THE DE-ASHING OF HIGH TEST MOLASSES USING CONTINUOUS ION EXCHANGE AT THE TONGAAT-HULETT REFINERY

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Abstract

The Tongaat-Hulett Refinery has been supplying AECI Bioproducts with high test molasses for use as a fermentation feedstock in the manufacture of lysine. The ash content in the high test molasses has caused bottlenecks in the lysine plant. A process to remove the ash was jointly developed by Tongaat-Hulett Sugar Ltd and AECI Bioproducts, and a commercial plant using continuous ion exchange technology (ISEP®) was installed at the Tongaat-Hulett Refinery. The principles of ISEP® technology, aspects of piloting, features of the commercial plant design, and the operation and performance of the plant are described.

Introduction

Fermentation processes use a carbohydrate raw material such as sucrose, glucose and/or fructose derived from the sugar or corn industries. AECI Bioproducts is a producer of the amino acid lysine and derives its carbohydrate raw material from high test molasses (HTM) supplied by the Tongaat-Hulett Refinery. HTM is manufactured by blending jet 4 liquor, a product of the fourth refinery white boiling(s) with a first or second recovery boiling molasses. Due to cost considerations HTM is preferred over raw sugar as the raw fermentation material but does have the disadvantage of incurring higher downstream processing costs. Various options to upgrade HTM were investigated. Since inorganic ash is the main impurity that causes bottlenecks in the lysine process it was proposed that the molasses be deashed using ion exchange. A joint technology development team was formed by Tongaat-Hulett Sugar and AECI Bioproducts to develop and commercialise the deashing technology.

The continuous ion exchange system (ISEP®) manufactured by Advanced Separation Technologies (AST, USA) was chosen to perform the deashing operation. The advantages of the ISEP® system over the traditional fixed bed resin plant include lower resin volumes, decreased regeneration chemicals, reduced effluent volumes and increased resin life (Rossiter, 1991). Many of these systems have been installed in other countries for the demineralisation of liquid sugars in the corn wet milling and high fructose corn syrup industries (Ahlgren, 1997). Only two ISEP® systems were installed in South Africa prior to the deashing plant at the Tongaat-Hulett Refinery; at AECI Bioproducts and African Products, Klipriver. However, this is the only known commercial application of the ISEP® deashing technology on cane sugar refinery molasses in the world. Previous studies conducted by Tongaat-Hulett Sugar (Hubbard and Dalgleish, 1996) have shown that there are significant cost advantages of the ISEP® unit compared to the fixed bed plant in the resin decolourisation process at the Tongaat-Hulett Refinery.

This paper gives an overview of the ISEP® deashing technology and describes the implementation of the technology from scale-up to design and operation of the plant. The pilot plant work was done during 1998 and the design, construction and commissioning of the plant in 1999 and 2000.

Process chemistry

An ion-exchange process is used to remove ash from the HTM. A strong acid cation resin removes sodium, potassium, calcium, magnesium and other cations and produces hydrogen ions which result in mineral acids being formed. The pH of the solution drops during this step. A weak-base anion resin is then used to neutralise and remove the mineral acids that have been produced by the cation exchanger and this results in the pH of the feed HTM being restored. Other substances such as colour and organic acids are also removed by either an ion exchange or adsorption mechanism. The ion exchange process is depicted in the following equations.

Strong acid cation exchange reaction

$$RSO_3^-H^+ + Na^+Cl^- \rightarrow RSO_3^-Na^+ + H^+Cl^-$$

('R' indicates the resin matrix)

Weak base anion exchange reaction

$$RCH_2(CH_3)_2N + H^+Cl^- \rightarrow RCH_2(CH_3)_2NH^+Cl^-$$

Similar reactions occur for the other cations and anions.

After the cations and anions have been removed the resin needs to be regenerated with chemicals. Hydrochloric acid is used to regenerate the cation resin while sodium hydroxide (caustic soda) is used to regenerate the anion resin. Hydrochloric acid is used as it prevents precipitation of calcium salts in the resin bed due to the high solubility of chloride salts. The hydrochloric acid is diluted to 7% $^m/_m$ while the caustic is diluted to 5% $^m/_m$ before being used as regenerants. An excess of chemical is normally required to regenerate the resin completely, but this excess is very low in the ISEP® process. The regeneration process is given by the following equations:

Table 1. Resin specifications.

	Cation Resin	Anion Resin
Manufacturer	Rohm & Haas	Rohm & Haas
Name	Amberlite IRA 252RF H	Amberlite IRA 92RF
Type	Strong acid cation, macroporous styrene DVB	Weak base anion, macroporous polystyrene
Max. operating temperature	90°C	90°C
Total capacity (100% usage)	1,7 eq/litre	1,6 eq/litre

Strong acid cation regeneration exchange reaction

$RSO_3^-Na^+ + H^+Cl^- \rightarrow RSO_3^-H^+ + Na^+Cl^-$

Weak base anion regeneration exchange reaction

$RCH_2(CH_3)_2NH^+Cl^- + Na^+OH^- \rightarrow RCH_2(CH_3)_2N + Na^+Cl^- + H_2O$

Other regenerants such as ammonia and nitric acid can also be used and a fertiliser can be produced from the regeneration streams instead of effluent.

The resins shown in Table 1 were used for the deashing of HTM. These resins are typical for this application.

ISEP® Technology

The ISEP® unit consists of 30 ion exchange vessels mounted on a rotating carousel. The vessels are connected to the ISEP® valve which has 30 rotating ports which connect to the rotating vessels via flexible hoses, and 30 stationary ports which are connected to the various feed streams with fixed piping. The vessel diameter for the HTM plant is 0,6 m and the height is 1,3 m. A more detailed description of the functioning of the ISEP® unit is given by Hubbard and Dalgleish (1996). The units used at the Tongaat-Hulett Refinery are of the indexing type, i.e. the carousel and vessels turn continuously while the valve moves over short periods (indexes). This is different to the old units where the valve also turned continuously. A cycle is completed when each vessel has passed through 30 ports. Movement over one port is termed a 'mini-cycle'.

Each ISEP® unit is divided into several zones:

Adsorption: In this zone the ions are adsorbed onto the resin as the columns move through the zone.

Adsorption wash/Sweeten off : The resin is washed with water to remove the residual HTM.

Regeneration: The ions that have been adsorbed are stripped by a chemical regenerant.

Regeneration wash: The resin is washed with water to remove all residual regenerant.

The HTM plant has been configured in a way that the recycle of streams is maximised. The adsorption washwater or sweetwater is used to dilute the incoming HTM feed while the regeneration washwater is used to dilute the chemical regenerants. In this way water usage and effluent volumes are minimised.

A typical flowsheet is given in Figure 1. The HTM is passed through nine vessels of the cation exchanger and then a further nine vessels of the anion exchanger. In order to increase the deashing, the HTM is passed for a second time through both the cation and anion exchangers. An additional pass can also be used if very high efficiencies are required and several other configurations are also possible. The HTM flows countercurrent to the resin and this makes high levels of deashing possible. High levels of regeneration at low chemical excesses are also possible due to the multistage counter current flow arrangement of the ISEP® system.

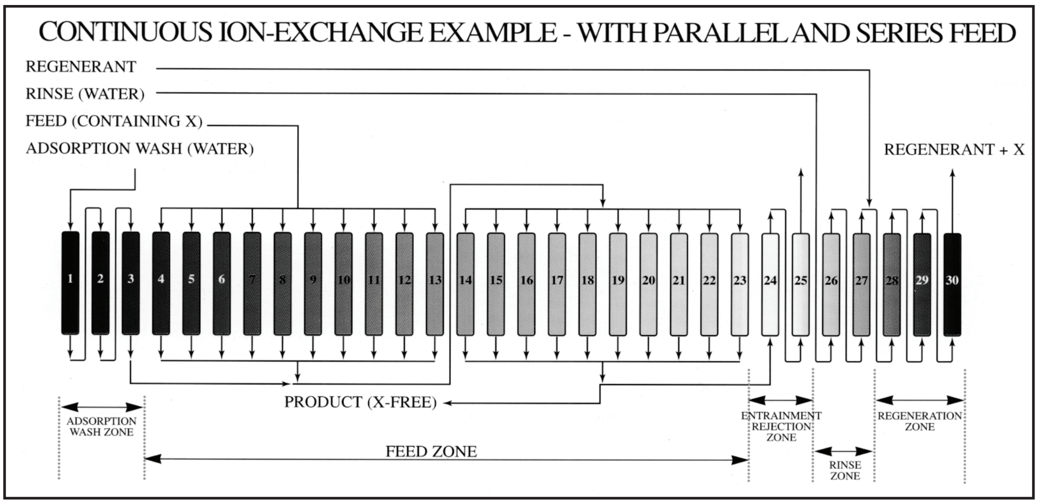

Figure 1. Typical flowsheet configuration (courtesy AST).

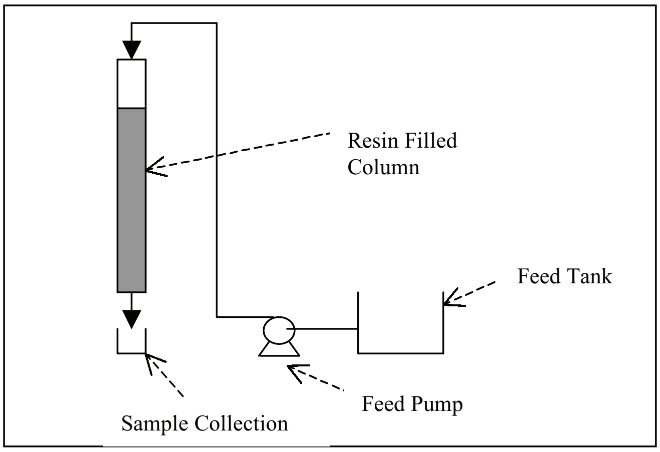

Figure 2. Scale-up equipment configuration.

Scale-up

Before the design and construction of the ISEP® unit, fixed column and pilot plant tests were conducted. Firstly, fixed column testing was used to dimension and cost the application. Thereafter, pilot testing was used to confirm operating and engineering design parameters giving confidence in the full-scale plant design and operation.

Fixed column tests

These tests were carried out using 25 mm diameter columns. The equipment configuration is shown in Figure 2.

Feed was passed through a column filled with resin and samples were taken of the liquid exiting the column. The following data were obtained from column tests:

- Adsorption breakthrough data on resin capacity and adsorption kinetics.
- Elution profile data on elution time and peak eluate concentration.
- Wash profile data on wash kinetics and wash tailing tendencies.

The above data were then used to derive a preliminary ISEP® design, which had to be confirmed through pilot plant tests.

Pilot plant tests

The aim of these tests was to demonstrate the actual process developed from the fixed column trials. The pilot plant configuration, together with operating and engineering parameters, was matched as closely as possible to that for the envisaged commercial plant. The important operating parameters are temperature, representative feed material and regenerant quality. The important engineering parameters are bed depth, fluid bed velocities, zone configuration, cycle time, resin residence time in each zone and fluid residence time in each zone (see Table 2). It is often impossible to match the length to diameter ratio of the pilot plant columns to that of the commercial plant columns as the resin bed height is similar to that of the full-scale unit. Proper liquid distribution of fluid is therefore important for the full-scale plant.

Process design

HTM is supplied to AECI Bioproducts as a partially inverted product. This is done by diluting the HTM to 55^0 Brix and inverting it using yeast. The HTM is then concentrated back to 78^0 Brix before being supplied to the lysine plant. The optimum location of the deashing plant was determined to be after the brixing down step, as this minimises further evaporation costs. The deashing plant has been designed to match the offtake of the lysine plant with a capacity to process 170 tons/day of HTM and 4,5 tons/day of ash. The design ash load is in excess of the expected average flow but caters for seasonal variations. The on-line time efficiency was assumed to be 95% based on experience gained on other ISEP® units. The design specifications of the deashing plant are summarised in Table 3.

The operating temperature of the plant is 60^0C. This is largely governed by pressure drop limitations as the ISEP® valve can only handle a maximum inlet pressure of 5,2 bar (g). Since the brix of the material is to a large extent fixed, the only parameter that can be varied is temperature. The temperature is then chosen to produce the viscosity that will result in an acceptable pressure drop and flow to be achieved. It should be noted that operating at 60^0C results in high inversion, but since inversion is the next process step, this is not of concern.

Table 2. Scale-up parameters on the cation unit.

Cation IX Scale-up parameter	Units	HTM Hulref	Pilot plant
Adsorption			
Volumetric treatment ratio	Bed volume	5,5	5,5
Resin capacity utilisation	%	70	70
Fluid velocity	m/h/pass	3,1	3,9
Fluid residence time	Min	12,5	11.8
Resin residence time in ads zone	Min	270	260
Regeneration			
Fluid velocity	m/h/zone	5,4	4,4
Fluid residence time in regeneration zone	min	29	31
Resin residence time in regeneration zone	min	60	65

Table 3. Design specifications for the HTM deashing plant.

		Design
Flow 78° Bx HTM	tpd	170
Ash	%	2,65
Ash	tpd	4,51
Ash removal	%	95
HCl (32%)	tpd	6,8
NaOH (50%)	tpd	4,8
Water	tpd	149
Steam	tpd	12
Effluent	tpd	112
Cycle time cation	hrs	4,8
Cycle time anion	hrs	4,6
Cation/anion adsorption wash	Bed volume	1,33
Cation regeneration wash	Bed volume	1,24
Anion regeneration wash	Bed volume	1,77

The plant has been designed for 95% ash removal based on pilot plant studies. The design also takes into account the gradual reduction in resin capacity during the course of operation due to reduced regeneration efficiency as well as long-term fouling of the resin. The plant is also designed to enable varying excesses of chemicals as well as concentrations to be used. A cross-regeneration step has also been designed to defoul the resins intermittently. This process involves passing dilute acid over the anion resin and dilute caustic over the cation resin for a full cycle.

The effluent from this process is derived from the chemical regeneration steps and consists mainly of a salt solution. In order to meet environmental criteria, as well as to save energy costs, the effluent is cooled to below 44^{0}C by using incoming process water. This heat recovery system is effected by a plate heat exchanger. The effluent from this process has been tested and found to be suitable for disposal into the sea.

The deashing plant is controlled by a fully automated system utilising a Yokogawa distributed control system (DCS). Based on an ash analysis of the feed, a resin flow is calculated. The chemical flows are then calculated based on the resin flow, and the washwaters are determined on the basis of the dilution required. In addition to the normal steady operation of the plant, several other states are defined in order to cater for the various possible plant conditions such as temporary shut, emergency shut and idle. A complex algorithm is also required to manage the indexing of the ISEP® valve and rotation of the carousels, which is critical to the successful operation of the plant.

Plant performance

The plant exhibited unusual operating characteristics from start-up, as it was unable to deash the HTM fully at high resin capacity utilisation and minimal regenerant excesses. These conditions were met during the original piloting of the HTM deashing process in 1998 and repeat pilot work during 1999.

Plant commissioning began at the end of October 1999 and was completed in January 2000. The deashing plant on-line time was poor during the early stages of commissioning, with mechanical efficiency figures of 50%. Between January and mid March 2000 the plant ran intermittently while the problems with the carousel positioning system were being rectified. Subsequently the plant operated with reasonable mechanical reliability. Other commissioning issues included resin fouling due to stop/start operations as well as distributor problems.

The steady operation of the plant was also plagued by frequent blockages in the cation ISEP® regeneration zone. This was attributed to potassium chloride precipitation. After a severe blockage a column was opened and a white crystalline material was found in the resin bed and piping; this was analysed and was confirmed to be mainly potassium chloride. The regeneration wash water is used to rinse the column leaving the regeneration zone free of acid. This rinse water, which varies in concentration, is subsequently used to dilute the con-

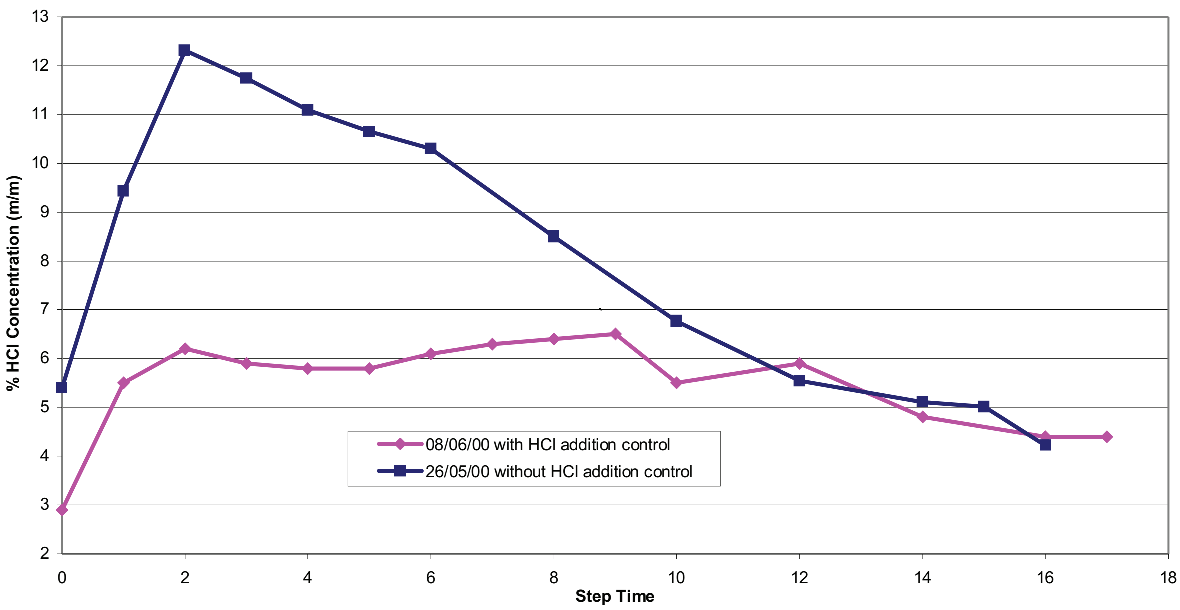

Figure 3. Acid profiles of dilute regeneration feed into the cation ISEP® regeneration zone.

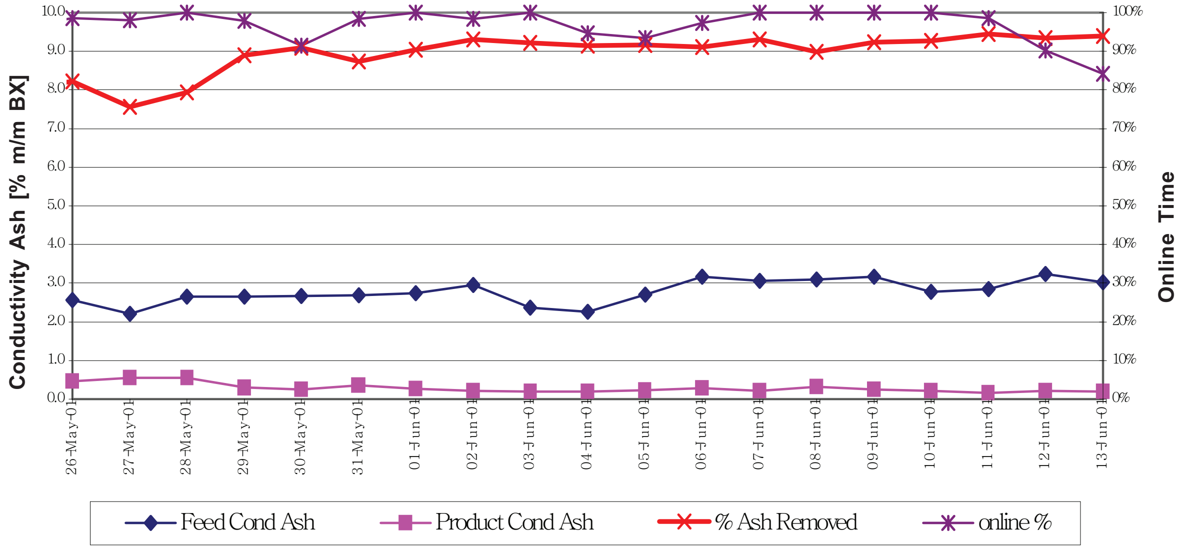

Figure 4. Deashing plant performance.

centrated hydrochloric acid regenerant via an in-line mixer. Over a mini-cycle, an acid concentration profile is then generated on the dilute acid regenerant stream. For about half the mini-cycle the acid concentration was above 8% $^{m}/_{m}$ potentially allowing potassium chloride to precipitate in the cation ISEP® regeneration zone and block flow. Laboratory tests indicated that potassium chloride readily precipitated when acid concentrations were in excess of 8% $^{m}/_{m}$. The acid concentration profile is shown in Figure 3.

To compensate for the acid returning with the regeneration wash, the acid addition control loop on the DCS was recoded with a 'ramp function' to lower the concentrated acid addition rate during the first half of a mini-cycle. The recoding ensured that the overall amount of concentrated acid added based on the chemical excess required was correct over the full mini-cycle. With the concentrated acid 'ramp function' the acid concentration into the regeneration zone was maintained below 7% $^{m}/_{m}$ as shown in Figure 3. Implementing the 'ramp function' has eliminated the regeneration wash water flow stoppages.

The plant has since operated with high mechanical reliability as depicted in Figure 4. Currently overall time efficiencies are exceeding design assumptions. Chemical and regeneration efficiencies are also good. Although the process was initially unable to reach the design specification in terms of deashed HTM, the problem has been resolved and the level of deashing is currently in excess of 90%.

Some performance characteristics of the deashing plant are:

- Conductivity ash removal >90%
- Colour removal 75%
- Organic non-sugar removal 60%
- Inversion 31%
- Sugar losses <0,1%

Conclusions

The HTM deashing plant is currently performing at close to 100% mechanical efficiency despite the problems that were encountered during the commissioning phase. Deashing efficiencies are also good and the benefits to AECI Bioproducts of utilising deashed HTM have been substantial.

The deashing technology has demonstrated that it is not only possible to remove ash from a cane sugar refinery molasses stream but that the ion exchange process can also remove colour as well as organic non-sugars. These characteristics make it possible for this technology to be applied to other streams in the sugar manufacturing process, e.g. clear juice (Fechter *et al.*, 2001). A process (patent pending) is currently being developed by Tongaat-Hulett Sugar and AECI Bioproducts to produce white sugar at a raw sugar mill using this technology as a key process step.

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