REFEREED PAPER

THE BENEFICIATION OF REFINERY MOLASSES INTO LIQUID SUGARS USING ION EXCHANGE TECHNOLOGY AT HULETTS REFINERY

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Abstract

The handling of raw sugar refinery molasses is a problem most sugar refineries are faced with. To this end, many processing options have been proposed and evaluated over the years. The advantages of such processes include the beneficiation of a low value stream, the reduction of recovery crystallisation and recovery house operations, the reduction of a low purity sugar recycle stream and an increased overall refinery throughput. The processing option discussed in this paper is the beneficiation of refinery molasses into liquid sugars. A process utilising continuous and batch ion exchange technology for de-ashing, inversion and decolourisation, followed by evaporation and carbon treatment, was developed, trialled and implemented. Return syrup is currently being treated using this process at the Huletts Refinery to produce a medium/high invert liquid sugar.

Keywords: liquid sugars, beneficiation, return syrup, ion exchange, waste stream, de-ashing

Introduction

The stand-alone Huletts Refinery recognised the need to reduce the volumes of refinery molasses being generated, in order to assist with the handling of this material. The sales volumes of refinery molasses had reduced significantly in recent years and future sales prospects did not look positive. Alternative uses or customers for this stream needed to be found. In response to this challenge, a proposal was put forward to utilise the decommissioned continuous ion exchange unit at the refinery to produce a liquid sugar from the return syrup stream. The return syrup stream was selected because it was the least concentrated ash stream, and would prove to be a good starting point to test the proposed process. Previous work by Rousett and Paillat (2009) had utilised decolourised melt liquor to produce a liquid sugar.

The production of medium to high invert liquid sugars from return syrup was ideally suited to the set-up at the Huletts Refinery. Singh et al. (2012) had listed the alternative options for handling refinery molasses and highlighted the capital requirements for such a process. However the decommissioned continuous ion exchange plant was already available, together with its resin inventory. The resin capacities of the remaining resin in the plant were tested.
and deemed to be suitable for the required duty. Percival and Schuler (1986) had tested such a process utilising a white syrup feedstock and batch ion exchange columns in a laboratory environment. They had concluded that ion exchange resins could be used to invert sucrose and to produce liquid invert syrups. The challenge in this case was to do this on a high colour (10000 ICUMSA units) and high ash (3.5% m/m) stream.

**Process description**

Based on previous experimental, pilot plant and plant scale work, the flow sheet shown in Figure 1 was proposed, and laboratory tests were setup. The return syrup specifications used as guidelines to setup process performance targets are shown in Table 1.

![Figure 1. Process flow diagram for liquid invert sugar using ion exchange.](image)

**Table 1. Return syrup specifications.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brix</td>
<td>75-76% Brix</td>
</tr>
<tr>
<td>Colour</td>
<td>7500-10000 ICUMSA units</td>
</tr>
<tr>
<td>Invert %</td>
<td>2.5-3.0%</td>
</tr>
<tr>
<td>Conductivity ash</td>
<td>2.5-3.0%</td>
</tr>
</tbody>
</table>
A summarised liquid sugar product specification is shown in Table 2. This was used as a guideline to ensure that the proposed process met the required specifications. A high invert product was chosen as it was felt that once the process was well defined, then the inversion control parameters could be fine-tuned to achieve the desired lower inversion percentage.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brix</td>
<td>79.0-81.0% Brix</td>
</tr>
<tr>
<td>Colour</td>
<td>&lt;100 ICUMSA units</td>
</tr>
<tr>
<td>Composition</td>
<td>Mono-Fructose 47%</td>
</tr>
<tr>
<td></td>
<td>Glucose 47%</td>
</tr>
<tr>
<td></td>
<td>Disaccharides 6%</td>
</tr>
<tr>
<td>pH</td>
<td>3.5-5.5</td>
</tr>
<tr>
<td>Conductivity ash</td>
<td>&lt;0.1%</td>
</tr>
</tbody>
</table>

**Discussion of laboratory results**

*Continuous ion exchange (de-ashing)*

The first unit operation to be tested in the laboratory was the de-ashing of return syrup. This operation had been successfully carried out at plant scale as part of the High Test Molasses (HTM) de-ashing plant at the refinery (Ahmed et al., 2001). In this case it was merely a verification that the old resin in the plant was still capable of carrying out this duty. Due to the anionic resin going out of production, alternative resins were also tested. These tests were also aimed at maximising colour removal and sucrose inversion. Resins exhibiting characteristics similar to the current plant resins as well as characteristics that would aid in colour removal were sought from different suppliers and tested. The cationic resin was kept the same whilst the anionic resin was varied in each laboratory run. See Figure 2 for results of the testing of different resins for de-ashing.

Figure 3 shows the results obtained with regards to colour removal for the de-ashing resin tests. These tests were carried out in a batch mode in the laboratory. The results were plotted against bed volumes (BV). A bed volume is defined as the total volume liquid passed through the column divided by the total volume of resin in a column. The BV allows a dimensionless measure of flow through a bed. This is useful when comparing the flows through different resin bed volumes.

Resin A was the resin from the plant, and proved to be able to still maintain the level of de-ashing required. Resins D and E were found to be viable replacements should the need arise. Resin D was about 2.5 times more expensive than resin E. Resin F was the alternative resin offered by the supplier, and also seems to be a good replacement.
Batch ion exchange (polishing)
The polishing de-ashing duty was selected to be done via batch ion exchange. A batch operation, although more capital intensive, does allow for more flexibility in the process. Since the polishing process is able to be run at higher treatment ratios than the bulk de-ashing process, thus requiring a lower resin volume, the batch operation was the more viable option in this instance. The polishing operation is designed to remove the specific remaining impurities that are not removed during the preceding de-ashing process. Due to the higher ash and colour loads from the feed into this process, de-ashing and decolourisation needed to be optimised across each unit operation without much room for a trade-off between the two. The
objective for these tests was to select a resin that was capable of polishing off the remaining ash as well as maximising colour removal.

Figures 4 and 5 show the de-ashing and colour removal results obtained during this phase of testing. Resin H proved to be an excellent decolouriser, but did not satisfy the de-ashing requirements. It was decided to use resin I for this duty.

**Figure 4. Polishing de-ashing results (BV = bed volume).**

**Figure 5. Polishing colour removal results (BV = bed volume).**

*Resin inversion*

At this point in the process, it was necessary to ensure that the feed stream to this process was ash free. Any residual ash would load up the inversion resin and thus cause a decrease in the
inversion performance (Percival and Schuler, 1986). Laboratory tests indicated that optimum inversion conditions for this process were achieved at 45°C, for a feed stream at 40°Brix and to minimise hydroxymethylfurfural (HMF) formation. HMF is an unwanted impurity as it adds to the colour of the product. Flow characteristics through the resin bed were also taken into account when selecting the type of resin to test in order to ensure optimum inversion conditions. A macro-porous and a gel resin which were being used in another process but for a similar application at the refinery, were tested.

**Batch resin decolorisation**

At this point in the process there should be negligible ash in the intermediate stream, thus de-ashing ability should not be a factor here. However, Bento (1999) presents two main mechanisms involved in sugar colourants fixation into styrenic resins. The first mechanism is the ionic bond between anionic colourants and resin fixed ions, which requires some ion exchange capacity. The second mechanism utilises the hydrophobic interaction between the colour bodies non-polar part and the styrenic divinyl-benzene resin matrix. Therefore the resins selected for testing on this duty were a mixture of adsorbent resins as well as a few with ion exchange capability.

Davis (2001) states that “Resins do not remove as broad a range of colourants as activated carbons, but are more specific.” It was these specific colour bodies that were targeted to be removed during this step. The melanoidins and alkaline degradation products of fructose (ADF) products are removed via ion exchange resins (Davis, 2001). The return syrup feed to this process had already undergone carbonatation, strong base acrylic anion resin decolorisation and crystallisation, so the colour bodies present should predominantly be melanoidins, caramels, ADFs and colour precursors as defined by Godshall (2000), thus justifying the choice of resin decolorisation.

An additional factor taken into account when selecting resins to be tested was the pore structure of the resins (Gula and Paillat, 2006). This pore structure determines the specific colour bodies that get removed and it is believed that, with the correct pore structure, the need for granular activated carbon (GAC) will be reduced and maybe even eliminated. The resin selected for this duty has a specific pore structure that was found to be optimal for the duty required. Resin H, as shown in Figure 5, was selected for the resin decolourisation duty.

**Discussion of one ton plant trial**

The laboratory results were analysed and a viable process flow was then proposed for a one ton plant trial. The one ton plant trial was proposed in order to mitigate any risks that could be incurred during scale-up. It could also provide further insight into the technology being utilised for this process. The relevant equipment was then identified and setup at the refinery. The continuous ion exchange was substituted with batch ion exchange for this trial, due to the ISEP plant not being re-commissioned at this stage. A total of 11.6 tons of return syrup was processed as part of this trial. The trial was conducted on a batch basis with one ton flow bins being used to store the feed, intermediate and product streams. The results obtained are summarised in Table 3. During this trial the resin decolorisation was done before the polishing application; however, the low decolorisation results achieved forced a rethink of this process. The resin used for decolorisation during this trial was also not resin H, which was the preferred resin for this duty. This unit operation was then moved to after the polishing and inversion step in the final process flow sheet. To maximise the resin decolorisation, the feed stream essentially needed to be ash free.
Table 3. One ton plant trial results.

<table>
<thead>
<tr>
<th>Unit operation</th>
<th>Average performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>De-ashing</td>
<td>95%</td>
</tr>
<tr>
<td>De-ashing colour removal</td>
<td>83%</td>
</tr>
<tr>
<td>Resin decolourisation</td>
<td>55%</td>
</tr>
<tr>
<td>Polishing de-ashing</td>
<td>99%</td>
</tr>
<tr>
<td>Polishing colour removal</td>
<td>74%</td>
</tr>
<tr>
<td>Inversion</td>
<td>93%</td>
</tr>
<tr>
<td>GAC colour removal</td>
<td>-17%</td>
</tr>
<tr>
<td>PAC colour removal</td>
<td>67%</td>
</tr>
</tbody>
</table>

The GAC treatment did not work well during this trial, possibly due to the age of the carbon, as well as the carbon being close to the end of its production cycle. A powdered activated carbon (PAC) was then used to get the product within the colour specification of less than 100 ICUMSA units. The laboratory tests had shown that the colour specification could be achieved without the use of PAC and with the use of resin H. Having achieved the desired product specifications after the one ton trial, confidence was achieved in continuing to a full scale plant.

Discussion of plant scale results

The results obtained from the laboratory and one ton plant trial indicated that the process was viable. It was then decided to retrofit this plant into the refinery. The ISEP de-ashing plant was then re-commissioned and the new resins selected for polishing, inversion and resin decolourisation were installed. The complete return syrup liquid sugars plant was then commissioned. A description of the results being obtained from each unit operation is given below.

Continuous ion exchange (de-ashing)
The mechanical reliability of the plant was significantly improved by studying the most common modes of failure experienced previously and better engineering solutions being implemented. There were initial problems experienced with the indexing mechanism of the ISEP valve, but these have since been resolved with a new system being put into place. This has decreased instances of ash leakage significantly.

- An improved regenerant wash water accept/reject system was implemented. The implementation of a water recovery system is the next objective.
- The plant has averaged 91% ash removal, with a significant improvement being experienced during recent runs. The design target was 90%.
- The de-ashed product colour has averaged 899 ICUMSA units. The design target was 1000 ICUMSA units. The feed colour varies between 7000-10000 ICUMSA units.
- Inversion across this plant has not been measured consistently, but the few measurements taken have indicated an inversion of between 40-50%.
- Problems with air in the system have been experienced, and significant effort has gone into the installation of air bleeds at the required exit points.

Batch ion exchange (polishing), inversion
This process proved difficult to control due to the initial ash leakage being experienced across the de-ashing plant. A polishing application generally runs at a high treatment ratio, thus resin
volume is reduced for the same throughput. The treatment ratio can be defined as the volume of syrup that can be passed through the resin before the resin gets fully loaded, divided by the volume of resin. Due to the higher than expected ash input, this plant loaded up much faster and resulted in ash leakage onto the inversion resin. This resulted in lower than expected inversion. Due to this operation being operated in batch mode, the unplanned regenerations put stress on the throughput targets of the plant. The de-ashing process was then optimised further, which resulted in lower ash levels being passed onto the polishing resin. This resulted in the polishing and inversion plants producing on-specification products.

- This section of the plant has since averaged >95% ash removal.
- The product colour out of the polishing section has averaged 111 ICUMSA units.
- The colour removal has averaged 87%.
- The inversion obtained has averaged 92% inversion.

**Batch resin decolorisation**

This section of the plant is also operated in batch mode. Due to the good colour removal results being obtained across the de-ashing and polishing plants, this plant has been able to achieve its required duty easily. During instances of higher colour out of the polishing plant, this plant has been able to reduce the colour to below the specification colour of less than 120 ICUMSA units.

The intention is to reduce or even eliminate GAC from the process. This, however, does not seem to be sustainable at present, possibly due to the variation in types of colour bodies coming through the process. The process needs to be robust enough to cope with the varying characteristics of the colour bodies being removed. There have been sustained periods where GAC is not required; however, this is not always the case. More optimisation work will continue in this section with the aim of removing the last 20 units of colour, thus eliminating the need for GAC.

**Granular activated carbon**

The GAC plant has produced a liquid sugar of 75 ICUMSA units average colour. The colour specification as shown in Table 2 is <100 ICUMSA units. It is therefore believed that further optimisation work on resin decolourisation would result in the elimination of GAC or, at the very minimum, the use of GAC only in instances of high colour that the resin cannot remove. The GAC plant is split, with one bottle placed before the falling film evaporator and one after.

**Conclusions**

The process described in this paper has been proven to be able to produce a high invert liquid sugar from return syrup that meets the stipulated product specifications. The de-ashing plant has consistently produced on-specification de-ashed product. Initially, the ash leakage from the de-ashing plant placed an extra load on the polishing plant, which resulted in lower inversion being experienced. This was rectified by optimising the regeneration wash recycle streams and since then the polishing and inversion plant has also produced on-specification product. The decolourisation across the polishing plant has been higher than expected, thus reducing the load on the decolourisation plant. However, due to the variation in colour bodies that could be experienced it was felt that the process needs to be robust enough to cope. The
resin decolourisation and GAC plants therefore remain online. The final product has thus consistently been produced on specification.

For Huletts Refinery, the production of liquid sugar from refinery return syrup is a commercially viable process relative to its current capability to recover and recycle the raw sugar. The benefits are from full sugar recovery (including invert), savings in steam and other costs related to crystallisation versus the treatment cost to purify refinery return syrup to liquid sugar. The experience thus far has shown that the commercial assumptions made in the design process are achievable. However, further experience with the process and optimisation are still necessary to make a final conclusion based on long term data.

Future work will include optimisation of the resin decolourisation plant, with the intention of eliminating or reducing the GAC requirements. It would also be ideal to be able to switch on the GAC plant only when variations in colour bodies occur that require GAC treatment for removal.

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REFERENCES


