

REFEREED PAPER

FINE LIQUOR COLOUR: HOW DOES IT AFFECT ENERGY, CAPACITY AND SUGAR LOSSES?

VAWDA AS, SARIR EM AND DONADO CA

*CarboUA Ltd, 9635 Cresta Drive, Los Angeles, CA, 90035, USA
avawda@carboua.com sarire@carboua.com andresdonado@carboua.com*

Abstract

In today's competitive sugar refining environment, refiners are spending more time and attention to improve their conversion costs. This means energy, maintenance and chemical usage are constantly being measured and improved. As sugar refining consists of a series of separation processes, any inefficiency has a knock-on effect on operating costs.

Impurity removal by separation and crystallisation are the most important process operations in a refinery. This paper studies the main separation processes, namely clarification, decolourisation and crystallisation to demonstrate where poor separation contributes to excessive costs of processing. The results of various tests are analysed and conclusions are made for refiners to manage their chemical and fuel costs.

Keywords: Colour removal, ion exchange (IX), high performance adsorbents (HPA), granular activated carbon (GAC), powdered activated carbon (PAC)

Introduction

Cost efficient manufacturing is a top priority in today's cost-conscience enterprise. It is now a norm to measure every aspect of cost in every unit operation. There is still a long way to go to fully integrate every cost aspect, the details of which extend further than raw and finished goods. The major conversion cost of raw sugar to refined sugar includes the following:

- Manpower
- Repairs and maintenance
- Utilities
- Packaging
- Sugar losses
- Depreciation.

By far the most important aspect is the understanding that in order to control it, one has to measure it. This means that full control of every production detail from raw goods to final product, is now vital to the profitability of the business. For the refinery manager, there are certain important items under his control which, if left unchecked, can eat up substantial profits and, occasionally, turn profits into losses. The most important item on this list is process control.

It is the process control, or the lack of it, which will determine the amount of fuel consumed and the tonnage of sugar lost.

The following areas will be discussed with respect to process control efficiency and the corresponding financial gain or loss:

- Affination
- Clarification
- Decolourisation

Affination

Affination is not practised in South Africa due to the use of VHP sugar as feedstock. Affination, where practised, is the first separation process in the sugar refining process. It is commonly applied to low pol raw sugar with a colour higher than 1800 ICUMSA (International Commission for Uniform Methods of Sugar Analysis). It entails the mingling of raw sugar with warm syrup, which dilutes the molasses coating around the sugar crystal to form magma. This magma is centrifuged to separate the crystals from the syrup, thus removing the greater part of the impurities from the input raw sugar and leaving the crystals ready for the next stage, melting.

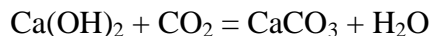
The control of the affination process is critical, as over-washing dissolves additional sugar which must be boiled multiple times at the recovery house before the sugar can be recovered again. Each time sucrose is dissolved, it is impossible to fully recover it all. This phenomenon is measured as recycle and it is the quantity of sugar passing through the melter in addition to the weighed raw sugar. Typically, about 50-60% colour removal is achieved across affination and a significant amount of ash and suspended matter removal is also achieved.

Clarification

Liquor clarification is essentially a pre-treatment for the decolourisation stage of sugar refining. The overall refining objective is the removal of turbidity, colour and ash. The two major processes are either carbonatation or phosphatation.

Description of the carbonatation process

The mechanism of carbonatation was described by Bennett (1974) in a series of experiments conducted in the 1970s. He demonstrated that the impurities are trapped within the growing calcium carbonate crystal.



The process consists of adding milk of lime (an aqueous slurry of calcium hydroxide) to the raw melt solution prior to it entering a reaction vessel. The amount of lime is in the range of 0.2-1.2% on sugar solids. Carbon dioxide gas is bubbled into hot liquor (75-85°C) in saturators, under controlled conditions of pH and temperature.

Description of the phosphatation process

The mechanism of phosphatation is primarily the flocculation of impurity particles. The majority of colloids in nature are negatively charged (anionic) and so the addition of cations like calcium neutralises these charges and allows flocculation to take place. Therefore anionic colour bodies are most effectively removed by this process, and some soluble colours are absorbed by the tri-calcium phosphate. The process consists of adding phosphoric acid to hot raw melt at 0.015-0.035% P₂O₅ on brix, then neutralising this with lime saccharate.

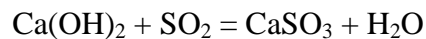
The reaction produces a precipitate of tri-calcium phosphate, to which is added a flocculant to coagulate it (Bennett, 1974):



The precipitate is very fine and is suspended in high density liquor which is difficult to filter; therefore, the liquor is aerated by dispersed air. The precipitate adheres to the air bubbles and is subject to flotation in a clarifier. The precipitate and other debris floating to the surface are scraped off as a scum.

Description of the sulphitation process

The mechanism of sulphitation is a reaction of sulphur dioxide with calcium hydroxide in the sugar solution to precipitate calcium sulphite. It is common to use absorption towers where limed liquor comes in contact with sulphur dioxide gas. Sulphur dioxide is usually produced in a sulphur burner fed with elemental sulphur.



The process incorporates colour in the precipitate and sulphur dioxide is a reducing agent which provides a bleaching effect.

Decolourisation

There are basically four types of decolourisation systems:

1. Granular activated carbon
2. Ion exchange
3. High performance adsorbents and powdered activated carbons
4. Bone char.

Activated carbon

The principal mechanism is that of adsorption. Activated carbon has an enormous surface area. Activated carbon colour removal relies on surface forces to adsorb colourants. (Dominguez and Hyndshaw, 1977). Activated carbon for sugar refining is made from bituminous coal and other vegetable material such as coconut shells. It is not specific and removes all colour including colour precursors, organics and odours. It requires a substantial amount of heat for regeneration thereby releasing gases to the atmosphere (Davis, 2001).

Ion exchange

Ion exchange resins used in the sugar industry as decolourisers are of the strong base anionic type, with quaternary amine functional groups. They are operated in the chloride form. There are two basic mechanisms for colorant fixation to strong base anions: (i) ion exchange resins, where ionic bonding between anionic colorants and the resin's fixed charges take place, and (ii) hydrophobic interaction between non-polar parts of the colorant and the styrene divinyl benzene resin matrix. Since most sugar colorants are anionic in nature, being charged negatively, strong base anionic resins are efficient decolourisers. However, both mechanisms can affect the same colorant molecule in amplified ionic binding.

Adsorption of sugar colorants to ion exchange resins are governed by:

- Colorant molecular weight
- Charge density
- Type of charge (highly anionic, weakly anionic, amphoteric or weakly cationic)
- Degree of hydrophobicity
- pH
- Ionic strength of the medium.

Resins are regenerated by desorption using a 10% NaCl solution (for acrylic type resin) or a mixture containing 10% NaCl and 0.5% NaOH (for styrenic type resin). The NaCl solution dehydrates the resin, forcing out the exchanged and adsorbed colour bodies (http://purolite.com/customized/uploads/purolite_sugar_cane%20111909%20final_js.pdf). Resin regeneration results in the pollutant being released.

High performance adsorbents (HPA)

Similar to powdered activated carbon (PAC), the principal mechanism is that of adsorption. PAC has an enormous surface area and complex porous structure that provides very good adsorption properties. HPA presents improvements against regular PACs, from structure to raw material and activation methods.

While regular carbons have surface areas of 800-1200 m²/g, HPA typically has a surface area of 1200-1700 m²/g (or more, depending on the case). Additionally the pore structure is especially designed to have the proper configuration (ratio between 'micro' and 'meso' pores) to allow more efficient adsorption in sugar solutions.

Another important difference between HPA and regular PAC is that HPA has integrated specific chemical groups to its surface, thus enhancing the capacity to remove other impurities that PAC has difficulties in removing. PACs are already highly efficient for removal of a wide variety of different colour bodies in sugar. With the advent of HPA (both carbon based and synthetic), the amount of impurities that can be removed is even more. This way, better colour removals have been achieved with HPA, or the same colour removal has been maintained but at much lower dosages (Donado, 2013).

The spent adsorbent is not regenerated, and is usually disposed of at a landfill site. It uses very little water and hardly any energy, therefore no pollution in the form of water or gases.

Bone char

Bone char is an adsorbent primarily made from cow bones. The bones are pyrolysed in the absence of oxygen at up to 700°C in a kiln. Regeneration takes place in kilns similar to granular activated carbon although at a lower temperature. Bone char is used in a sugar refinery as both a decolourising and de-ashing agent. The ability to remove ash is peculiar to bone char compared to granular activated carbon. The removal of ash is an advantage, as it reduces the level of scaling later in the evaporator and vacuum pan heating surfaces. Removal of contaminants occurs in the following manner. Firstly, species can become incorporated within the hydroxyapatite lattice substituting for Ca or CO₃²⁻. Secondly, species can interact with reactive groups on the surface of either carbon or hydroxyapatite (<http://www.sandia.gov/water/2005vendors/BrimacCarbonServices.pdf>).

Discussion*The cost of poor colour removal*

The previous paragraphs have covered two processes, clarification and decolourisation. Both processes have certain decolourisation efficiencies. If the final product is EU specification of maximum 50 ICU colour, the final colour of fine liquor has a financial implication, i.e. the cost of processing a fine liquor of ICU 500 colour will be much more expensive compared to a fine liquor of 100 ICU colour.

Experimental procedure to determine sugar colour at different wash % massecuite

The following work was done at refineries in Africa and Europe. Most of the work was conducted at a large sugar refinery in the Middle East and some of the data was collected from two other refineries, where high fine liquor colours were available.

From a set of nine Silver Weibull 1500 centrifugals, sugar is discharged into a screw conveyor arranged to move sugar in two directions towards two inclined screw conveyors. Wet sugar samples were extracted at strategic points. The samples were taken according to a pre-set wash water setting. The samples were analysed for ICUMSA colour.

The results showed a general relationship $y = 151.14x^{-0.479}$, where y is the sugar colour and x the wash time (Figure 1).

This was done using R1 massecuites between 450 and 550 ICU. In this particular case, the colour bottomed out at around 35 ICU indicating no further benefit beyond 2.5% wash on massecuite.

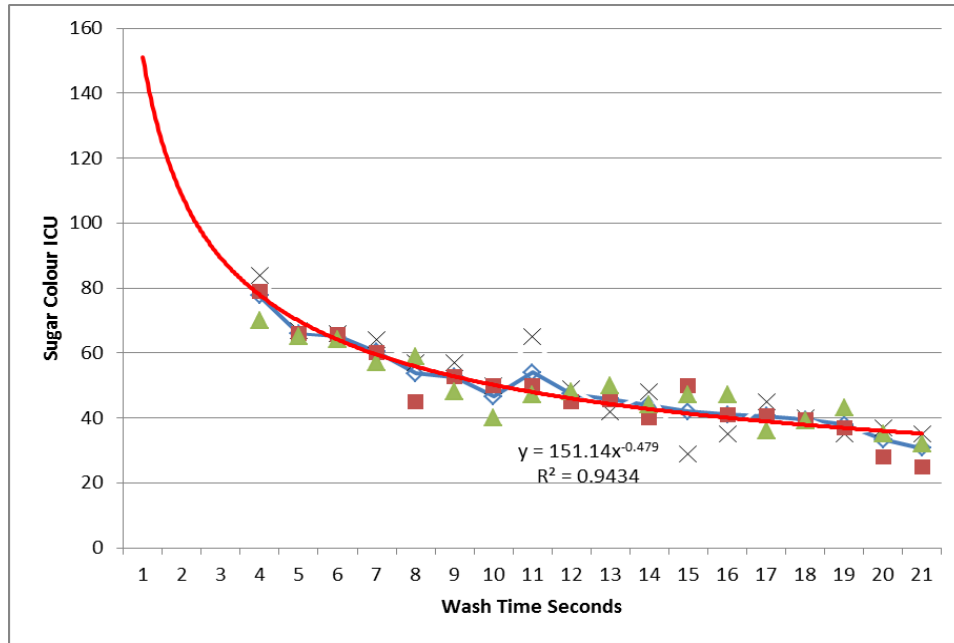


Figure 1. Sugar colour vs Wash for Massecuite between 450 and 550 ICU.

Figure 2 shows the wash water usage for massecuite of different colours, collected from various refineries.

The wash times were converted to volumes based on the centrifugal manufacturer’s nozzle data. The various refineries had different massecuite colours and the wash water consumption data was collected noting the massecuite colours. The refineries were all targeting EC colour specification between 35-45 ICUMSA colour units.

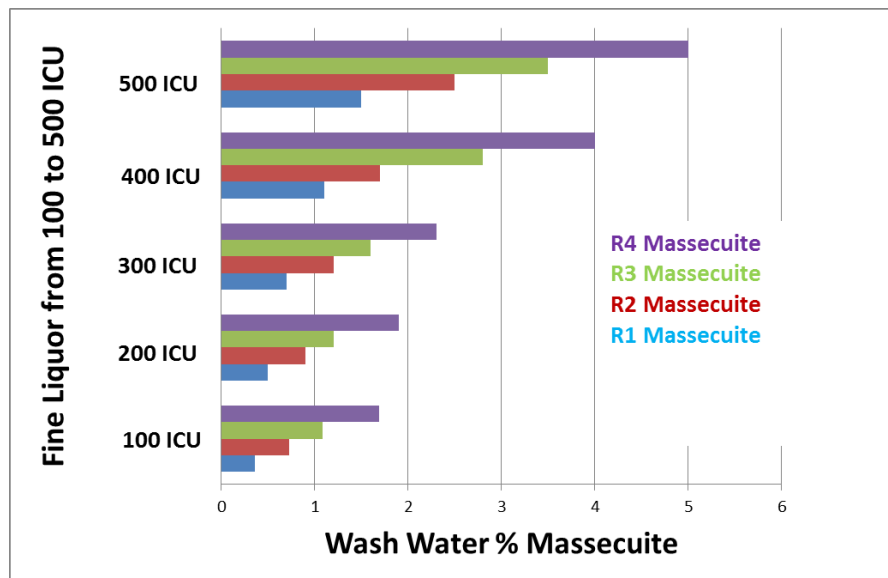


Figure 2. Wash time required for different massecuite colours.

The negative impact of high colour and high washing inside the centrifugal

While crystallisation is a very efficient separation process, over-washing can undo the good work done in the pans. The colour is basically distributed in three different regions of the crystal (personal communication¹).

On the *surface* there is a layer of mother liquor. When this is washed off the crystals, this layer will be reduced gradually and the colour will decrease and asymptotically approach the average colour of the two next regions.

Crystal surface. Here the colour does not change much. Once the surface layer has been washed off, further washing will change the colour very slightly.

Kernel. Here there is a smaller or larger amount of colorants, depending on the seeding and start of crystallisation.

Sucrose is highly soluble in water, and the solubility increases with temperature.

Charles (1960) experimentally determined the solubility of sucrose in water and derived the following equation:

$$C = 64.397 + 0.0725T + 0.002057T^2 - 9.035 \times 10^{-6} T^3$$

where

C = % sucrose in the saturated solution

T = temperature (°C).

The solubility of pure sucrose is often expressed as the percentage of dissolved solids by weight, but for purposes of comparison of the solubility, the ratio 'sucrose to water' is preferable. This relationship generally means parts of sucrose per 100 parts of water and is referred to as the number of solubility.

This equation was used to compute the sucrose dissolved in wash water at actual temperatures measured at the molasses receiving tank located below the centrifugal station. Using the volume of wash water consumed, a spreadsheet was created to compute the water usage, the sucrose dissolved and the energy required for evaporating the water. A summary of this is shown in Table 2 using the cost assumptions shown in Table 1.

¹ B. C. Nielsen, Neltec, personal communication, April 2014.

If we make the following assumptions, the cost of high fine liquor colour can be computed.

Table 1. Assumptions for this model.

Item	Value
Refinery capacity tpd	1000
Sugar colour ICUMSA	40
Steam cost per metric ton	USD 15
Water cost per m ³	USD 1.1
Sugar per metric ton	USD 500
Number of white boilings	4
Refinery overall yield	97%
Centrifugal capacity (kg)	1750

Table 2. Summary of the theoretical annual consumption of water, steam and sucrose loss.

Fine liquor colour (ICU)		100	200	300	400	500
Wash % massecuite*	%	3.9	4.5	5.8	9.6	12.5
Water usage	m ³	2 603	3 871	5 173	8 198	11 061
Sucrose dissolved	tons	9 206	13 694	18 298	29 000	39 127
Cost of steam	\$/ton	40 856	60 773	81 201	128 696	173 638
Cost of water	\$/m ³	2 863	4 258	5 690	9 018	12 167
Cost of sucrose loss**	\$	138 094	205 415	274 462	434 997	586 901
Total cost	\$	181 813	270 447	361 353	572 711	772 706

*Total of all centrifugal wash water on R1, R2, R3 and R4 massecuites.

**Based on the assumption that the total crystallisation process yields 97%.

Options for improving colour removal

All conventional colour removal processes have different operating costs, capital costs, process effectiveness, ease or complexity of operation and environmental issues.

There are two areas where colour removal can be enhanced, clarification and decolourisation. Typical colour removal in the clarification station ranges from 25-50% while decolourisation stations can remove between 65-85% additional colour. Both these numbers can be improved upon by the use of adsorbent technology.

In the case of improving colour removal in phosphatation processes, there are several high performance adsorbents available to add to the liquor stream. Some of these are added at the melt stage to enhance phosphatation colour removal, while others are added after the clarifier.

In the case of improving colour removal in the carbonatation process, there are also several specially engineered high performance adsorbents that may be added to the post carbonatation liquor, i.e. at the filter supply tank.

In both cases, the adsorbents are available in liquid and solid forms; some are carbon based while others are synthetically made.

High performance adsorbents (HPAs) can combine different purification mechanisms such as adsorption, occlusion, coagulation, adsorption and oxidation. In most cases colorants are physically removed from the process. As the spent adsorbent is not regenerated, but disposed of, it is very important to note that HPA requires much lower dosages than traditional PAC and colour precipitants, thereby making it cost effective (Donado, 2013) An example of colour removal conducted in the laboratory is shown in Figure 3.

A sample of filtered carbonated liquor was subjected to progressive dosages of HPA to reach low liquor colours in the approximate range of 300 to 500 ICUMSA. The experimental procedure is shown in Appendix 1.

In Figure 3, it can be seen that starting with filtered carbonated liquors of 1140 and 755 ICUMSA, respectively, the liquor colours are shown to be reduced by the progressive application of the adsorbent, to 490 and 285 ICUMSA, respectively. It can also be seen that there is a good correlation between the dosage of adsorbent and the corresponding liquor colour.

Excessive washing in centrifugals is the cause of the following problems:

- Less sugar directly to the silo
- Smaller crystals due to dissolution
- Loss of sugar to molasses due to repeated re-crystallisation
- Loss of sugar to inversion (undetermined loss) due to recycling of sucrose
- Increased energy consumption due to reprocessing and evaporation
- Loss of process capacity due to high recycle.

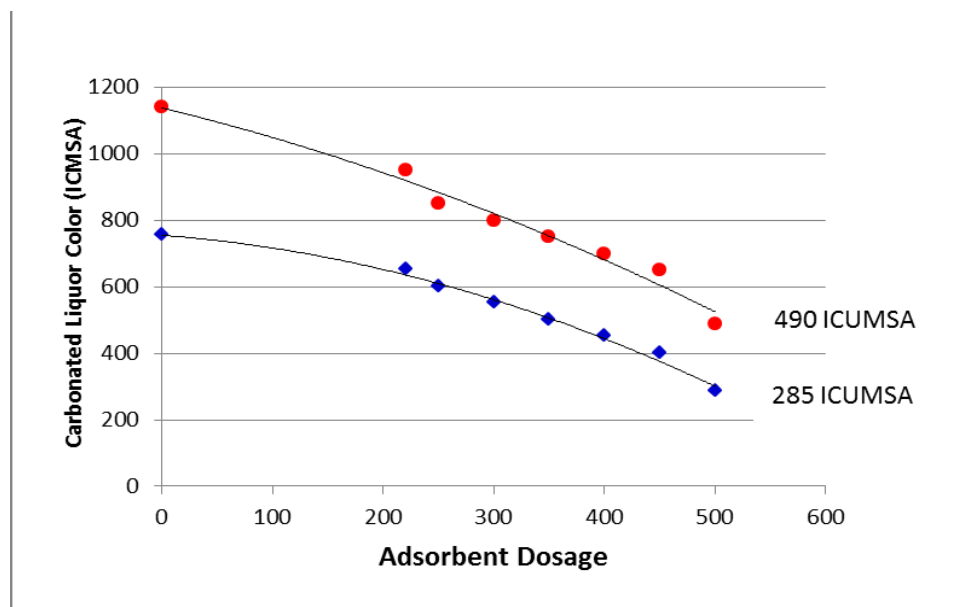


Figure 3. Dosages of adsorbent to reach 490 and 285 ICMSA units.

Using the spreadsheet, data was computed for a 1000 tpd refinery comparing the utilities required for fine liquor at 100 against 500 ICUMSA. The results are summarised below:

One day:

85 metric tons of sugar is dissolved daily, which could have been sent to the silo.

24 m³ additional water is used daily.

24 metric tons of additional steam is used daily.

2.1 metric ton of additional sugar lost into molasses daily.

One year:

29 750 metric tons of sugar is dissolved annually, which could have been sent to the silo.

8 400 m³ additional water is used annually.

8 400 metric tons of additional steam is used annually.

735 metric tons of additional sugar lost into molasses annually (0.46%).

One year costs:

Water cost additional \$9 240 per year.

Extra heating and evaporation cost \$126 000 per year.

Sucrose lost to molasses \$367 500.

Conclusion

This paper has shown that poor decolourisation comes at a significant cost by demanding excessive amount of centrifugal wash water. An attempt has been made to show the economic impact of high wash water consumption. Refineries should strive to maximise their colour removal processes and use process aids where justifiable. A study should be conducted where the sugar loss is measured at different wash water % massecuite by actual weighing of the sugar discharged from the drier.

REFERENCES

- Bennett MC (1974). Physical chemistry of phosphatation and carbonatation. *Int Sug J* 69: 68-73.
- Charles DF (1960). Solubility of pure sucrose in water. *Int Sug J* 62: 126-131.
- Davis SB (2001). The chemistry of colour removal. *Proc S Afr Sug Technol Ass* 75: 332.
- Dominguez, A.R. and Hyndshaw, A.Y. (1977). Activated carbon for refining sugar. *Proc. Int. Soc. Sugar Cane Technol.*, 16: 2645–2656.
- Donado CA (2013). High performance adsorbents for liquid sugar manufacture. Internal Report, CarboUA Ltd, Los Angeles, CA, 90035, USA. pp 2-3.

Appendix 1. Laboratory test to evaluate colour removal: Carbonatation liquor

Measure 500 mL of fresh hot carbonatation filtered liquor into two 1000 mL glass beakers.

One is the control and the other is for testing.

Measure and record the initial temperature, pH, conductivity, brix and colour.

Add the required amount of adsorbent.

Heat to 75-85°C and stir continuously for 20 minutes.

After 20 minutes, use a coarse filter paper to separate the carbon from the liquor, thus ceasing further adsorbtion.

Analyse and report data in the table below:

Adsorbent	0 ppm	500 ppm	1000 ppm	
g/500 mLs	0	0.21 g	0.42 g	
Time (min)	0	20	20	
Temp (°C)				
pH				
Conductivity				
Brix				
Colour				

Calculation of ppm

ppm: mg of adsorbent per kg of sugar solid in solution.

At 65 Brix, 1000 mL of liquor contains $1000 \times 1.3 \times 0.65 = 845$ g of sugar.

500 ppm is 500×845 g/million = 0.42 g.

0.21 grams per 500 mL liquor (500 ppm)

Maintain beaker at 75-85°C and stir continuously.