DIRECT PRODUCTION OF WHITE SUGAR AND WHITESTRAP MOLASSES BY APPLYING MEMBRANE AND ION EXCHANGE TECHNOLOGY IN A CANE SUGAR MILL

By

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Abstract

A process to produce both direct white sugar as well as a fermentable sugar feedstock from sugar cane has been developed by Tongaat-Hulett Sugar and AECI Bioproducts. The development of the process as well as the results from pilot plant work carried out is described. This process focuses on juice rather than molasses as a raw material for purification, and involves ultra-filtration, de-mineralisation and de-colourisation. The ultra-filtration has been evaluated on ceramic and stainless steel membranes. The ion exchange uses ISEP technology. The de-mineralisation uses a strong acid cation followed by a weak base anion resin. The de-colourisation is based on an acrylic strong base anion resin in the chloride form. Sugar has been produced from the pilot plant which meets all the specifications of conventionally produced white sugar. The sugar recovery increased by more than 7% if compared to a raw sugar mill and back-end refinery. The improved crystallisation properties of the de-mineralised juice enable the conversion of the existing crystallisation capacity of the raw sugar mill boiling to the production of increased white sugar production with no additional capacity.

Introduction

The potential for increasing revenue at a raw sugar mill lies in three main areas:
1. Improve the quality of the sugar produced and ultimately eliminate the re-melting and further processing of the raw sugar to white sugar.
2. Increase the overall recovery of sugar from the juice.
3. Unlock the value of products contained in the molasses.

White sugar is currently produced through the manufacture of an intermediate raw product that is re-dissolved, filtered, de-colourised and re-crystallised. While the traditional refining process is a relatively cheap, simple and effective purification, it suffers from additional processing costs and sucrose losses. Several possible processes have been developed that will produce white sugar directly from cane juice, as well as recover more sugar (Clarke, 1996; Kearney, 1996; Kwok, 1996; Lancrenon and Herve, 1988; Monclin, 1996;aska and de Lataillade, 1994). However, none have been implemented on an industrial scale.

Various investigations have been carried out on molasses de-sugarisation (Davis et al., 1997; Lancrenon and Herve, 1988; Paanen, 1996; Ramm-Schmidt, 1988; Buckley and Norton, 1991; Saska and de Lataillade, 1994). Much of the research into molasses de-sugarisation can be applied to juice clarification as similar unit operations are applied. This is also evident from the literature references.

Cane molasses is used as feedstock of carbohydrates to the fermentation industry. The impurities contained in the molasses add complexity and cost to the fermentation processes. In the upgrading of cane molasses, only softening of cane molasses has been commercially implemented (verbal communication). As part of the study into molasses de-sugarisation ion exclusion chromatography, nano-filtration and ion exchange were investigated. From these preliminary investigations, it became clear that the upgrading of molasses, as a fermentation substrate, was not commercially feasible at the current world pricing of molasses and raw sugar.

In 1997, Tongaat-Hulett Sugar Limited (THS) and AECI Bioproducts (Pty) Ltd (ABP) combined their resources to develop a process that is able to achieve direct white sugar (EEC2 specification), increase sucrose recovery, and upgrade the value of final molasses as a fermentation feedstock. The process would have to be commercially viable at world open market pricing for raw sugar, the white sugar margin and cane molasses. This paper describes the development of the white sugar mill process (patent pending) and includes results from pilot plant work conducted at THS Felixton raw sugar mill from 1997 to 2000.

Definition of terms

White sugar mill —
Cane raw sugar mill which includes the new unit operations of membrane filtration, de-mineralisation and de-colourisation and its products are white sugar and whitestrap molasses

White juice or syrup —
Cane clear juice or syrup after membrane filtration, de-mineralisation and de-colourisation.

Whitestrap molasses —
high-grade molasses produced from exhausted white juice.

KEYWORDS: White Sugar, Ion Exchange, Membrane Technology, Whitestrap Molasses.
Flowsheet development

Additional juice purification steps are a prerequisite for producing white sugar directly from cane juice. Juice purification prior to crystallisation has the advantages of additional sucrose recovery (less molasses produced), higher crystallisation rates and lower mill maintenance costs, e.g. reduced evaporator scaling. From the fermentation feedstock and overall recovery perspectives, inorganic ash is the impurity of major concern. Chromatography (Kearney, 1996; Thompson, 1994; Saskia, 1995) and ion exchange de-mineralisation (Kim, 1997; Lancrenon and Herve, 1988) are two well-established technologies which would allow the separation of ash from the juice.

Chromatography

The ion exclusion chromatography process has been commercially implemented in the beet industry with the objective to separate sucrose and a secondary product, Betaine, from beet molasses. If chromatography is applied to cane molasses, the removal of suspended solids and softening is a pre-requisite. The separation on the chromatography is achieved through dilution with water over the simulated moving bed. The substantial amounts of added water will require evaporation.

The typical resin volume required is 90-130 m$^3$ resin/(tonne of brix/h) treated with the feed typically at 60 to 70 brix. In chromatography terminology, this equates to 0.01-0.015 m$^3$ feed/m$^3$ resin.h. The product brix is about 5 to 15 brix in the case of juice separation. To achieve the objectives of both the sugar producer, i.e. sucrose recovery, and the fermentation substrate consumer, i.e. low ash invert sugar, at least two separations are required. The chromatography process, thus, about trebles the evaporation load if compared to a standard raw sugar mill. The cost and design of the evaporation station is thus an important part of this process.

Ion exchange de-mineralisation

Ion exchange with the objective to de-mineralise liquid sugars has been commercially implemented in the corn wet milling (CWM) and high fructose corn syrup (HFCS) industry. This is normally followed by an adsorbent step to remove odour and taste. The advantage of ion exchange is that substantially all of the inorganic ash as well as organic acids are removed in a compact system. The typical resin volume required is 2.3-4.6 m$^3$ resin/(tonne of brix/h) treated with the feed typically at 20 brix (1-2 m$^3$ feed/m$^3$ resin.h). The ion exchange resin volume is thus more than an order of magnitude less than the resin volume required for chromatography.

The main disadvantage of ion exchange is the use of chemicals to regenerate the resin and the disposal of the mainly inorganic salt effluent. This disadvantage can be substantially eliminated with the use of chemicals suitable for the production of fertiliser. If nitric acid and ammonia are selected as the chemicals, the ion exchange regenerant product can be used as a liquid fertiliser. As the cane fields are fertilised after ratooning, the processing of cane would be balanced with the application of the fertiliser. The process described here was developed using hydrochloric acid and caustic but the resin selection was based on the fertiliser option.

Upgrading of high test molasses (HTM)

The current carbohydrate source for AECI Bio-products is high test molasses. The first step of the joint sugar technology project between AECI Bio-products and Tongaat-Hulett Sugar was to develop the de-mineralisation of high test molasses from the Hulett's Refinery. Ion exchange based on a strong acid cation and weak base anion resin was successful in the cost effective de-mineralisation of the molasses. A commercial plant is operating at Hulett's Refinery.

In addition to removing more than 95% of the inorganic ash from the HTM, approximately 80% of the HTM colour and 60% of the non-sugar organic impurities were removed. Colour removal during de-mineralisation is also reported by Dymond (1948) and more recently by Saskia (1995) and Shore et al. (1988).

The combined impact of de-mineralisation removals on cane juice is an increase of about 6% in juice purity. This leads to an improvement in the overall recovery of sucrose by more than 7% if compared on the basis of white sugar (new process versus back end refinery added to a raw sugar mill).

Technology development program

Although the key technology in the new process is ion exchange de-mineralisation, the development work also covers ultra-filtration, ion exchange de-colourisation, and crystallisation. Ultra-filtration is required to protect the ion exchange resins from fouling due to the components present in the cane juice. It has the additional benefits of removing some impurities from the juice and ensuring that the white sugar turbidity specifications are satisfied. Ion exchange de-colourisation is included because de-mineralisation alone is not able to produce a white juice of sufficiently low colour to allow direct white sugar production. Crystallisation studies were needed to quantify the impact of de-mineralised syrups on factory crystallisation, and to test the quality of the white sugar produced. The proposed flowsheet is depicted as a block flow diagram in Figure 1. Each step is described briefly in the following sections.

In parallel to the laboratory and pilot plant program, the basic engineering design of the complete plant was progressed, as well as the detailed design of the new unit operations. This allowed different development options to be assessed on the basis of commercial viability throughout the development program.

Stream selection

The sizing of both the ultra-filtration and ion exchange units is determined by hydraulic design considerations. In order to minimise equipment cost the optimal brix or total solids concentration must be selected. The volumetric flow rate decrease is
inversely proportional with increasing brix but the viscosity increases exponentially with increasing brix as illustrated (but not quantified) in Figure 2. The capital optimum for ultra-filtration is a maximum brix flow and for ion exchange a minimal pressure drop. A practical consideration in selecting the brix level is the configuration of the multiple-effect evaporation train and plant steam balance. Based on these considerations, the process was optimised in the range of 20 to 25 brix.

Membrane filtration

Membrane filtration was piloted on a batch and a continuous single stage pilot membrane separation plant provided by NIRO Inc. The membranes evaluated were ceramic membranes provided by Applexion (CarboSep) and USFilter and stainless steel membranes by Graver Technologies. The pore size of the ceramic membranes ranged from 200Å to 1.4 µm. The channel size of the ceramic membranes varied from 3 to 16 mm. The pore size and channel size of the stainless steel membrane was 0.1 µm and 16 mm respectively.

The objective of the ultra-filtration development program was to minimise the membrane area while protecting the resins from fouling components present in the juice and maintaining white sugar quality. The selection of the pore and channel size as well as the operating parameters determine the permeate flux. The permeate flux is increased by increasing temperature, transmembrane pressure and cross flow velocity for any given type of membrane within a limited range. Specific cleaning in place (CIP) protocols have been developed for both ceramic and stainless steel membranes to deal with variations in juice quality over the season.

The pilot plant operated on ceramic membranes during the 1999 season. During the 2000 off-crop (diluted stored syrup) and season, the pilot plant operated mainly on stainless steel membranes. The ceramic membranes have been evaluated in detail by the vendor and no abrasion of concern was detected. The final membrane life can only be determined at full scale. Both membrane systems are suitable for the application and the final selection is based on commercial considerations.

De-mineralisation

The implementation of the ion exchange process on ISEP technology as described by Rossiter and Riley (1997) and provided by Calgon Carbon Corporation has the following advantages:

- Substantially reduced resin inventory if compared to standard fixed bed technology. This is achieved through increased cycle rate of the ion exchange process or increased resin flow rate. Despite this increased cycling rate, the resin life is not negatively impacted. In the Lysine and HFCS applications, the ISEP technology has
largely displaced the traditional fixed or Simulated Moving Bed technologies.

- The multi-stage counter-current flow arrangement of the liquid streams to the resin flow makes it possible to achieve 95% de-ashing and 90% regeneration of resin at low chemical excesses of less than 20%.
- The wash and rinse steps can be effected efficiently, reducing evaporation and effluent disposal load.
- The ISEP technology can also be modified and applied to chromatography (Rossiter, 1999) and ion exchange de-colourisation of carbonatated liquor (Hubbard and Dalgleish, 1996).

The de-mineralisation process was evaluated at both laboratory and pilot plant scale. The pilot plant consisted of two ISEP units with all the required auxiliary equipment. The first unit contained a strong acid cation exchange resin and the second unit a weak base anion exchange resin. The de-mineralisation resins, which were successfully evaluated over the 2000 season, were Amberlite 252RF and Amberlite IRA92RF, supplied by Rohm & Haas. The resin life exceeded the South-African milling season of 36 weeks. Juice feed colour was in the range of 15 000 to 20 000 ICUMSA. The de-mineralisation process was optimised to remove 80% of the juice colour consistently, the majority of which is adsorbed on the weak base anion exchange resin.

The use of a strong acid cation exchange resin leads to sucrose inversion but this can be reduced to less than 0.5% if the process is operated below 15°C. To achieve this low operating temperature, a heat recovery and refrigeration step is required. Low levels of inversion are crucial to minimise sucrose losses and to meet the invert specification of EEC2 white sugar.

**De-colourisation**

The de-colourisation ion exchange utilises a strong base anion exchange resin in the chloride form. The resin evaluated was the acrylic IRA958 supplied by Rohm & Haas. The flow sheet is based on the ion exchange de-colourisation process used in the refining process as described by Getz (1988), MacDonald and Thompson (1996) and Hubbard and Dalgleish (1996). The process required substantial optimisation to cope with the high colour load and white juice colour specification of less than 300 ICUMSA. Figure 3 illustrates that this has been achieved most of the time on the pilot plant. The resin life exceeds one milling season of 36 weeks.

Alternative methods of colour removal were also considered. These were chemically regenerable granular activated carbon (GAC), adsorbent non-functional resins, styrenic strong acid cation exchange resins in the sodium form and conventional crystallisation. The use of GAC was studied further but the low treatment ratio of 0.3 m³feed/m³adsorbent.h and the low pH required to achieve high capacity and high levels of colour removal rendered this an impractical solution. Crystallisation is effective and the sugar produced by the second crystallisation from the re-melted
sugar of a de-mineralised syrup easily meets all the quality criteria of EEC2 specifications.

**Crystallisation**

The juice was concentrated in a single effect rising film vacuum pilot plant evaporator.

As crystallisation of sucrose has evolved over many years, limited information is available on scale-up. A fully automated steam heated batch pan was thus built by scaling down the key equipment parameters based on commercial crystallisers. The batch pan was calibrated against known mill and refinery streams. The white juice properties were between those of the A-pan feed and brown liquor from the refinery. Figure 4 illustrates this for the relationship of boiling point elevation versus crystal content.

The syrup was then processed in a batch pan and a four stage boiling scheme was simulated. Figure 5 plots affinated sugar colour versus feed colour for the first boiling. The regression of colour transfer data as achieved on the pilot crystallisation compares very favourably with the relationship derived by Lionnet (2000) for industrial scale refinery crystallisation. The sugar produced from the white juice by the first boiling meets all the quality criteria of EEC2 specifications.

**Conclusion**

The process is technically and commercially feasible and achieved the objective of producing white sugar at increased recovery and a high-grade whitestrap molasses.
This conclusion is based on:

- The membrane separation step has been proven on ceramic as well as stainless steel membranes. The performance data were repeatable over two seasons.
- The use of the continuous counter current ion exchange technology (ISEP) facilitated the process intensification of the ion exchange steps. This leads to the minimisation of ion exchange resin whilst achieving high product quality targets, minimal chemical excesses, and minimal water use. This leads to minimised effluent.
- The crystallisation rate improves such that existing raw sugar mill crystallisation capacity is more than sufficient to produce white sugar. The boiling-scheme is similar to a refinery or beet sugar factory, and the raw sugar mill boiling house thus requires re-arrangement.
- The use of nitrogen based regeneration chemicals has been proven at laboratory scale and will be evaluated at pilot plant scale during the 2001 season, thereby providing a largely effluent free process.
- The de-colourisation of juice to 300 ICUMSA can be achieved with standard ion exchange de-colourisation resins, chemically regenerable granular activated carbon, non-functional resins or crystallisation. The final selection is based on commercial considerations.
- The new unit operations can be integrated into the evaporation train.
- Additional benefits are the increased pan floor capacity and reduced fouling of the evaporator stations downstream of the new process.

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LA FABRICATION DU SUCRE BLANC DE CANNE EN SE SERVANT DE MEMBRANES ET DE RÉSINE ÉCHANGEUSES D'IONS

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Resumé
Tongaat-Hulett Sugar et AECI Bioproducts ont développé un procédé pour produire du sucre blanc et une mélasse fermentable à partir de la canne. On décrit le procédé et on donne des résultats obtenus à l’échelon pilote. La matrice première est le jus, et non la mélasse, pour la purification qui comprend l’ultra-filtration, la déminéralisation et la décoloration. Pour l’ultra filtration on s’est servi des membranes céramique et en inox. Les résines font parties d’un procédé ISEP, et la déminéralisation est basée sur des résines acides cationiques, suivies par des résines basiques anioniques. Pour la décoloration on s’est servi de résines acryliques basiques et anioniques. On a produit du sucre, à l’échelon pilote, qui a toute les qualités d’un sucre blanc conventionnel. La performance est meilleure par plus de 7% comparé à celle d’une sucrerie et rafinerie. Comme la cristallisation est améliorée grâce à la déminéralisation on a pu se servir de l’équipement de la sucrerie pour produire tout le sucre, sans augmenter la capacité.

Mots clefs: Sucre blanc, résine, membrane, mélasse.
PRODUCCIÓN DE AZÚCAR BLANCO DIRECTO Y SUS MIELES POR APLICACIÓN DE TECNOLOGÍAS DE MEMBRANA E INTERCAMBIO IÓNICO EN INGENIOS DE CAÑA DE AZÚCAR

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Resumen

Un proceso para producir azúcar blanco directo y sus mieles fermentables, a partir de caña de azúcar ha sido desarrollado por Tongaat- Hulett Sugar y AECI Bioproducts. Se describen el desarrollo del proceso y los resultados de los trabajos desarrollados a nivel de planta piloto. Este proceso se centraliza en el jugo más que sobre las mieles como materia prima para la purificación, e involucra una ultra-filtración, desmineralización y decoloración. La ultrafiltración se evaluó utilizando membranas de cerámica y de acero inoxidable. Para el intercambio iónico se usó la tecnología ISEP. Para la desmineralización se usó un ácido catiónico fuerte seguido por la base débil de una resina aniónica. La decoloración se fundamentó en el uso de una resina aniónica clorada fuertemente básica. El azúcar producida a nivel de planta piloto cumplió con todas las especificaciones del azúcar blanco producido convencionalmente. La recuperación de azúcar al ser comparada con ingenios que producen azúcar crudo y lo refinan, se incrementó en más de un 7%. Las mejoras en las propiedades de cristalización del jugo desmineralizado permiten convertir la capacidad existente de un ingenio de azúcar crudo a una producción incrementada de azúcar blanco sin aumento en la capacidad en tachos.

Palabras claves: azúcar blanco, intercambio iónico, tecnología de membranas, mieles.