concerned.

With alternate technologies being considered, for example one step white sugar production, the individual ash constituents from throughout the process will be altered and hence the consequent effect on exhaustion will be of importance. The effects of the four main inorganic cations, viz. calcium, potassium, magnesium and sodium on exhaustion have therefore been studied and the results are reported. In addition, the effects of glucose, fructose, dextran and starch were also studied.

Finally, the growing and processing of sugar beet with cane has been considered in South Africa and hence the effect of cane and beet molasses blends on exhaustion has been investigated.

Experimental procedure

The tests were done on the target purity difference (TPD) apparatus, the design and operation of which have been thoroughly discussed previously (Bruijn, 1977, Bruijn *et al.*, 1980; Rein and Smith, 1981). The exhaustion test essentially consisted of concentrating molasses under vacuum (-95 kPag) to approximately 87% (m/m) dry solids in order to reduce the viscosity effects (Bruijn, 1977) and then adding castor sugar and crystallising for a time period at 40°C. After crystallising, the sample is separated in a nutsch filter and the extracted molasses is analysed for true purity (sucrose/dry solids). This purity is known as the equilibrium purity.

The target purity is calculated by using the formula derived by Smith (1995), viz:

$$\text{Target purity} = 43{,}1 - 17{,}5\left(1 - e^{-0{,}74\left(\frac{F+G}{A}\right)}\right) \qquad (1)$$

where F is the fructose, G is the glucose and A the sulphated ash (% m/m) of the molasses.

To eliminate any difference in the molasses composition from different areas in South Africa, all the tests were done on subsamples from one large batch of representative molasses. The results were then confirmed by repeating some of the tests on a different batch of molasses. The following tests and procedures were involved.

Application of the target purity formula

Molasses samples from various mills as well as composite samples were subjected to the exhaustion test in order to apply the target purity formula to a wide range of samples. The target purity formula (Equation 1) was used to calculate a purity of final molasses based on the fructose, glucose and ash levels in the molasses. This implies that if the final molasses can be fully exhausted (according to the experimental procedures described above) then it should reach the target purity. The experimentally measured equilibrium purity will then be equal to the calculated target purity.

Crystallisation time

Molasses samples were boiled to similar dry solid levels and left to crystallise for two, three, four and five days in order to establish the optimum exhaustion time. There were four replicates for each time period.

Ash effects

A survey of the composition of ash in molasses from different factories was made. For comparison, samples of Colombian molasses and overseas beet molasses were also included. The results were used to select four ash constituents for the investigation, viz. calcium, potassium, magnesium and sodium. The concentrations of the four species are shown in Figure 1, where the most striking observation is the low concentration of potassium in the Colombian sample. This could be due to different processing conditions used in Colombia. Possible reasons for this were not investigated.

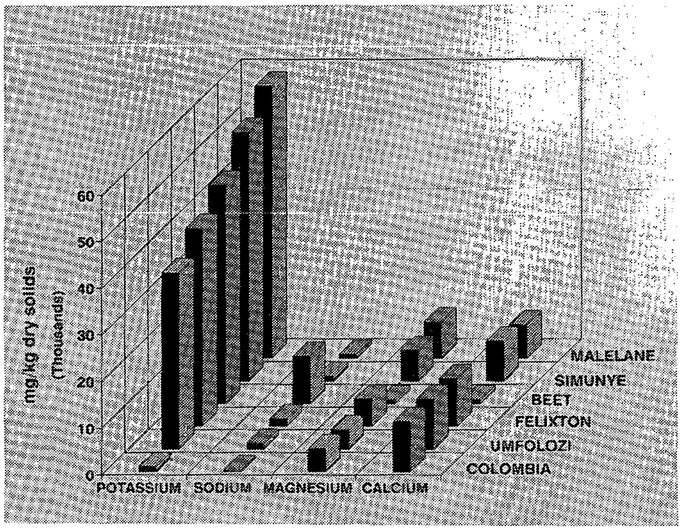

Figure 1. Ash composition of molasses.

In order to test the effects of individual ash constituents on exhaustion, subsamples of molasses were individually spiked with different levels of each constituent added as chlorides, and exhausted in the usual manner. The addition of ash to the molasses changes the purity of the molasses and hence an appropriate amount of sucrose was added with the ash, to maintain the purity at the same level.

Reducing sugar effects

Glucose and fructose were added to molasses subsamples at different levels but in the same ratio as the background level and the subsamples were exhausted. Again sucrose was added to keep the purity at the same level. Fructose and glucose were also spiked separately and the molasses samples were exhausted.

Dextran/starch effects

Subsamples of molasses were spiked with various levels of dextran (industrial grade; molecular weight 5 to 40 million) and exhausted as above. Because of the small quantities added to the molasses, there was no significant change in the purity and hence no sucrose needed to be added. Potato starch was tested in a similar manner. Potato starch was used for the tests because this starch is used to obtain the calibration curve against which all starch analyses are compared to.

Cane/beet blends

Beet molasses samples from four countries were obtained and added at four levels to cane molasses on a mass/mass basis and exhausted in the usual way.

Results and discussion

Application of the target purity formula

The results in Table 1 show that, in most cases, the experimental equilibrium purity as obtained by the exhaustion procedure and that predicted by the target purity formula (Equation 1) are in good agreement. This confirms the viability of the method.

Table 1. Application of target purity formula.

Sample	$\frac{F+G}{A}$	Original molasses purity	Target purity (from Eq. 1)	Experimental equilibrium purity	Difference (target – equilibrium)
Composite	0,66	38,9	36,5	36,3	-0,2
Composite	0,65	38,9	36,4	36,6	0,2
Composite	0,96	40,2	34,2	34,3	-0,1
Pongola	0,87	39,4	34,9	34,9	0,0
Umfolozi	0,34	37,2	39,3	39,2	-0,1
Umfolozi	0,34	37,6	39,2	38,4	-0,8
Felixton	1,10	37,1	33,4	33,5	-0,1
Sezela	1,08	36,9	33,4	33,6	-0,2
Union Co-op	0,79	38,0	35,5	35,2	-0,3
Union Co-op	0,69	36,9	35,5	34,6	-0,9
Union Co-op	0,80	37,3	35,2	35,1	-0,1
Swaziland	1,14	38,2	33,1	33,7	0,6
Swaziland	1,12	37,8	33,2	33,7	0,5
Swaziland	1,16	38,6	33,0	33,8	0,8
Zimbabwe	0,72	38,4	35,8	34,5	-1,3
Reunion	0,31	43,9	39,5	40,3	-0,8

Crystallisation time

The results have been averaged and are shown in Figure 2. They indicate that three days (72 hours) is the optimum time for complete exhaustion to occur.

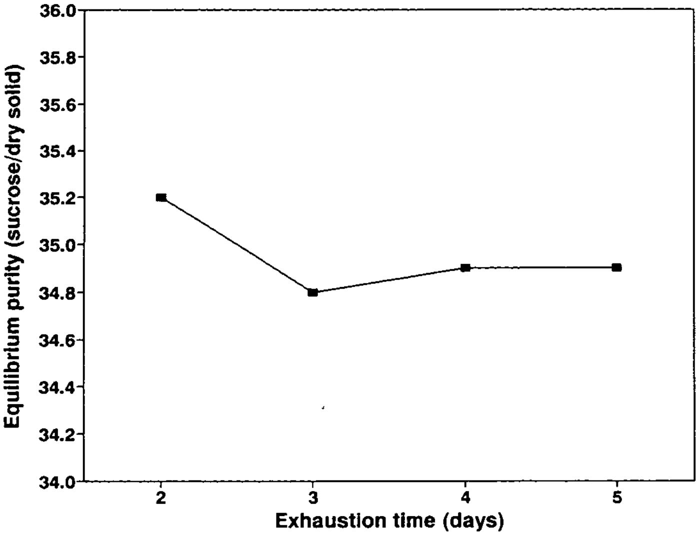

Figure 2. Effect of crystallisation time on equilibrium purity.

Ash

The main objective of this work is to compare the melassigenic effects of potassium, calcium, magnesium and sodium. Obviously, these cations cannot be added on their own and in this work, the chlorides have been used. The effect from the Cl^- ion itself needs to be considered. As the concentrations (mg/kg dry solids) of both the cations and the chloride in the spiked samples are known, it is possible to plot equilibrium purities versus the concentration of chloride in the molasses, as done in Figure 3. The plot shows three distinct sets of results, for sodium, potassium and calcium plus magnesium as the cation associated with chloride. It thus appears that it is not the chloride ion which has the overriding effect. It is therefore the cation attached to chloride which determines the melassigenic effect.

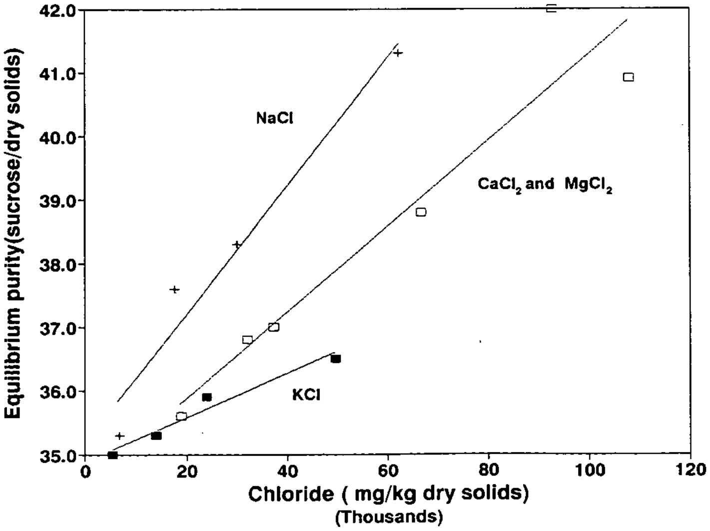

Figure 3. Equilibrium purities measured with various chloride concentrations, from added NaCl, KCl, $CaCl_2$ and $MgCl_2$.

Regression equations have been used to estimate the effect of the cations by regressing equilibrium purity versus the concentration of the chloride (mg/kg dry solids) associated with that cation. The results are shown by Equations 2, 3 and 4, for chloride in sodium chloride, calcium and magnesium chlorides, and potassium chloride, respectively.

Equilibrium purity (Na)

$$= 35{,}2 + 10{,}1 \times 10^{-5}\,\mathrm{Cl}^- \qquad (n = 4;\ r^2 = 0{,}96) \qquad (2)$$

Equilibrium purity (Ca+Mg)

$$= 34{,}5 + 6{,}75 \times 10^{-5}\,\mathrm{Cl}^- \qquad (n = 6;\ r^2 = 0{,}92) \qquad (3)$$

Equilibrium purity (K)

$$= 34{,}9 + 3{,}41 \times 10^{-5}\,\mathrm{Cl}^- \qquad (n = 4;\ r^2 = 0{,}96) \qquad (4)$$

Assuming that the chlorides have a negligible effect on exhaustion, it is possible to express the effect of the cations on exhaustion. The results are illustrated in Figure 4, and show potassium (as potassium chloride) to have a lower melassigenic effect than sodium and calcium (as chlorides).

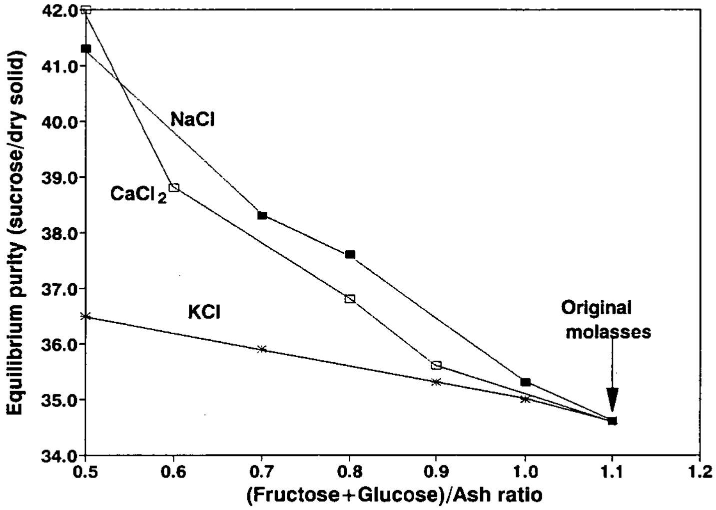

Figure 4. Equilibrium purities measured on molasses spiked with NaCl, KCl and $CaCl_2$ plotted against the (fructose+glucose)/ash ratios of the molasses.

Reducing sugars

The addition of reducing sugars (fructose and glucose) results in the expected lower equilibrium purity (Figure 5). With the limited data available at the high fructose plus glucose addition levels, the effect seems to be asymptotic which needs to be confirmed. The effect of the individual components of the reducing sugars is shown in Figure 6, and no significant differences between fructose or glucose with respect to 'exhaustion' is apparent. However, the decreasing trend in the equilibrium purity from the original molasses when either reducing sugar is added is again evident.

Dextran

The addition of dextran to the molasses samples showed two clear effects. Firstly, at the same dry solids the viscosity of the molasses increased and secondly the dry solid levels in the boiled-down molasses were decreased. The viscosity effect is illustrated in Figure 7, where it is clearly evident that, at the same dry solid concentration and temperature, viscosity increases linearly as the concentration of dextran is increased from 6 200 mg/kg solids (background level) to 16 000 mg/kg dry solids.

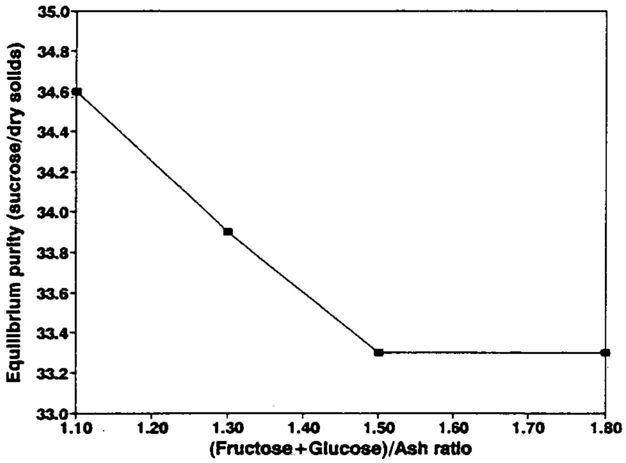

Figure 5. Equilibrium purities measured on molasses spiked with a mixture of fructose and glucose.

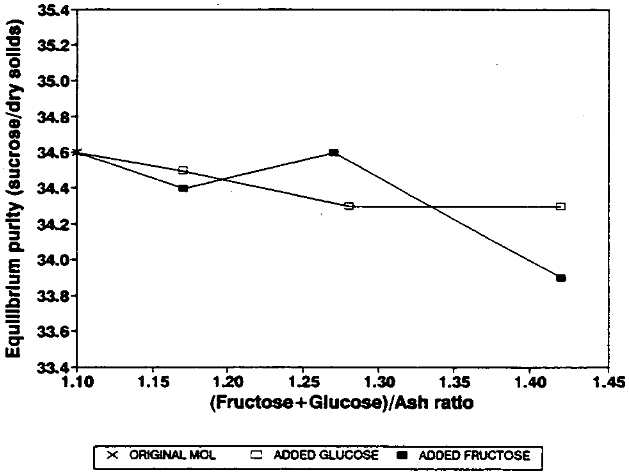

Figure 6. Equilibrium purities measured on molasses spiked with fructose or glucose, separately.

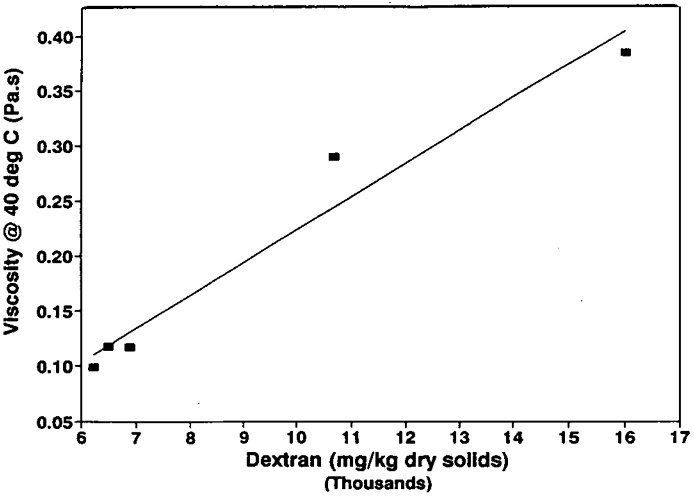

Figure 7. Effect of dextran on molasses viscosity at the same dry solids level.

The second effect is shown by the data in Table 2. There is no doubt that the equilibrium purity increased as the concentration of dextran rose as illustrated in Figure 8. The latter is, however, associated with lower dry solids in the boiled down molasses, which is known to result in higher equilibrium purities. It is therefore impossible to establish that viscosity alone is responsible for the poorer exhaustion.

Table 2. The impact of dextran on boiled down molasses.

Dextran mg/kg dry solids	$\frac{F+G}{A}$	Dry solids %	Equilibrium purity
8 229	0,8	87,4	34,6
9 767	0,8	88,6	34,8
11 646	0,8	88,1	35,1
13 020	0,8	88,5	35,3
14 032	0,8	86,7	35,4
20 097	0,8	85,1	37,0

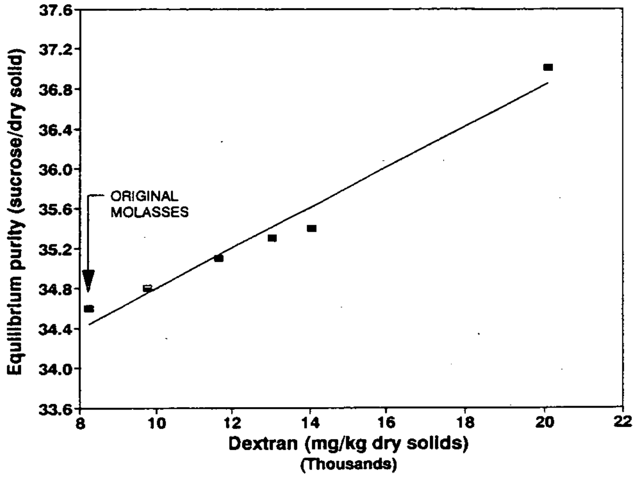

Figure 8. Equilibrium purity on molasses spiked with dextran.

Starch

The addition of potato starch to molasses samples shows a very small increase in the equilibrium purity, which could probably be due to a viscosity effect. This needs to be investigated further. These results are shown in Figure 9.

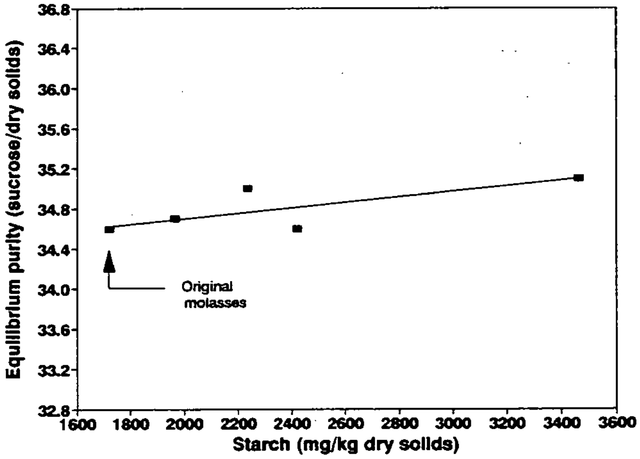

Figure 9. Equilibrium purity on molasses spiked with starch.

Cane/beet molasses blends

Exhaustion tests on cane molasses spiked with beet molasses show high equilibrium purities and hence lower exhaustions. These findings were confirmed with beet molasses from four different beet processing countries. The averaged results are shown in Figure 10.

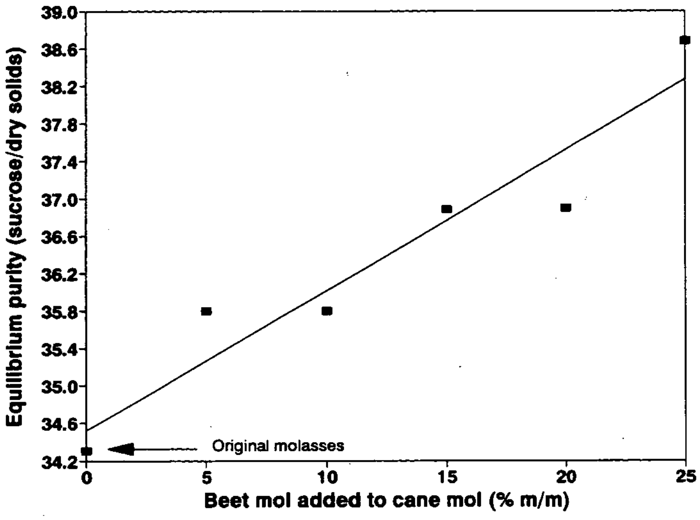

Figure 10. Equilibrium purity on molasses spiked with cane/beet molasses blends.

Beet molasses exhausted in these tests may be different to beet molasses obtained from beet/cane processing and hence may have a different composition. The ash composition of beet molasses shown in Figure 1 has similar potassium levels but much higher sodium levels and lower magnesium and calcium levels when compared to cane molasses. This difference in ash composition may be due to the different process, e.g. carbonatation being used in the beet industry. All the tests were carried out using three days as exhaustion time. Cane/beet blends may probably require longer exhaustion times that still need to be verified.

Conclusions

Exhaustion tests on final molasses from South Africa, Swaziland, Zimbabwe and Reunion Island have shown that the target purity formula applies well in all cases. Considering that the experimental error in such a test is expected to be fairly high, the purity differences obtained (see Table 1) are considered to be acceptable; this confirms the applicability of the target purity formula.

The results obtained in this investigation show that the relative melassigenic effect of the cations studied is:

$$\mathrm{Na^+ > Ca^{2+},\ Mg^{2+} > K^+}.$$

The first observation that can be made is that this is contrary to the findings in the beet industry. This is surprising and will need confirmation. Another aspect requiring more work is that related to the effect of the anion. In view of these two points, the above results must be viewed as preliminary.

Reducing sugars (fructose and glucose) have a favourable impact on exhaustion, however, there is no significant difference in equilibrium purity between fructose and glucose.

Dextran was shown to have a large influence on viscosity and on evaporation, hence having an adverse effect on exhaustion. Starch appears to have no measurable effect on exhaustion.

The addition of beet molasses to cane molasses results in lower exhaustions. Longer exhaustion times than those used in these tests (3 days) need to be used to confirm this.

Acknowledgements

The guidance of Mr GRE Lionnet and the numerous analyses carried out by the Analytical Services and Chemical Divisions of the SMRI are gratefully acknowledged.

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