NOVEL CHARACTERISTICS OF THE ARi COUPLED LOOP CHROMATOGRAPHY PROCESS (ASSBT 1999)

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Introduction

The observation that ionizable compounds can be separated from non-ionic compounds by passage through ion exchange resins was introduced by the Dow Chemical Company in 1953[1]. This effect was termed "ion exclusion". In 1956 the application of this concept to sugar purification was demonstrated[2]. Asher determined that both ionic materials and color could be excluded from resin. The sucrose could therefore be purified. By 1963 it was clear that the large organic molecules in molasses are also excluded[3]. It was also understood that sugar juices should be softened prior to exclusion.

In 1965 J.B. Stark of the U.S.D.A. reported a research program designed to determine if in addition to these excluded impurities, which elute before sucrose, other impurities might be eluted after sucrose and therefore enable additional purification[4]. Using industrially scalable equipment Stark discovered that amino acids and betaine elute after the sucrose and therefore demonstrated that these components could be additionally separated and collected via the chromatography of beet molasses. It is notable that the same general type of resins used in these tests are still in use today for the chromatography of molasses, i.e., low crosslinked strong cation resins in monovalent form.

From this early work the general elution order of components was determined and can be described as comprising quickly moving excluded material (e.g. salts, color and high molecular weight compounds) followed by sorbed components which are retarded in their movement (e.g. sucrose, followed by betaine and amino acids). With this simple batch process, the molasses component fractions are collected as they exit the chromatography column.

Simulated Moving Bed Chromatography of Beet Molasses

While these pioneering discoveries were made using batch chromatography, the more recent application of simulated moving bed operation to molasses separation has been dependent upon the same elution order. As with batch chromatography, the excluded components travel quickly through the resin bed and exit from the leading end of the internal separation profile. This waste by-product is referred to as raffinate and contains the majority of the molasses nonsucrose. In opposition to this effect, the sucrose is sorbed by the resin which leads to the usual retardation of its movement. As a result, the sucrose is separated from the majority of the nonsucrose and is removed from the tailing area of the separation profile. This purified material is referred to as extract.

The opposing effects of nonsucrose exclusion and sucrose retardation are responsible for the economic success of industrial molasses desugarization.

An Obstacle to Obtaining Increased Sucrose Product

Although the majority of the molasses nonsucrose is favorably excluded, what occurs in a simulated moving bed to the sorbed nonsucroses - such as betaine and amino acids? Because both the sucrose and these small molecules exhibit sorption, a mutual contamination is observed. For example, the major contaminants in the sucrose fraction (extract) from a chromatographic separator are these small organics. Similarly, if a small organics fraction is taken, it is contaminated with sucrose. The unavoidable cross contamination results in a significant reduction of subsequent crystalline sucrose recovery.

Note that the product sucrose recovery is dependent upon both the separator extract purity/recovery combination and the subsequent crystallization recovery. The sensitivity of these variables can be determined by the following equation[5]:

(1) $Z = R (1 - Me/mE)$

Where:

Z = overall crystallized sucrose recovery including both separation and crystallization
R = separator recovery/100
E = separator extract purity/100
M = molasses purity/100 after extract crystallization
e = 1-E
m = 1-M

As an example, a separator purity/recovery combination of 90/90 will yield an overall crystalline product recovery of 75% of the sucrose entering the separator (assuming molasses purity = 60). It is clear that small increases in separator extract purity and recovery will have a significant effect on the recovery of crystalline product and that there is a very large amount of sucrose which is not being recovered by present state-of-the-art simulated moving bed separators. The Coupled Loop process was primarily developed to provide a significant increase in crystalline sucrose recovery.

Coupled Loop Separation of Molasses – Elimination of Cross Contamination

The ARi Coupled Loop process[6] applied to beet molasses has been designed with several characteristics opposed to the conventional methods for chromatographic separation of sucrose. For example, in a first simulated moving bed the sucrose is forced to exhibit exclusion rather than sorption behavior. It therefore is collected together with the excluded nonsucrose ordinarily separated from the sucrose.

From a conventional point of view, this result would be considered disastrous. As a rule, any sucrose in the waste byproduct (raffinate) is strictly minimized. However the new method purposely forces 99+% of the sucrose into the raffinate. We have discovered that under proper conditions, this contrary method results in a nearly complete separation of the usual contaminating organics (e.g., betaine and amino acids) from the sucrose. This means that the long standing problem of sucrose/small organic cross contamination is never encountered.

Free of the ordinarily problematic cross contamination, the sucrose/raffinate material can be easily separated in a second simulated moving bed. The result is an unusually high purity extract. The Coupled Loop process typically produces extract in the 95 to 97 purity range. Consequently the overall recovery of crystalline sucrose as determined by equation (1) is

significantly increased compared to conventional separation.

Additional contrary factors

At first sight, it would appear that the Coupled Loop configuration would lead to excessive costs due to large system size and unacceptable water use due to multiple separation. However because of other contradictory characteristics this is not true.

We have discovered the "backwards" separation to be an extremely efficient procedure. The loading, i.e., nonsucrose fed per unit time per unit of resin, is 3x or more the loading of a conventional simulated moving bed. This means the "backwards" separator is 1/3 or less the size of a conventional system. Ordinarily, such high loading would seriously deteriorate separation. Full scale industrial operation has demonstrated that the overall Coupled Loop process operates with resin inventory equivalent to a single conventional simulated moving bed.

With respect to water use, it is conventionally understood that the small organic contaminants can be separated somewhat more efficiently from the sucrose if water is added to a simulated moving bed at excessive levels. However with the "backwards" operation we have found a nearly complete separation of the small organics from the sucrose using *less* water than conventional operation. Remarkably, the water use is about 70% less than a standard separator which incorporates the usual sucrose retardation effect. Due to this unusual result, overall Coupled Loop water use is comparable to that for a single conventional simulated moving bed.

Another contradictory characteristic is the formation of a very large steady state inventory of well separated small organics in the "backwards" separator. These components (including betaine and amino acids) are specifically the material difficult to separate from sucrose. It is peculiar that purposely maintaining these components in the separator at an extremely high steady state concentration results in their improved separation from sucrose. In a conventional simulated moving bed this concentrated inventory of sucrose contaminants does not exist.

Other unique observations include a decrease in pressure drop and an improvement in product quality as equilibrium is approached. Ordinarily, pressure drop increases and product quality deteriorates somewhat as a simulated moving bed is loaded to steady state.

Implementation

The ARi Coupled Loop process has been evaluated at industrial scale and its purity/ recovery benefits have been verified. Presently, full scale installations are being implemented at three sugar companies in the United States. The capacities of these systems will be, respectively, 350, 525 and 600 tons/day of 80% DS molasses.

Conclusion

For the last 40 years the effectiveness of the chromatographic separation of sucrose from molasses has been fundamentally dependent upon the sorption/retardation of sucrose. ARi's Coupled Loop system has incorporated a reversal of this principle along with several other contradictory factors in order to provide improved separation efficiency.

References

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