PROCESS FOR MANUFACTURING LIQUID SUGAR
FROM CANE MOLASSES

H. J. Hongisto
Finnish Sugar Co. Ltd.
Kantvik, Finland

ABSTRACT

A process has been developed for the manufacture of liquid sugar from cane molasses by means of a chromatographic separation method. Unlike the few ion exchange processes applied to cane molasses, the chromatographic separation process fractionates the molasses into two parts, one rich in sugars and another in which the nonsugars are concentrated. It is recommended to invert the sucrose in the molasses before separation. The recovered total sugar fraction can be further treated to different kinds of commercial first-class invert liquid sugars.

INTRODUCTION

The application of the chromatographic separation for the desugarization of cane molasses was for the first time presented to the XVI Congress of this Society in Sao Paulo in 1977 (Hongisto et al11). Since then some additional papers have been written on the subject by Hongisto et al2,4 and Schneider3. In these articles two aspects have been emphasized:

1. The process greatly differs from the few ion exchange processes recommended for cane molasses in order to produce liquid sugar. These are all handicapped by severe waste water problems caused by the removal of the nonsugars and the regenerants. In the chromatographic separation processes, the bulk of nonsugars is separated into a residual molasses fraction which can be utilized either as cattle feed or as fertilizer (Fig. 1).

2. The importance of the pretreatment of cane molasses prior to separation. Whatever the target - granulated or liquid sugar - the molasses has to be free from components that may deteriorate the actual separation process.

The purpose of the present paper is to describe the chromatographic molasses desugarization process when it is applied to the production of liquid sugars and syrups.
**EXPERIMENTAL PROCEDURE**

**Pretreatment of Molasses**

The general arrangement for pretreatment is shown in Fig. 2. It has two purposes: to remove turbidity and Ca-and Mg-ions. If the colloidal impurities were not removed, they would fill up the voids between the resin beads in the separation columns and deteriorate the separation.

**FIGURE 1.** Basic cane molasses desugarization process

**FIGURE 2.** Pretreatment of cane molasses.
Defecation consisting of phosphatation and centrifugal clarification has been practiced. Fig. 3 shows the factory scale equipment. A decanter centrifuge with a screw conveyor that can transport the flock without breaking it has been selected.

**FIGURE 3.** Pretreatment plant for cane molasses.

Cane Molasses can contain fairly high amounts of divalent ions. This hardness has to be decreased to a level of about 0.1% Ca + Mg molasses d.s. to prevent the separation resin - which is originally in sodium form - from going into a devalent form. The necessary decalcification partly takes place in the defecation process but the final removal of the divalent ions is performed by cation exchangers.

The filtration is either carried out by a suitable deep-bed filter or pressure filtration is used.

**Separation**

In the chromatographic desugarization process cane molasses is fractionated into its different components in columns filled with suitable adsorbent. The basic phenomena behind this fractionation have been discussed by Melaja et al.\(^5\) and
Schneider. It is a question of a large spectrum of different adsorption, diffusion and exclusion phenomena. In principle no ion exchange should take place although the adsorbent is a special cation exchange resin. The behaviour of the different components in the column has been expressed by the distribution coefficient (Hongisto 4).

\[ K = \frac{C_i \text{ in the adsorbent phase}}{C_i \text{ in the solution}} \]

where \( C_i \) = concentration of component \( i \).

The bigger \( k \) is, the more the component is retained in the resin bed. In cane molasses separation \( k \) increases in the order nonsugars, oligo-saccharides, sucrose, glucose, fructose (Fig. 4). A consequence of this is that there is a greater difference between the nonsugars and reducing sugars than between the nonsugars and sucrose. This gives the idea to invert the sucrose in order to increase the capacity. In our pilot plant the inversion of sucrose in cane molasses has been carried out both by acid hydrolyses and enzymatically. A typical separation curve for inverted cane molasses is presented in Fig. 5.
Schneider. It is a question of a large spectrum of different adsorption, diffusion and exclusion phenomena. In principle no ion exchange should take place although the adsorbent is a special cation exchange resin. The behaviour of the different components in the column has been expressed by the distribution coefficient (Hongisto)

\[
K = \frac{C_i \text{ in the adsorbent phase}}{C_i \text{ in the solution}}
\]

where

\[C_i = \text{concentration of component } i.\]

The bigger \(k\) is, the more the component is retained in the resin bed. In cane molasses separation \(k\) increases in the order non-sugars oligo-saccharides, sucrose, glucose, fructose (Fig. 4). A consequence of this is that there is a greater difference between the non-sugars and reducing sugars than between the nonsugars and sucrose. This gives the idea to invert the sucrose in order to increase the capacity. In our pilot plant the inversion of sucrose in cane molasses has been carried out both by acid hydrolyses and enzymatically. A typical separation curve for inverted cane molasses is presented in Fig. 5.

![Diagram](image)

**FIGURE 4.** Chromatographic fractionation
The recovered sugar solution has to be further purified in order to have liquid sugar of the required quality. In the pilot plant experiments arrangement consisting of two "trains" of demineralization and decolorization columns (Fig. 6) are recommended. Different post-treatment decolorization have been tried in order to achieve high-quality products.

**Figure 5.** Separation of inverted cane molasses

**Purification**

**Figure 6.** Iron exchange and decolorization in the production of liquid sugar by means of the chromatographic molasses separation process
RESULTS AND DISCUSSION

The pre-treatment and separation of cane molasses have been experimented on full factory scale while the purification has been carried out in pilot plant tests.

Although the presented pre-treatment might be considered relatively complex, it is, in fact, a fairly easy and reliable way of making any cane molasses suitable for the chromatographic separation process. A few points are worth consideration:

- In the phosphatation the particle size of the phosphate precipitate is very small and, accordingly, separating it may be difficult. The use of suitable flocculant has proved necessary to achieve a good clarification of colloidal impurities.

- It has been feasible to use such amounts of phosphate that would be required to lower the calcium to the desired level. Besides, the magnesium content is hardly effected by phosphatation. It is more economical to use only the minimum amount of phosphate needed for sufficient clarification. Thus, there is still some 0.4 - 1.2% Ca + Mg on molasses d.s. in the solution after the centrifugal clarification.

- If the amount of the remaining calcium and magnesium is only some 0.5-0.8%, a weak carboxylic exchanger in alkaline metal form is used for softening. The divalent ions are eluted with acid, and the resin is transformed into the alkaline metal form by softened molasses, residual molasses and/or NaOH or Na₂CO₃. At this stage a considerable swelling takes place in the resin and special precautions have to be taken in order to avoid the mechanical breakage of the resin (conical column or countercurrent regeneration).

- If the hardness after the clarification is high (>0.8%), it is recommended to split the softening into two parts, i.e. to remove the bulk of the remaining divalent ions by a strong acid cation exchanger regenerated by the residual molasses fraction and to use the carboxylic weak exchanger for the very final deliming only.

- If the pressure filtration has to be used, the appropriate selection of filter aid must be emphasized. The particle size should be optimized in order to get sufficient throughput with minimal leakage of mud. Furthermore, the pores of the filter medium have to retain all the Kieselgur particles used. Even a small amount of diatomaceous earth in the feed solution causes severe problems in the separation.

- There is a certain sugar loss of about 3-4% in the mud. This can be minimized by washing the mud with water and by recentrifuging it. On the other hand, it can be added into the residual molasses and used as cattle feed.
SEPARATION OF CANE MOLASSES (inverted)

PRETREATED CANE MOLASSES
50.0 tons sucrose
22.0 tons reducing sugars
28.0 tons non-sugars

100.0 tons dry substance

TOTAL SUGAR FRACTION
% d.s.
Sucrose 47.27 92.8
Red. sug. 19.27
Non-sug. 5.19 7.0
D.S. 71.3 100.0
11% D.S.

NON-SUGAR FRACTION
% d.s.
Sucrose 2.73 19.3
Red. sug. 2.73
Non-sug. 22.81 80.7
D.S. 28.27 100.0
5% D.S.

INVERSION AND SEPARATION

TOTAL SUGAR FRACTION
% d.s.
Sucrose 0.3 95.0
Red. sug. 66.6
Non-sug. 3.85 5.0
D.S. 70.5 100.0
23% D.S.

NON-SUGAR FRACTION
% d.s.
Sucrose 1.8 7.5
Red. sug. 3.3
Non-sug. 24.4 82.5
D.S. 29.5 100.0
9% D.S.

FIGURE 7. Separation of cane molasses
It is recommended to add an enzymatic inversion to the pre-treatment in which case the separation plant capacity can be almost doubled compared to separation of non-inverted cane molasses. Inversion yield of over 96% can be achieved. The ketoses in cane molasses are also partly hydrolyzed.

In Fig. 7 the material balances are shown from typical cane molasses separations for further processing into liquid sugars. They differ from the separation for granulated sugar production in which an apparent sucrose purity of say 90% is obviously of the right order. When in this case liquid sugar is pursued, it is advisable to separate into higher purity of the order of 93-96% in order to make the removal of the remaining non-sugars easier. The total sugar yields exceed 90%.

Since fructose has a higher distribution coefficient than glucose, it can be to some extent enriched in the product fraction. By suitable cut-points it is possible to get fraction which contains 55% fructose on d.s. This liquid sugar is fairly similar to the 55% high fructose corn syrup.

The color of the product fraction in both the "inverted" and "not inverted" alternatives is of the same order depending on the raw material, being roughly 10-20% of the color of the raw molasses.

FIGURE 8. View of chromatographic separation plant in a Finnish sugar factory showing the control arrangement for the out following fractions.
In the described purification process it is possible to produce liquid sugar with a color less than 200 ICUMSA units and ash less than 0.03%. To produce liquid sugar of the higher quality with a color less than 50 ICUMSA units an additional post-decolorization after evaporation is necessary. This is done by activated carbon, a resin absorbent or by a mixed bed of strong acid and strong-base ion exchangers.

The required combination very much depends on the molasses to be treated and a tailor-made system is always necessary.

In the literature referred to the utilization of the residual fraction has been discussed. It can be considered as one of the many so-called condensed molasses solubles which are nowadays extensively used as cattle feed or liquid fertilizer. The fairly limited amount of the spent regenerants originating from the final purification by demineralization and decolorization can be combined with the non-sugar fraction from the separation and these can be evaporated together into residual molasses. This, in fact makes it possible to avoid pollution practically completely.

As far as the economy of the plant is concerned, feasibility studies for different circumstances have been made. In the following, an example is given for a 3-column plant in an Asian country (molasses inverted):

* Annual production estimate, operating period 8,000 h (333 days)

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Liquid weight</th>
<th>Dry substance</th>
<th>Total sugar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cane molasses</td>
<td>40,000</td>
<td>80</td>
<td>67</td>
</tr>
<tr>
<td>Product</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid sugar</td>
<td>26,700</td>
<td>70</td>
<td>99</td>
</tr>
<tr>
<td>(200 ICUMSA)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residual molasses</td>
<td>18,200</td>
<td>65</td>
<td>23</td>
</tr>
<tr>
<td>Pre-treatment sludge</td>
<td>2,240</td>
<td>45</td>
<td></td>
</tr>
</tbody>
</table>

Inversion gain and estimated loss are included in the calculation.

Regeneration wastes are discarded.
**Investments estimate**

- Main process equipment (imported) including decanter centrifuges, softening resins, filters, separation columns, separation resin, demineralization resins, evaporator, heat exchangers and instrumentation for plant. **6,000**

- Local equipment supply, such as softening columns, ion exchange columns, process tanks and agitators as well as pumps, piping, valves, etc. **970**

- Civil works, i.e., factory building, laboratory, office, maintenance workshop, canteen and well-fare facilities, etc. **750**

- Auxiliary functions: steam generation, electricity supply, compressed air, process and cooling water, sewage and the storage facilities for process chemicals, molasses, residual molasses and liquid sugar. **1,150**

- Installation **1,100**

- Interest during construction and start-up **400**

**Total investment cost estimate USD x 10³** 

**10,370**

**Operating cost estimate**

- Steam **64,000 t/a** **384**

- Electricity **2,800 MWh** **112**

- Water **3,000,000 m³/a** **3**

- Cooling water **2,400,000 m³/a** **502**

**Chemicals and resins**

- Phosphoric acid (100% H₃PO₄) **100 t/a** **80**

- Caustic soda (100% NaOH) **620 t/a** **155**

- Salt (NaCL) **160 t/a** **8**

- Hydrochloric acid (100% HCL) **580 t/a** **174**

- Flocculant **18**
- Enzyme: 57
- Softening resin replacement: 55
- Separation resin replacement: 95
- Demineralization resin replacement: 260
- Other chemicals: 50

Maintenance: 200

Operating personnel (continuous 3-shift)
- 1 dpt engineer, 4 head operators, 16 process workers,
- 1 instrument technician, 2 laborers: 70

Other operating costs: 50

Total operating cost: USD x 10^3 1,772

Production cost estimate: USD x 10^3

Raw material
- Molasses: 40,000 t, $30, 1,200
- Residual molasses: 18,200 t, $20, 364

Operating cost: 1,772

Capital cost
- Depreciation (10 years, 8% interest): 1,545
- Interest on working capital
  - (10% on 1,000,000): 100, 1,645

Production cost for 18,700 tons liquid sugar d.s.: USD x 10^3 4,251

Production cost for one ton of liquid sugar d.s. is USD 227. If an almost water-clear product is looked for the produced liquid sugar can be further decolo-
rized to less than 50 ICUMSA color with some additional decoloring equipment. The extra investment cost is of the order of USD 200,000, and the operating cost would increase by some 10-15 USD/ton of liquid sugar d.s.

Based on the above calculation and similar ones for other countries, it seems likely that the cost price of liquid sugar tends to be between 200 and 300 USD/ton d.s., mainly depending on the actual ex-factory molasses price. While cane molasses price has increased on the increased on the European market, the actual ex-factory molasses price is still low in many factories. The achieved price level of the liquid sugar competes successfully with the price of the 55% HFCS and other liquid invert sugars. In our opinion a molasses-based sugar production is still clearly the cheapest way to increase the sugar production in any country while one of the country's natural resources, i.e., sugarcane, will be maximally utilized for its original purpose, the production of sugar.

CONCLUSIONS

By means of the chromatographic molasses, desugarization process is possible to produce different kinds of commercial liquid sugars from the product fraction separated from final cane molasses. Depending on the requirements for the final product, different post-treatment processes, i.e., demineralization and decolorization, are necessary. The process consists of pre-treatment, actual separation, purification and evaporation. Depending on circumstances, the cost price for this kind of liquid sugar can be very competitive.

REFERENCES


Ha sido desarrollado un proceso para fabricar azúcar líquida a partir de melaza de caña utilizando un método de separación cromatográfica. A diferencia de algunos procesos de intercambio ionico aplicados a melaza de caña, el proceso de separación cromatográfica fracciona la melaza en dos componentes, uno rico en comienda invertir la sacarosa de la melaza antes de la separación. La fracción recuperada con todos los azúcares puede recibir otros tratamientos para convertirla en azúcar líquida invertida comercial de primera clase.