COOLING CRYSTALLIZATION OF RAW JUICE: SUCROSE SOLUBILITY TESTS.

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In order to try to answer a number of problems the sugar industry is having to address in recent years, an in-depth investigation was conducted to evaluate the possibility of directly crystallizing sucrose from raw juice (1, 2, 3). Naturally, such an approach would make it possible to completely eliminate any raw juice purification step.

The advantages coming from such a simplified processing scheme (Fig. 1) would affect environmental, economic, technological and process equipment areas of sugar production.

Concernig the environmental area, we should point out that, other than beet fluming and wash water, polluting wastes of solid, liquid or gaseous types come almost exclusively from juice purification plants on the whole. The total elimination of the usual purification steps would thus practically eliminate this problem, and in particular the increasing difficulties associated to sludge disposal. Moreover, the possibility of not extracting lime would certainly help to minimize problems related to the environment.

From the economic point of view the proposed technology undoubtedly involves either an energy saving because of the complete elimination of the full juice purification station and thus coke utilization for the kiln, or a saving in operating costs due to the simplicity of the process itself.

From the technology point of view, the problems related to the poor quality of beet grown under unfavourable climatic conditions are noticeably reduced. In fact, the problem of elimination of non-sugars in the purification step, which is particularly important for beet of poor quality, is completely overcome and has to be reconsidered.

From the process equipment angle, the beet processing scheme is completely simplified, as outlined above. Thus, the

proposed technology could offer the valid option of increasing the capacity of a sugar factory without building a new kiln or enlarging the traditional juice purification plant. Is this the first development step which can be expected from this type of technology which, only in the long run, could replace obsolete traditional plants. It should be obvious that this new technology would eventually be adopted in considering a total economic balance which, as well as determining white sugar yields, would take overall account of all the aspects mentioned above.

What is more, we have to bear in mind that all the non-sugars present in the beets, including the nitrogenous, phosphate and oxyacid components which are normally eliminated in purification, remain as such in the molasses. This as a result, improves its characteristics both as a raw material for biotechnological industries and as an animal feed.

Lastly, should the slightly acid conditions, at which both concentration and crystallization take place, promote a small amount of sucrose inversion, we have to take into account that the invert sugar is not completely destroyed as is the case during traditional juice purification. Thus it is almost totally found in the molasses. First and second product raw sugar, (see Fig. 1), would be affinated, dissolved, filtered and recrystallized in order to obtain commercial white sugar, as shown in Fig. 2.

The feasibility of the proposed project, as described in the literature cited above, is based on a complete modification of the traditional concentration and crystallization conditions: concentration is to be carried out at as low temperature as possible, whilst crystallization is run according to the cooling technique. Experiments on a semi-industrial pilot plant (Fig. 3) operated in close cooperation with the sugar industry, have to-date given encouraging results. Because there are no juice purification stages, it was predictable that the non-sugars normally eliminated in purification might change the sucrose solubility conditions experienced in the traditional crystallization process. The relatively high crystallization yields together with the low purities of the molasses which we obtained, allow us to forecast lower sucrose solubility values than those which are found in the traditional process. Such expectations are moreover supported by the fact that compounds which exert a well-known salting-out effect, such as invert sugar, magnesium ions and some nitrogen compounds, mentioning just a few, are present at rather high levels in the crystallization magmas coming from raw juice direct crystallization.

MATERIALS AND METHODS

In order to evaluate sucrose solubility conditions in the two steps of first and second crystallization we used a technique based upon the saturoscope principle (4).

We have carried out solubility tests at different temperatures, both on the concentrated raw juice to be crystallized to yield the first product, and on the concentrated run-off syrup to be crystallized to yield the second product (see Fig. 1). The juices were obtained from the pilot plant shown in Fig. 3 during 1991 campaign (3).

We varied the S/W values (S = sucrose, W = water) of such syrups, and the temperatures corresponding to their saturation were recorded.

In order to optimize the crystallization conditions and to evaluate the exhaustability of the molasses in respect of the non-sugars' influence on sucrose solubility under the crystallization conditions described above, we determined the molasses saturation function using the Polish Test criteria (5).

Because in such molasses all the non-sugars, which traditionally are eliminated in the purification stage, are present, we have supposed that Wiklund's rule (6) could not be valid. As is known, the Wiklund's rule points out that the saturation curve is independent of the temperature, and for this reason the Polish Test is carried out at a temperature of 80 °C. On the other hand, the validity of Wicklund's rule for traditional molasses is not conditioned by the fact that the effect of the non-sugars on sucrose solubility is independent of the temperature (7), but by the fact that the positive and negative effects exerted by the various non-sugars balance each other out. Therefore, we have applied the Polish Test at various temperatures and have properly extended the time of contact between crystals and molasses at the lowest temperatures.

Taking into account that, in the proposed technological scheme, crystallization is carried out by cooling, it becomes important to know the saturation functions throughout the whole cooling range. Consequently, we have calculated the solubility curves for the three temperatures of 80 , 60 , and 40 °C.

RESULTS AND DISCUSSION

Fig. 4 shows the results, obtained from the solubility tests carried out on concentrated raw juice and concentrated run-off syrup, in comparison with the solubility curve for pure sucrose solution. The pure sucrose solution data are those reported by Vavrinecz (8, 9) and were calculated by eq. /1/:

$$P = 64.447 + 0.08222 \times t + 0.0016169 \times t^2 - 0.000001558 \times t^3 - 0.0000000463 \times t^4 \quad /1/$$

where P = g sucrose in 100 g solution and t = temperature in °C. From the experimental data obtained the coefficients of eq. /1/ were properly modified in order to arrive at the solubility equations for concentrated raw juice (eq. /2/) and concentrated run-off syrup (eq. /3/), respectively:

$$P = 63.268 + 0.0795 \times t + 0.00167569 \times t^2 - 0.000001058 \times t^3 - 0.0000000463 \times t^4 \quad /2/$$

$$P = 62.750 + 0.081 \times t + 0.00163169 \times t^2 - 0.000001169 \times t^3 - 0.0000000358 \times t^4 \quad /3/$$

Using equations /2/ and /3/ it is possible to calculate solubility tables for raw juice and for run-off syrup as done by Smythe (10) for pure sucrose solution. However, we can only set up all the solubility tables related to the different purities corresponding to the various raw juices and run-off syrups tested. Of course, we must assume as valid the hypothesis that for different raw juices and run-off syrups of different purities, the effect of the non-sugars on sucrose solubility may be comparable. The tables so calculated for the different purities may be used to optimize the required concentration conditions at a given temperature, before adding the seed necessary prior to cooling crystallization. We were able to verify that such tables, prepared by using juices collected during the 1991 campaign,

could be fruitfully utilized in the same factory during the 1992 season. However, we cannot support the hypothesis that such tables have general validity expecially for very different regions.

Concerning the saturation coefficient (C) variation as a function of the non-sugar concentration, in Fig. 5, 6 and 7 the saturation functions determined at the three different temperatures of 80 , 60 and 40 °C, are shown. By using experimental data the a, ,b and c coefficients of the well-known equation /4/ (7) were calculated:

$$C = a \times N/W + b + (1 - b) \times \exp(-c \times N/W) \qquad /4/$$

so obtaining, for the three temperatures, the equations /5/, /6/ and /7/.

t = 40 °C

$$C = 0.0595 \times N/W + 0.8335 + 0.1665 \times \exp(- 1.56 \times N/W) \qquad /5/$$

t = 60 °C

$$C = 0.0280 \times N/W + 0.8410 + 0.1590 \times \exp(- 1.10 \times N/W) \qquad /6/$$

t = 80 °C

$$C = 0.0455 \times N/W + 0.8342 + 0.1658 \times \exp(- 1.30 \times N/W) \qquad /7/$$

It is quite clear that for the different temperatures and the whole variation range of the N/W ratio, the saturation coefficient is lower than 1 which is contrary to results for traditional molasses (Fig. 8). In fact for the latter, only at low N/W values is sucrose solubility lower than that of pure sucrose solutions. The curve of Fig. 8 for traditional molasses was calculated by using Grut's data (11) through eq. 8:

$$C = 0.178 \times N/W + 0.820 + 0.180 \times \exp(- 2.1 \times N/W) \qquad /8/$$

Therefore, we can infer that non-sugars, which are normally eliminated in purification, together with the albeit limited

amount of invert formed during the direct concentration of raw juice, remarkably decrease the sucrose solubility especially at high N/W ratio values. It would be interesting to establish just how the low values of solubility coefficients would go, and in particular at high N/W ratio values, if the non-sugars which traditionally remain after normal juice purification, were to be eliminated. We could propose that, as far as molasses exhaustion is concerned, the traditional purification step eliminates the less melassigenic non-sugars whilst the most melassigenic ones remain in solution. This conclusion can be confirmed by the negative influence exerted by magnesium ion and invert sugar on sucrose solubility (7). Magnesium, which enters the sugar factory through the beet, is almost quantitatively precipitated at the high pH existing during juice purification, whereas invert sugar is converted to acidic compounds, (e.g. lactic acid), all of them well-known as melassigenic substances.

Of course, low values of the solubility coefficients lead to low values of molasses purity. Fig. 9 shows the theoretical purity curves, calculated by using the solubility data from equations /5/ and /8/ relating respectively to our "experimental" molasses at 40°C and to traditional molasses. It can be seen that, particularly at the highest N/W ratio values, the purity differences are quite distinctive.

Returning to the variation of the saturation function with temperature, it can be seen in Fig. 10 that there is a trend-inversion going from N/W < 0.8 to N/W > 0.8. Whereas at 80°C the solubility values are always intermediate between those at 40 and 60 °C, at N/W < 0.8 the lowest solubility can be found at 40°C. On the other hand, at N/W > 0.8 the lowest C values occur at 60°C thus showing remarkably different values at the three temperatures. This finding is important when we are looking for the optimum cooling rate conditions during the first and second crystallization steps (see Fig. 1). In fact, during the first crystallization the N/W values are less than 0.8, whereas they are higher than 0.8 during the second crystallization. In particular, during the first crystallization stage we have to take into account that, during cooling, the saturation coefficient values tend to be higher at 60 °C although showing small variations. In contrast, during the second crystallization, the C values are lowest at 60°C, and the variations as a function of temperature become higher with increasing N/W ratios.

CONCLUSIONS

Our experimental results as a whole allow us:

- to account for the low purities of molasses obtained first of all on the laboratory scale and later with the pilot plant when adopting the raw juice cooling crystallization process.
- to account for the relatively high sucrose yields obtainable by using this new technology, which are comparable to those obtained in the traditional process.
- to have at our disposal "actual" solubility tables, both for the first and second cooling crystallization, which then allow us to optimize both the concentration and crystallization conditions.
- to know the solubility coefficient variation as a function of the temperature decrease and so being able to choose the optimum cooling profile.

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SUMMARY

In order to try to minimize some of the problems met with the sugar industry in the recent years, at least as far as pollution is concerned, the authors propose a new technology which make it possible to eliminate the traditional purification stage in beet sugar processing. In fact, most of the solid, liquid or gaseous wastes originating in sugar factories come from the various purification steps between the extractors and the vacuum pans. The new technology would make possible production of commercial white sugar directly from raw juice, after concentration under low temperature conditions, at high vacuum , and using cooling crystallization.

Since it was reasonable that, in the absence of the purification stage, the non-sugars remaining in the concentrated raw juice could change the sucrose solubility, tests on the latter parameter were carried out at different temperatures. Moreover, molasses saturation functions using the Polish Test criteria, were determined through the whole cooling range.

The salting-out effect exerted by certain non-sugars remaining in concentrated raw juice and run-off syrups accounts for the relatively high sucrose yields obtainable with the new technology as well as the low purities of the corresponding molasses samples. The working-up of actual solubility tests both for the first and second crystallization stages have allowed us to optimize both the concentration and crystallization conditions.

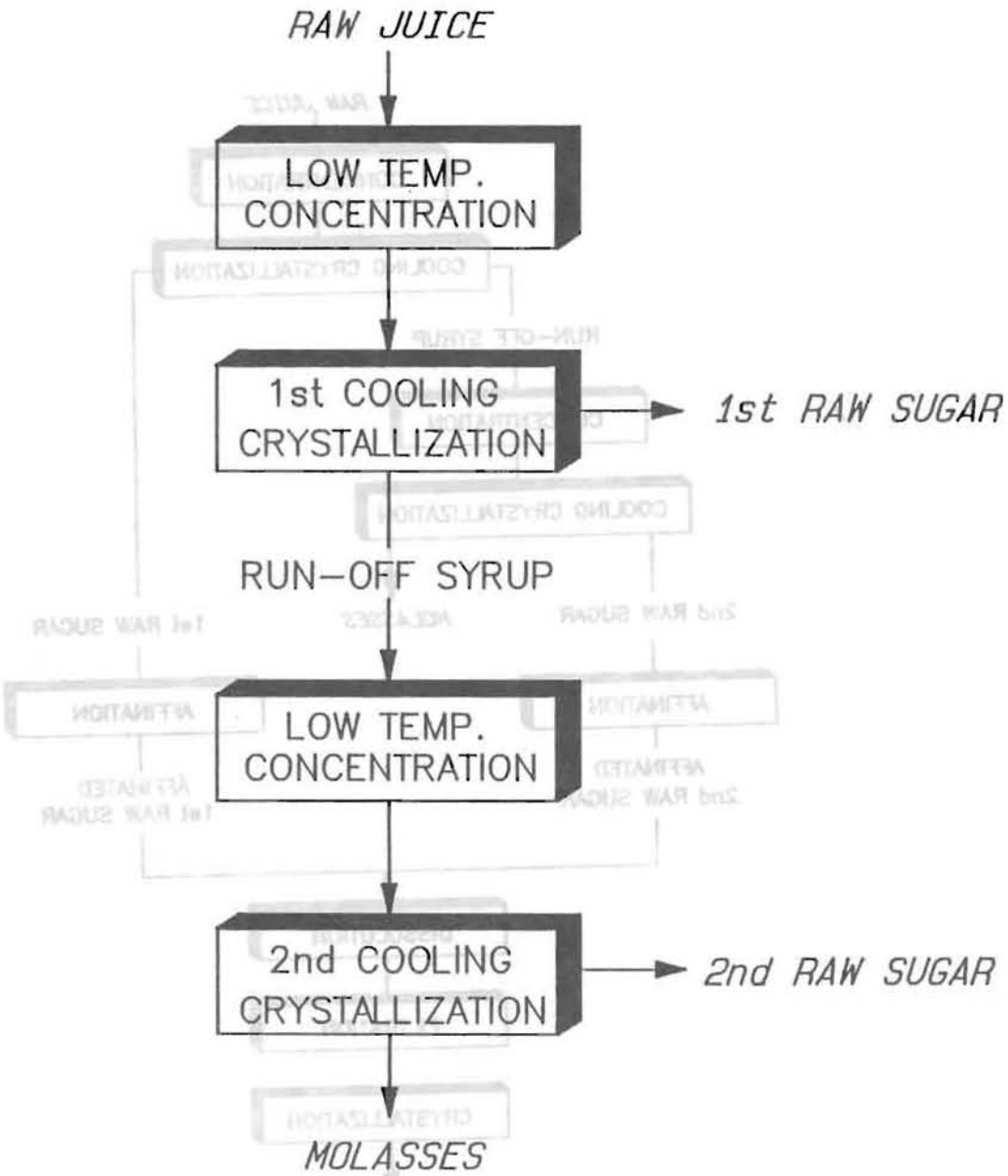


Fig. 1 - Flow diagram of the two-stage raw juice crystallization scheme.

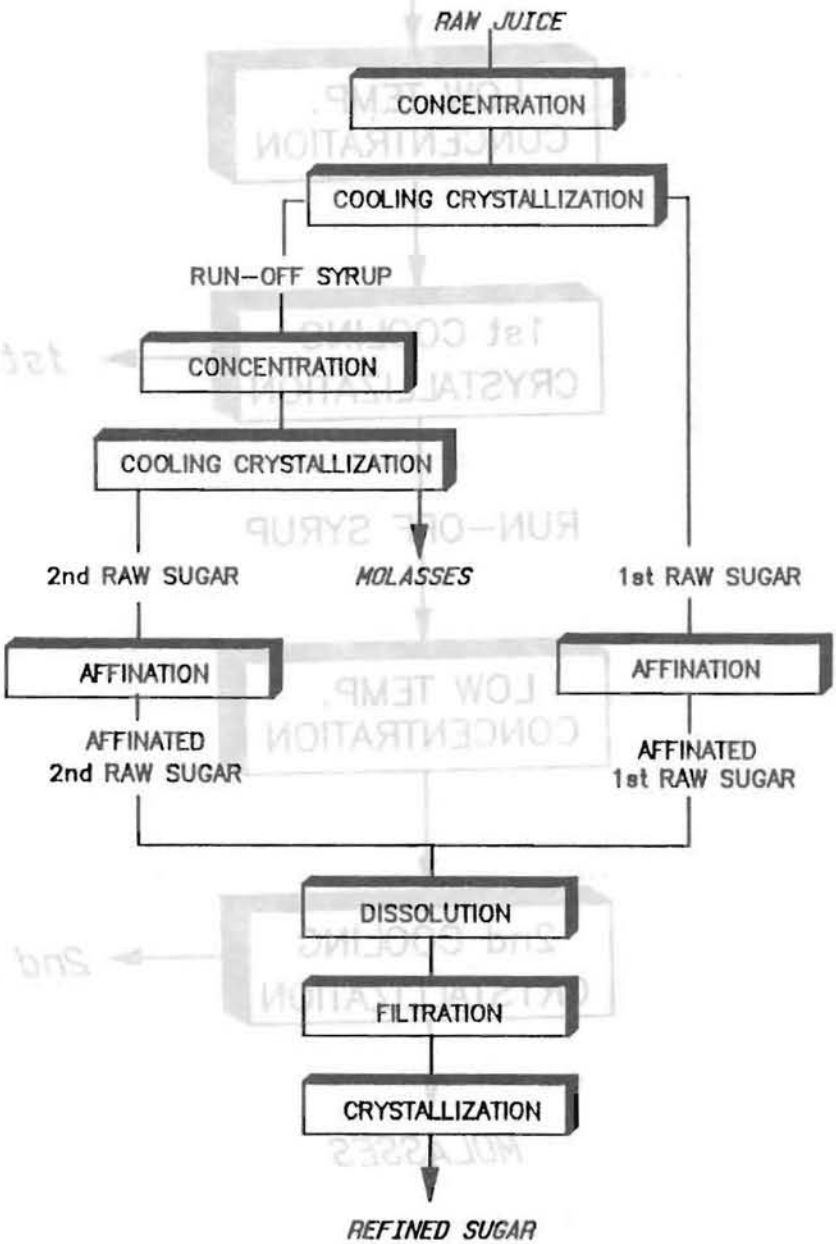


Fig. 2 - Flow diagram for producing refined sugar directly from raw juice by adopting cooling crystallization.

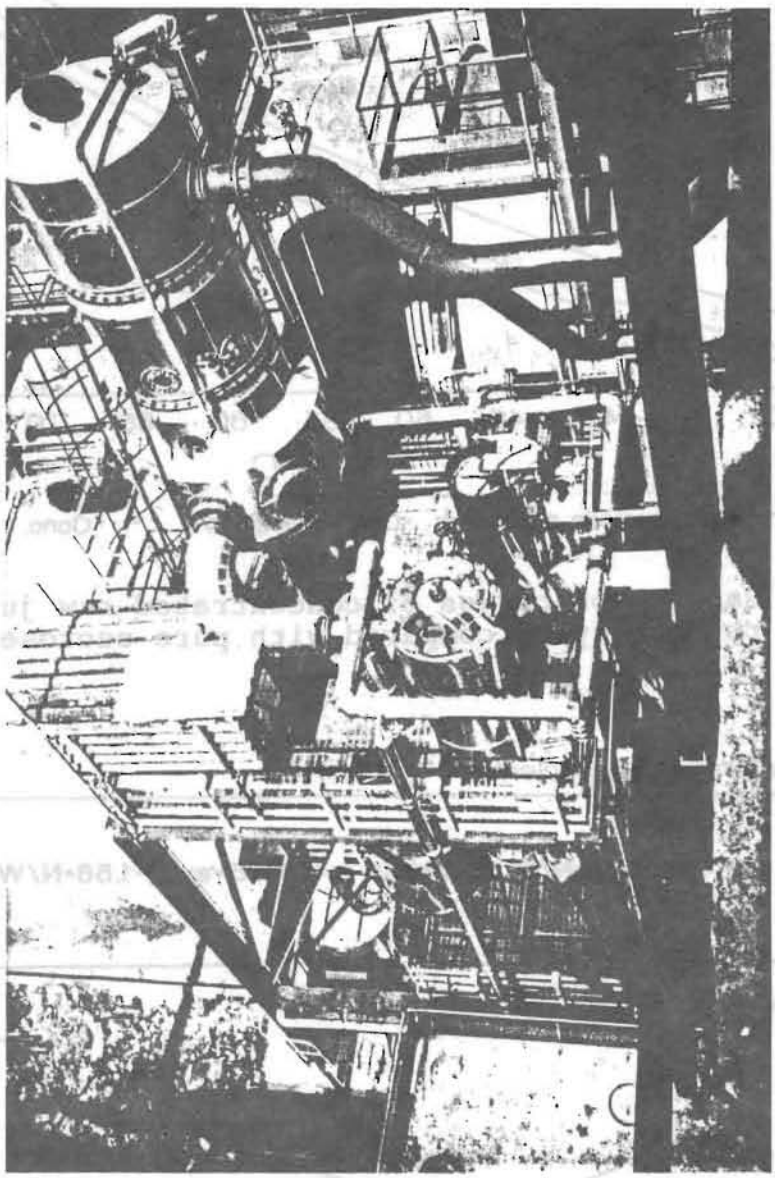


Fig. 3 - The pilot plant.

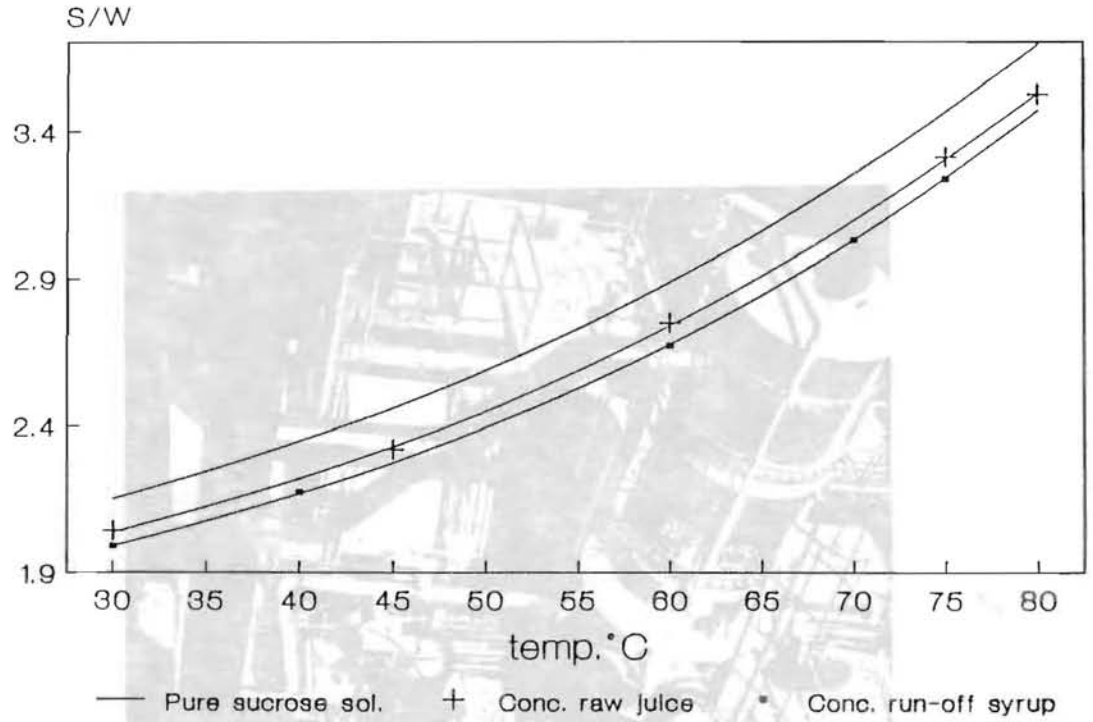
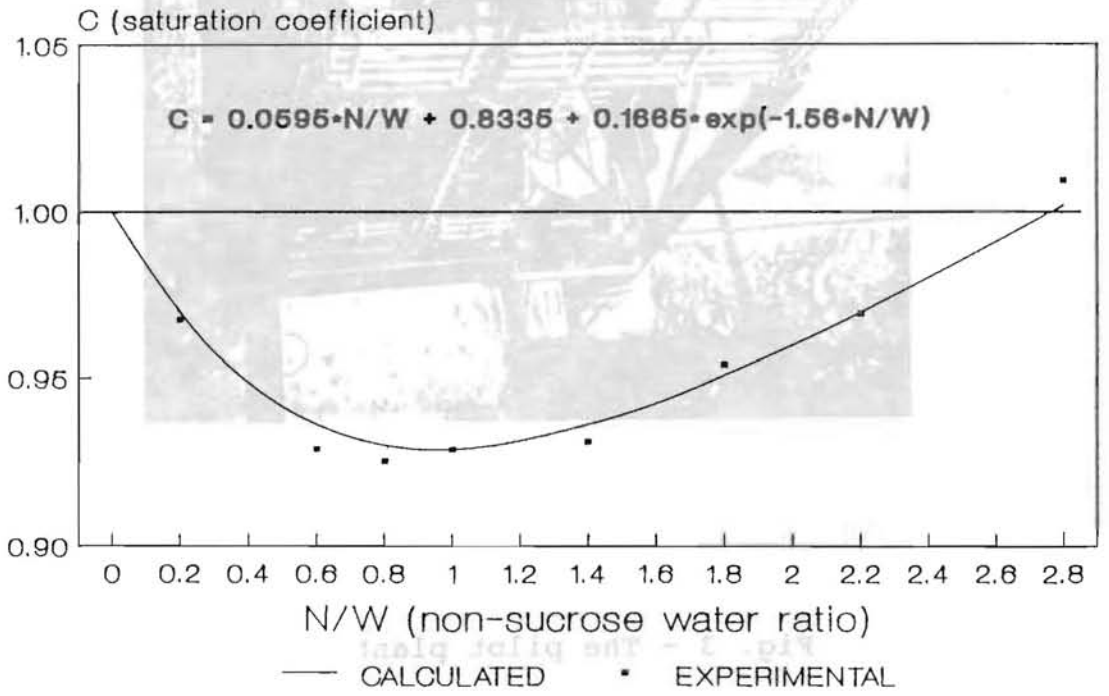
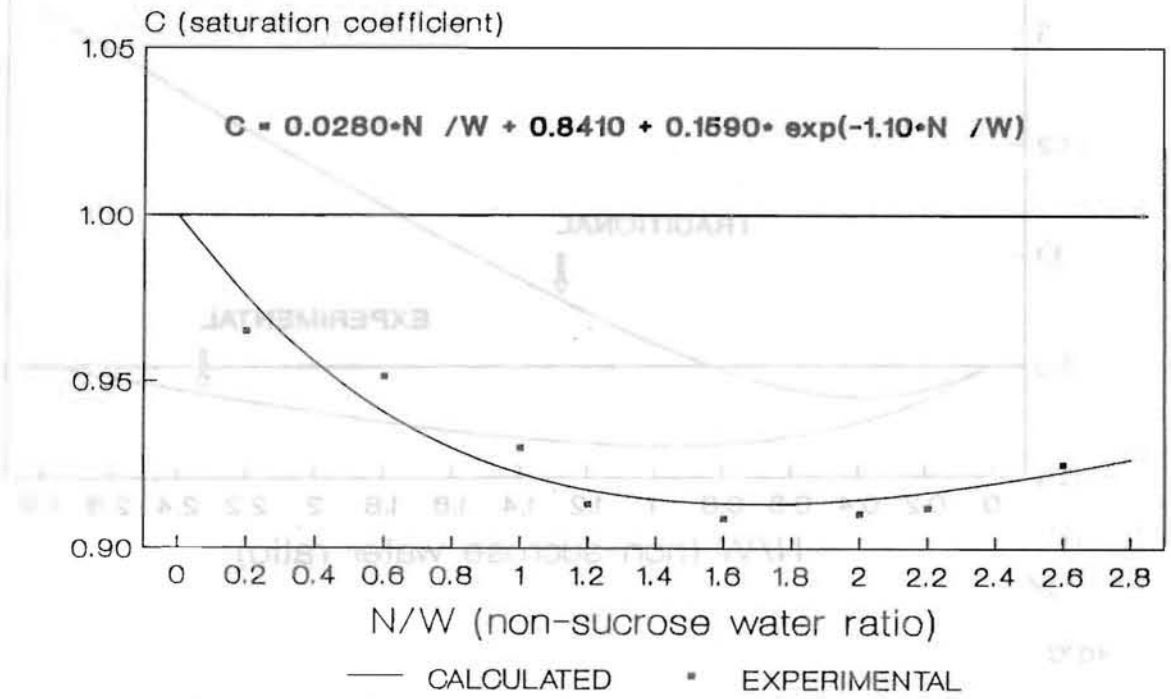


Fig. 4 - Saturation curves of concentrated raw juice and run-off syrup compared with pure sucrose solution.



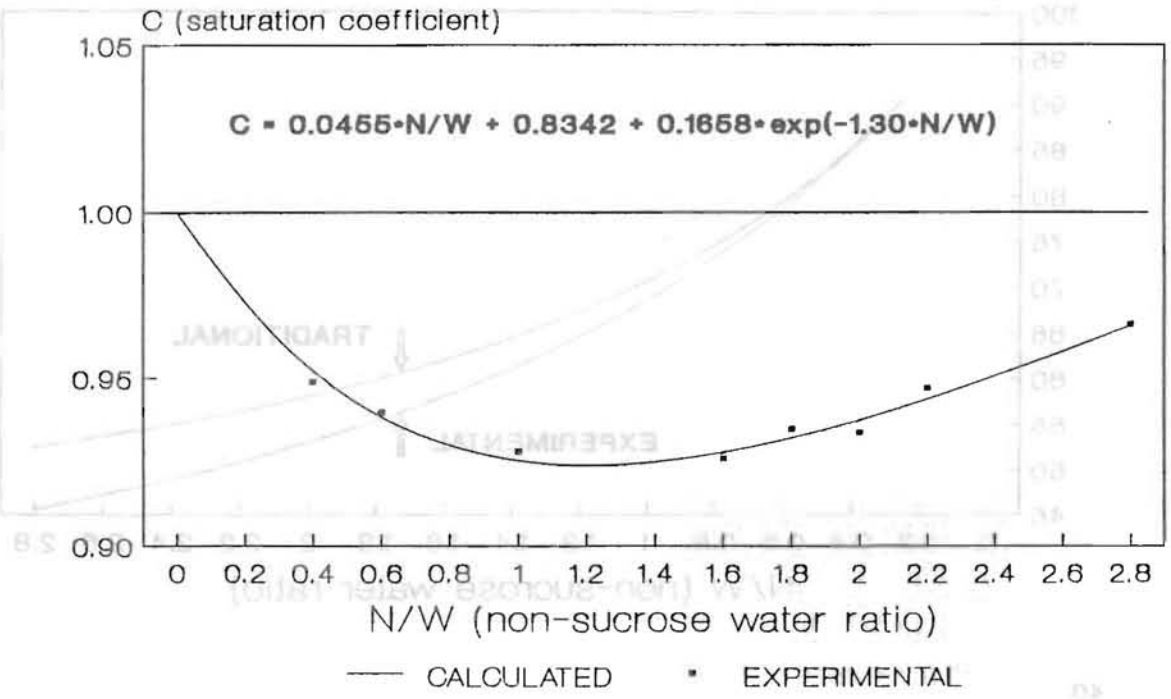
t = 40°C

Fig. 5 - Saturation function of the experimental molasses at 40 °C.



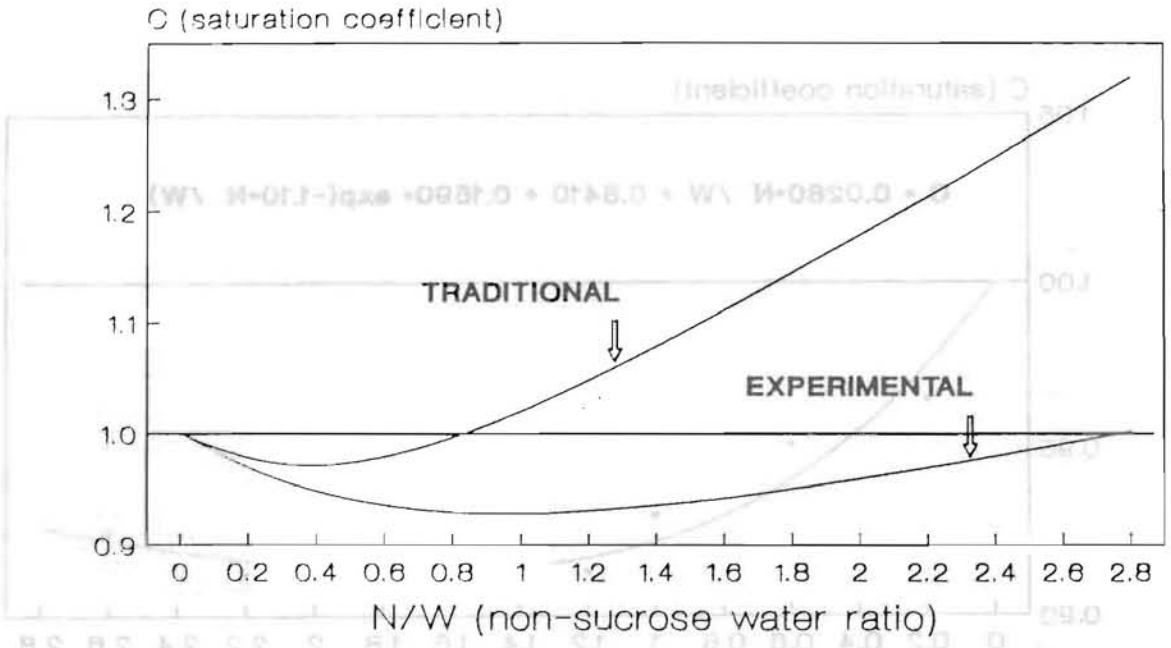
t = 60°C

Fig. 6 - Saturation function of the experimental molasses at 60 °C.



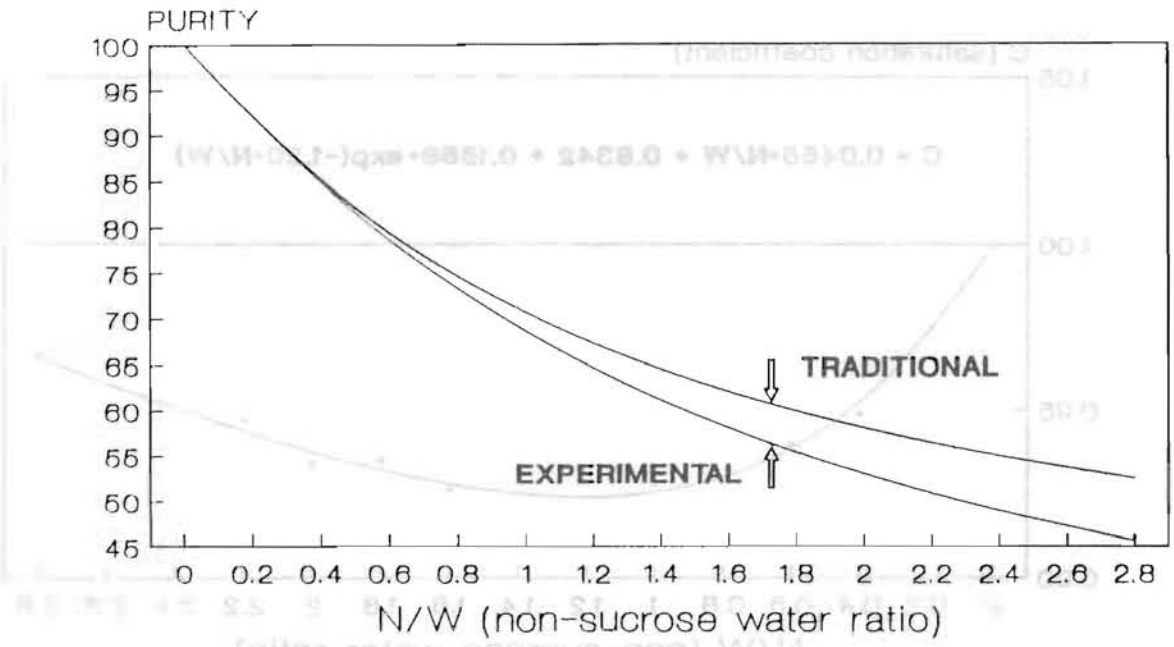
t = 80°C

Fig. 7 - Saturation function of the experimental molasses at 80 °C.



t - 40°C

Fig. 8 - Comparison between the saturation function of traditional molasses calculated by using Grut's data, and that obtained from experimental molasses at 40 °C.



t - 40°C

Fig. 9 - Comparison between the theoretical purity curves calculated for traditional and experimental molasses at 40 °C.

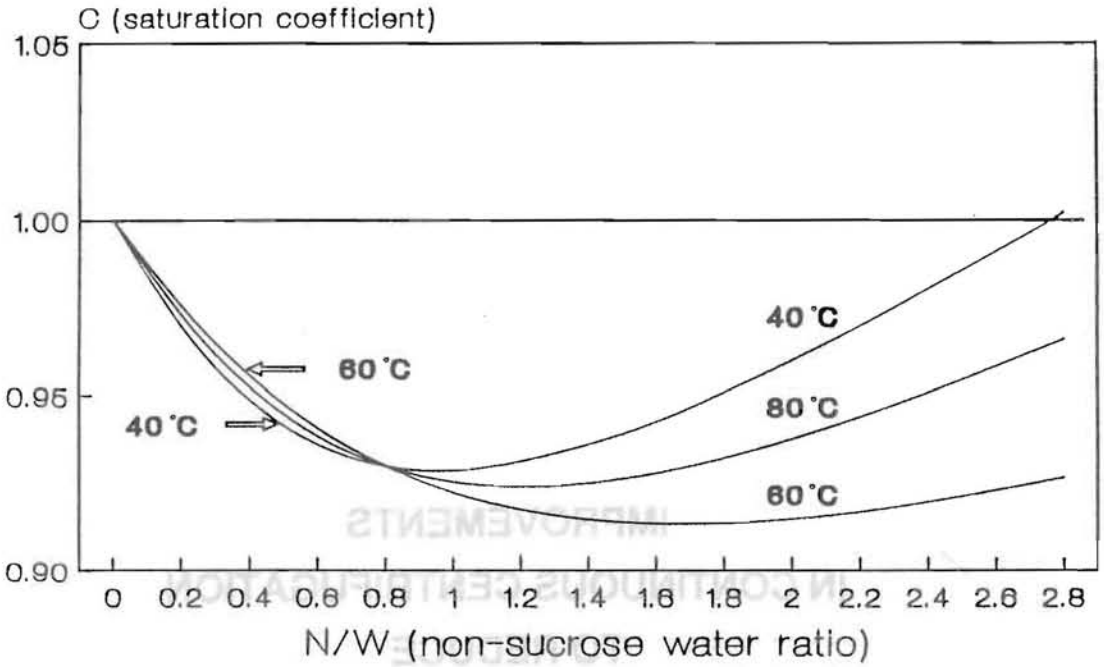


Fig.10 - Comparison between saturation functions obtained on experimental molasses at 40 , 60 and 80 °C.