The HPA System
A Simple Effective and Low Cost Decolourization System

Vawda, A.S, Sarir, E. M, Donado, C. A.
Presented by: Raja Khalique Hussain (Techniques Ltd)
CarboUA Ltd, 9635 Cresta Drive, Los Angeles, CA, 90035, USA
avawda@carboua.com, sarire@carboua.com, andresdonado@carboua.com

Abstract

Colour removal is one of the most important unit operations in sugar refining. Over the years, there has been a shift from one process to another. In the last three decades mostly ion exchange and granular activated carbon plants have been installed. However, a number of powdered activated carbon (PAC) plants have been established and their conversion to high performance adsorbents (HPA) has steadily increased. This paper describes the High Performance Adsorbent System and compares it with three other processes:

These processes are examined under the following subjects:

Capital cost
Operating cost
Decolourization Effectiveness
Process Flexibility
Environmental impact

The paper shows the principles of operation, highlights the advantages and dis-advantages, and provides a picture of the material and energy balance of three processes.

Keywords: Ion Exchange (IX), High Performance Adsorbents (HPA), Granular Activated Carbon (GAC), Powdered Activated Carbon (PAC) , colour removal, energy efficiency.

Introduction

The purpose of decolorizaton systems in a sugar refinery is to prepare the pan feed to a colour that would easily produce the final sugar colour to the required specification while employing the desired number of crystallization stages. Typically, a pan feed of between 150 to 250 ICU comfortably allows for four crystallization stages to produce a sugar colour between 35 – 45 ICU. Depending on the colour of the raw sugar and the choice of the primary clarification process, the feed colour to the secondary de-colourization process is usually between 500 – 1000 ICU.

There are several de-colourization systems currently in use:

1. Bone char
2. Granular Activated Carbon
3. Powdered Activated Carbon and High Performance adsorbents
4. Ion Exchange

Bone Char (BC)
Bone char is an adsorbent primarily made from cow bones. The bones are subjected to pyrolysis 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 both as a decolourising and a de-ashing agent. The ability of bone char to remove ash is peculiar to bone char compared to other decolourizing systems. . The removal of ash is an advantage, as it reduces the level of scaling later in the evaporator and vacuum pan heating surfaces. Removals of mineral content occur mainly by ion exchange on the hydroxyapatite lattice structure, substituting for Ca or CO_3. Secondly, species can interact with reactive groups on the surface of either carbon or hydroxyapatite.[1]

Granular Activated Carbon (GAC)
The principal mechanism is that of adsorption. Activated carbon has an enormous surface area. Colourants are physically adsorbed onto it by several forces, mostly Van Der Waals and London forces. Activated carbon for sugar refining is made from bituminous coal and other vegetable material like coconut shells. It is not impurity specific and removes all colour including colour pre-cursors, organics, odours etc. It requires substantial amount of heat for regeneration thereby releasing gases to the atmosphere[3].

Powdered Activated Carbon (PAC) and High Performance Adsorbents (HPA)
Powered activated carbon is made from a variety of vegetable and fossil fuel products. Powder activated carbon (PAC) has an enormous surface area and complex porous structure that provides very good adsorption properties. High Performance Adsorbents are similar to Powdered Activated Carbon, the principal mechanism is that of adsorption. HPA, however, presents improvements against regular PACs, from structure of raw material and activation methods.

While regular carbons has surface area of 800 – 1.200 m^2/g, a HPA is typically 1.200 – 1.700 m^2/g (or more, depending on the case). Additionally the pore structure is especially designed to have a better 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 to remove. PACs are already highly efficient for removal of a wide variety of different colour bodies in sugar. With the advent of HPA (Both types carbon based or synthetic), the amount of impurities that can be removed is even more. This way, better colour removals have been achieved with HPA or it maintains the same colour removal but at much lower dosages.[4] The spent adsorbent is not regenerated, but disposed of. It uses very little water and hardly any energy, therefore no pollution in the form of water of gases.

Brief Description of PAC and HPA Operations.
The de-colourization is effected by reacting the clear melt with PAC or HPA in a stirred tank for a minimum of 20 minutes. Powdered adsorbent is added at a rate of 400 – 1800 ppm together with body feed (Filter Aid) of the same concentration. The hot slurry is filtered through a

pressure filter or a plate and frame filter press. The de-colourized liquor will be collected in a fine liquor tank ready for evaporation. The adsorbent and filter aid is removed from the filter, after completing the duty cycle, which is normally of 5-10 hours; Five hours for PAC and 10 hours for the HPA. The filter is de-sweetened by back flushing with hot water. Depending on the type of filter employed, the cake can be disposed of wet or dry. The efficacy of HPA is different when fed with phosphatation clarified or carbonatation liquor. It has been observed that for the same colour duty, more carbon is demanded by phosphatation clarified liquor. (Activated carbon is not selective; color removal efficiency varies as function of other impurities present in the liquor to be treated. This can happen in both phosphatation and carbonatation refinery. It appears to be less obvious in carbonatation because carbonatation is a more efficient remover of impurities, so carbon can "focus" more on colour removal)[5]

Ion Exchange (IEX)

Ion exchange resins used in the sugar industry as de-colourizers 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 anion. Ion exchange resins: ionic bonding between anionic colorants and the resin's fixed charges, and hydrophobic interaction between non-polar parts of the colorant and the styrene di-vinyl benzene resin matrix. Since most sugar colorants are anionic in nature, being charged negatively, strong base anionic resins are efficient decolourizers[6].

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 exchanged and adsorbed colour bodies out[6]. Resin regeneration results in the colourants being released.

Capital Cost

Based on CarboUA experience in various plants around the world, data has been compiled to compare capital costs. The capital cost data used is about 7 years old and no capital price was obtainable for a bone char plant. However, due to the extra equipment of a bone char plant, multiple columns, sweet water evaporators etc, a modest factor of 10% above the capital cost of GAC.

The capital cost of GAC and char is higher than that of ion exchange, while the PAC or HPA plant is much cheaper. The information below illustrates the approximate capital cost of all four processes.

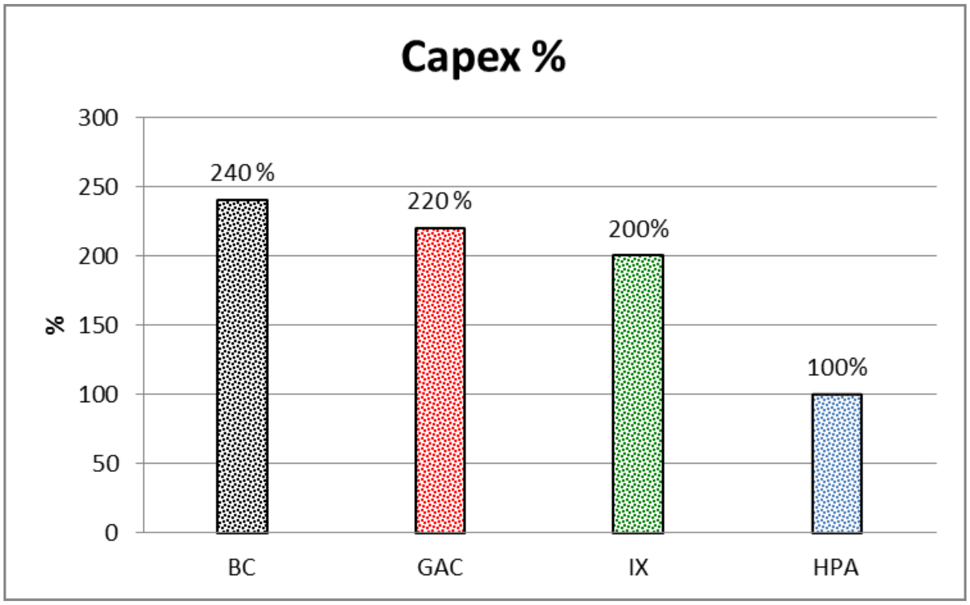

Figure 1. Capital cost comparison of all decolourization systems

The capital cost is also influenced by the size of the installation with bone char and GAC having the biggest foot print. Bone char and GAC also has a significant material handling system to transport the adsorbent to and from the kiln.

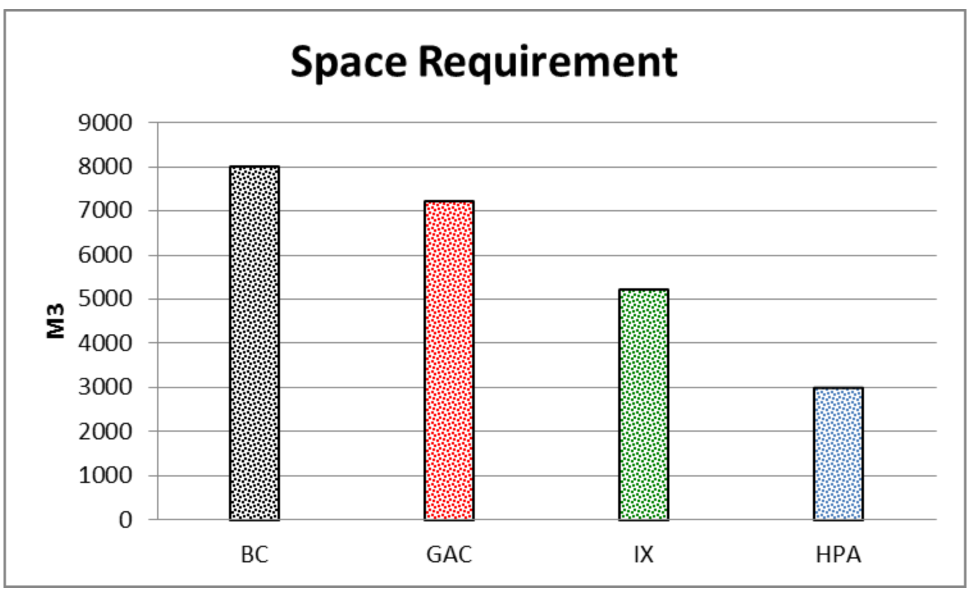

Figure 2. Space requirement of the various de-colourization systems

Comparative Operational costs

The operational cost of these processes mostly depends on the price of fuel, carbon, char, resin and salt. There is also the cost of waste disposal, repairs and maintenance. Comparison is also made difficult with the price of fuel and also the environmental regulations in different countries.

For the purposes of this report, we have conducted a cost comparison with the following criteria:

Clarified liquor colour: 600 ICU
Fine liquor colour : 150 ICU

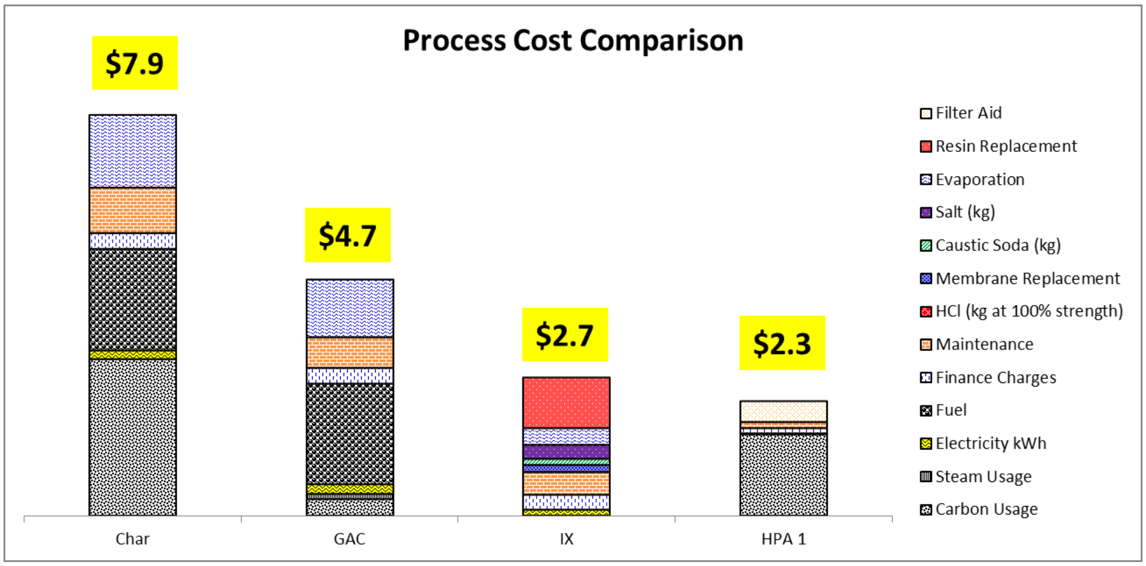

Figure 3. Operating cost comparison for all four processes in USD/MTRSO

The above comparison uses best quality consumables and international fuel prices, and the highest environmental standards. Kiln emissions and brine recovery systems all add to the capital and operating costs and since different countries have different standards; these can differ and thus influence the final capital and operating costs. Energy prices differ in different regions of the world[7].Such variations, like the cheap energy costs in the Middle East narrows the operational cost between GAC and IEX quite significantly.

For Char and GAC, besides adsorbent make up and reactivation, there is an additional cost of evaporating sweet water. Char has far more sweet water than GAC due to the higher adsorbent inventory and shorter cycle time. The cycle time for char columns is between 3 – 5 days[8]. Char inventory is typically 0.45 – 0.5 m3/MTRSO while GAC is 0.3 – 0.4 m3/MTRSO.

Decolourization Effectiveness

The first effluents from any of the four processes are very low in colour, often less than 20ICU. It is however, the average over the full cycle that has been considered for the comparison.

Carbon is not specific for any type of colour, but gives high overall colour removal 80 – 85% due to its enormous surface area. Direct comparison by carbon and bone char conducted at C&H in the 60s showed clearly the superiority of GAC over bone char with regards to colour removal. Both stations were run for 25 days in parallel, colour removal for carbon averaged 42% while the char filters averaged 30%. To maintain over 40% colour removal the char filters would have had only a 3 day cycle[9].

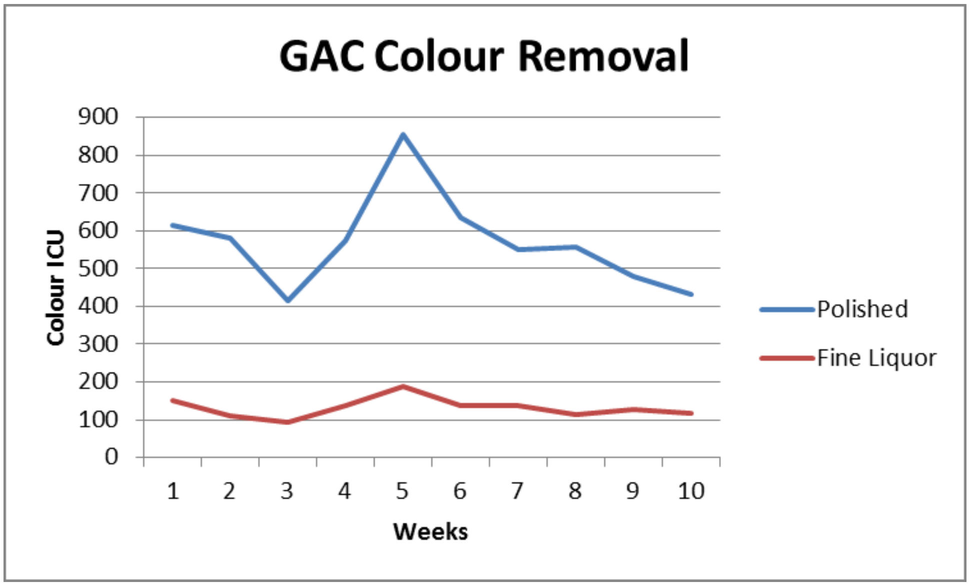

Figure 4. Typical Granular Activated Carbon two pass column colour removal data

IEX resins of the strong-base anionic type, with quaternary amine functional groups works slightly better when coupled with carbonatation compared with phosphatation. The reason for this is that the phosphatation process relies heavily on quaternary ammonium type decolourants, and they compete with IEX for the same colourants. IEX resins typically deliver colour removal of 65 – 70 when coupled with phosphatation, and 70 – 75% when coupled with carbonatation.

A case study of IEX performance in 2002 has been examined. Clarified liquor from a carbonatation refinery was de-colourized by being passed in series through two stages of acrylic ion exchange resin. The plant consists of five pairs of vessels of which four are on de-colourizing duty, with one being regenerated at any one time. The total cycle length is 30 hours, comprising 24 hours on de-colourizing and 6 hours for regeneration. The total colour removal was 56.7%

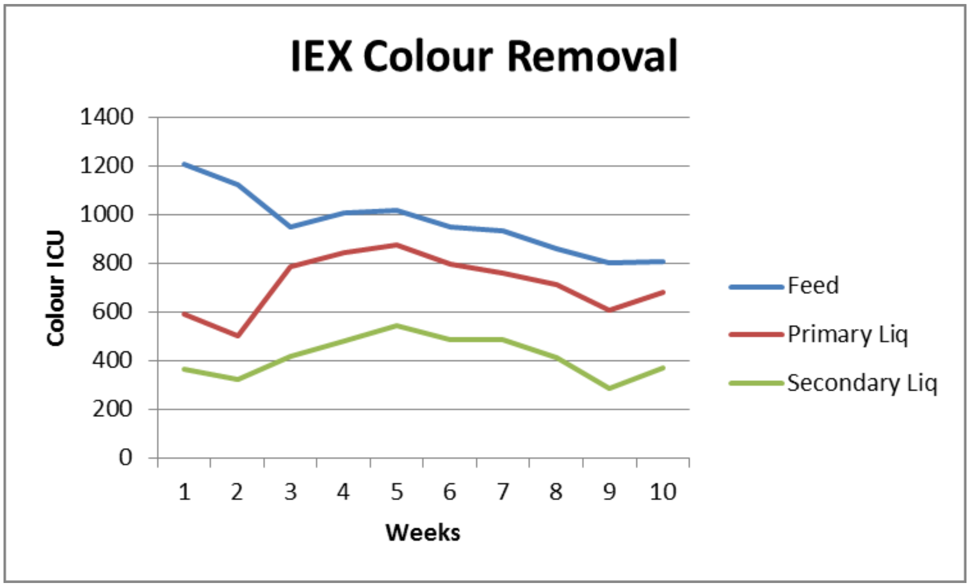

Figure 5. Typical ion exchange two pass colour removal data

Experience using HPA shows that the carbon consumption for phosphated liquors is 16.6% higher, than for carbonated liquors. The reason for this is not known. It is believed that carbonatation being the more effective clarification process, offers less impurities for the carbon to load on.

Consider a case study from 2013, involving a plant operating a HPA filter system serving clarified phosphate liquor and using HPA at 1200 ppm. The PAC removal data from 2009 is shown in figure two, while the 2013 HPA data is shown in figure three. The PAC consumption averaged 1800ppm. Filter aid is added 1:1 with both the adsorbents.

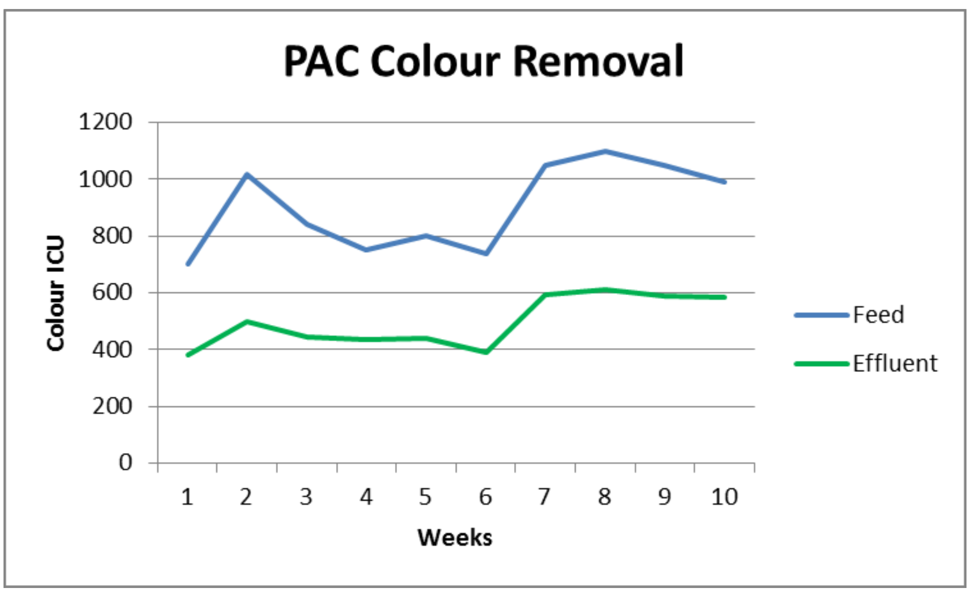

Figure 6. Typical PAC de-colourization performance

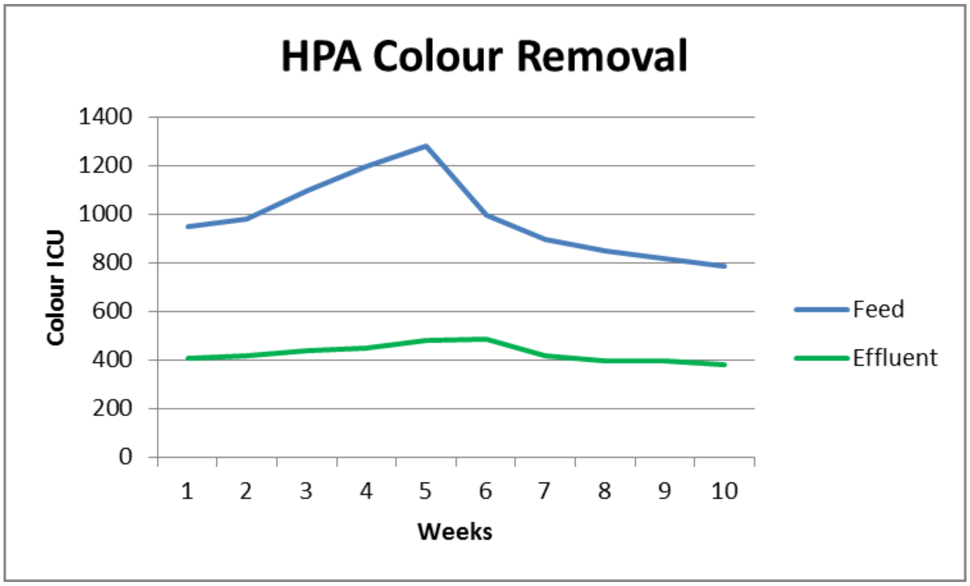

Figure 7. Typical HPA de-colourization performance

Despite the fact that the HPA and PAC were dosed at 1200ppm and 1800ppm respectively, the % colour removal for the ten weeks period assessed, was 56.3 and 45.0 respectively. Also the longer cycle time of the HPA resulted in significant savings in filter aid.

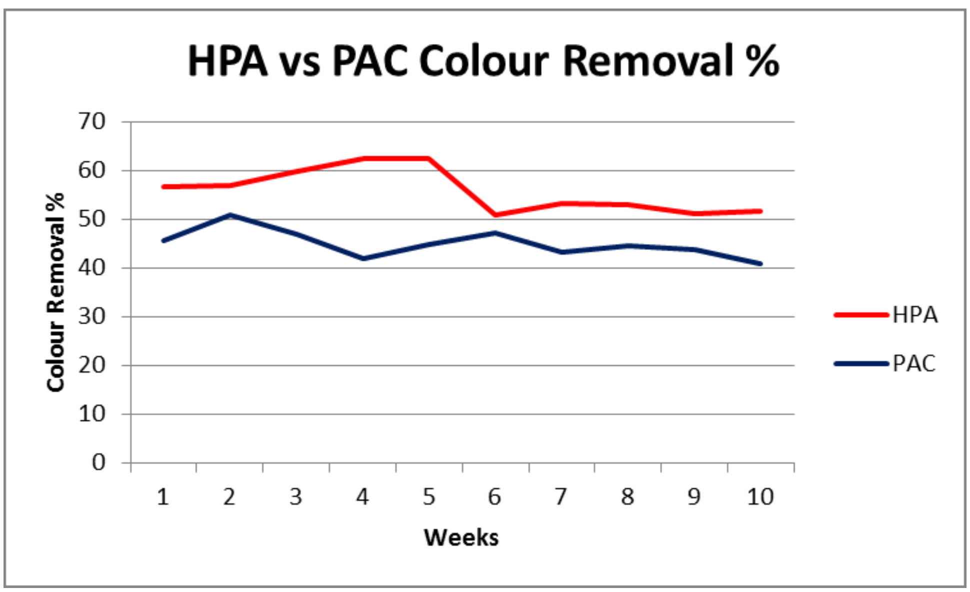

Figure 8. Performance comparison between HPA and PAC de-colourization capability

Process Flexibility

Process flexibility can be defined as the ability to deal with both foreseen and unforeseen changes in operational demand by varying the de-colourizing capacity to deliver the desired fine liquor colour.

The performance of the bone char plant is determined by both ash removal and colour removal. Changes in either parameter will affect the process; hence the bone char plant has a limited flexibility. GAC on the other hand is geared for colour removal only, hence it has greater flexibility.

Ion exchange is moderately flexible as it can be affected by solids carry over from the clarification system or by big changes in pH or ash.

The HPA or PAC has the highest flexibility. It has a high versatility because the dosages can be adjusted according to the colour removal needs. Neither changes in brix, ash or pH affects its performance. The high surface are of the carbon allows it to work very strongly at small doses.

Environmental impact

Both bone char and GAC employ kilns to regenerate the adsorbent. Environmental regulations vary quite widely from region to region, but essentially the target is to minimize any negative effect to the environment. Cyclones, wet scrubbers and fabric type systems have been used but the most effective still remains the afterburner system which incinerates any carbon dust emission. Unfortunately, this system consumes energy, up to 40% of the total energy required to fire the hearth. The remaining concern is the CO_2 emission which is a direct consequence of using gas or diesel as a fuel.

With IEX, the problem is the disposal of the high coloured, high BOD effluent after recovering the salt using nano filtration. There are two novel systems that have been reported by Rousset [10] using atmospheric pre-concentration using waste heat, and another process has been described by Srivastava[11] which employs a falling film evaporator in conjunction with a scraped film drier.
A second waste product from IEX systems is the spent resin, which has to be disposed of at a special chemical waste disposal site for hazardous wastes.

Figures, 9, 10 and 11 show the mass balance of GAC, IEX and HPA plants of capacity 2000 tpd. By far it can be seen that the different stations produce different types and quantities of waste products. GAC produced slightly more liquid waste compared to IEX. The HPA plant produced the least amount of waste and is considered to be the most environmental friendly.

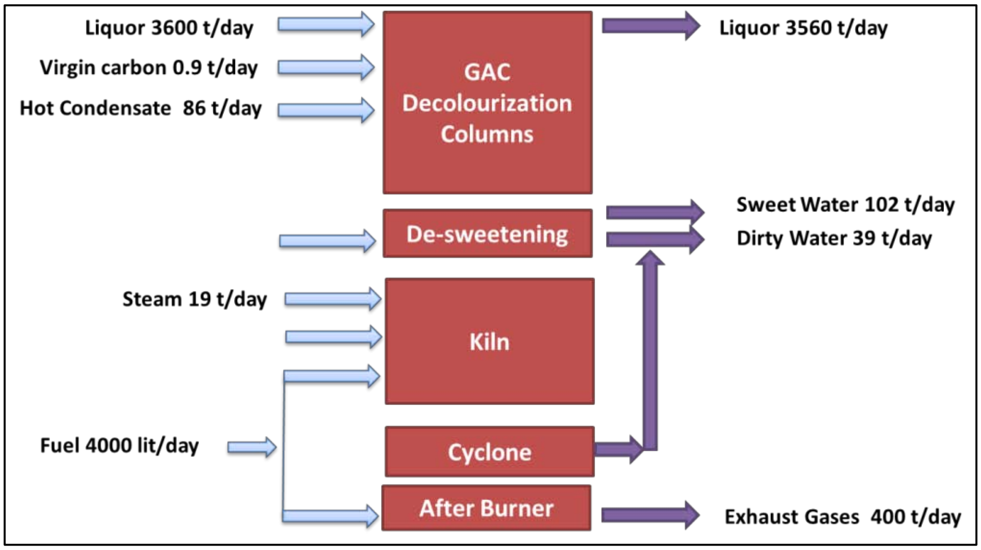

Figure 9. Typical mass balance of a 2000 tpd refinery using GAC (Adapted from Ahring6)

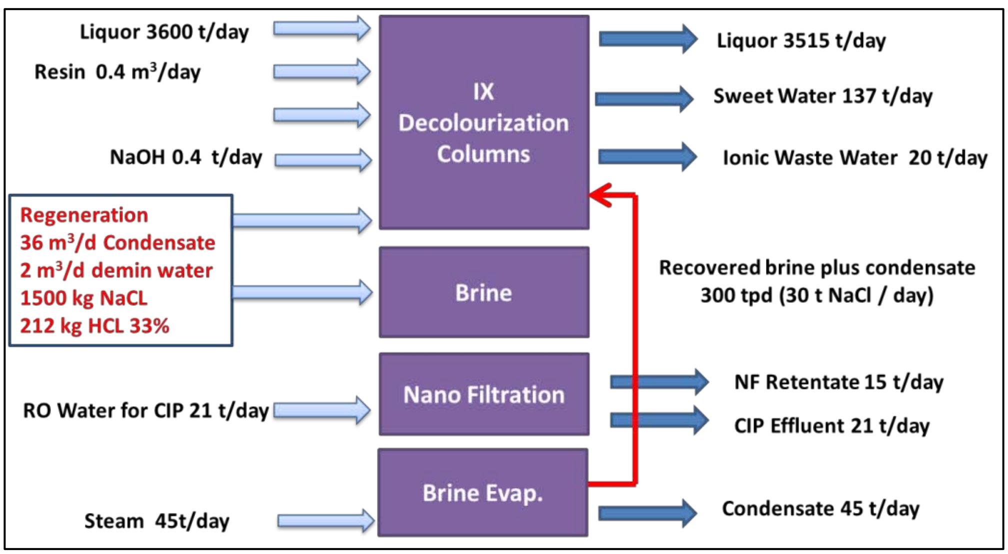

Figure 10. Typical mass balance of a 2000 tpd refinery using IEX. (Adapted from Ahring6)

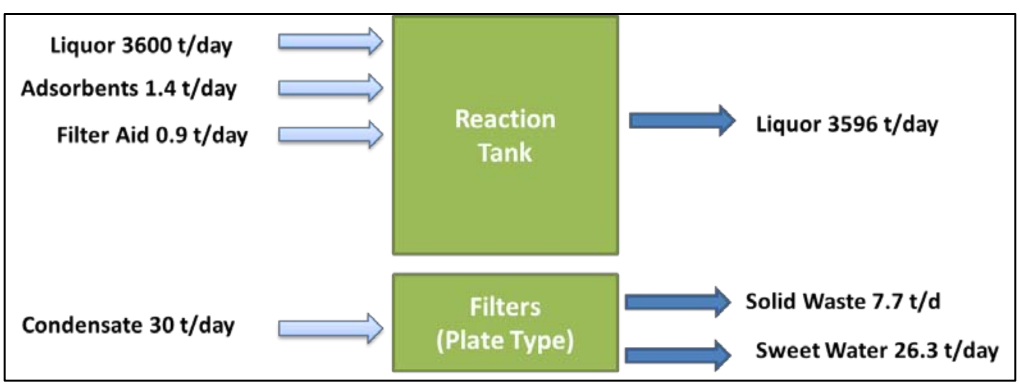

Figure 11. Typical mass balance of a 2000 tpd refinery using HPA

High Performance Adsorbent (HPA) Case Study

A sugar factory in South America has an attached refinery. The mill grinds 18,000 Tons of cane per day and the refinery produces 970 Tons of refined sugar per day.

The main stages of the refinery process are:

Melting station
Phosphatation Clarification
Treatment with Powder Activated Carbon
Press Filtration (Suchar Type Filters)
Evaporation
Straight Boiling scheme (4 strikes)

This refinery has two processes

1. Phosphatation
2. Powdered activated carbon (HPA)

The utilization of powder carbon (PAC) is a well-established purification method in sugar refining and sweetener processing. Its high purification efficiency and flexible method of application makes this technology highly suitable for sugar refinery.
After Phos-flotation process, clarified liquor is sent to the carbon reaction tank.
In this reaction tank, a carbon slurry (10-15% in water solution) is added continuously to the process to react with clarified liquor.
The amount of slurry (and therefore the dosage of carbon) is adjusted according the colour removal requirements. Filter aid is also added in the reaction tank at proportion of 1:1 PAC : Filter aid to facilitate the filtration and remove more turbidity.
The volume of the reaction tank allows a retention time of twenty minutes and the stirrer generates the necessary mixing action.
Once the HPA reacts and adsorbs the impurities, the treated liquor containing HPA and filter aid is filtered through a series of press filters. There is a secondary set of pre-coated filters functioning as safety filters.
The decolorized liquor is then collected in final liquor tank and a simplified flow sheet is shown in figure 12.

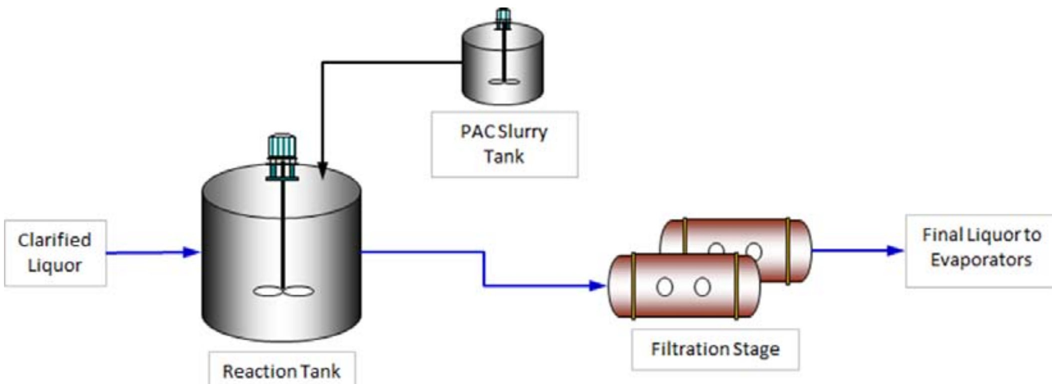

Figure 12. A simplified flow diagram showing the main components of the HPA system.

Table 1 shows the better colour removal when using HPA compared to PAC

	COLOUR PROFILE COMPARISON			MELTED Vs CLARIFIED		CLARIFIED Vs FILTERED		TOTAL (MELTED to FILTERED)	
	MELTED	CLARIFIED	FILTERED						
	IU	IU	IU	IU	%	IU	%	IU	%
HPA	920	572	269	349	37,74	303	53,02	652	70,79
PAC	917	619	253	299	32,37	365	59,08	664	72,46

The process is more cost efficient due to the reduction in the use of adsorbents and filter aid. It also produces better sugar quality due the removal of more than just the visible colourants, but due to the removal of colour pre-cursors. The refinery has also seen a significant drop in the colour rise across its evaporators.

Table 2 shows the improved final sugar colour and the reduction of adsorbents by 41%

	SUGAR	AVG CARBON
	COLOR	CONSUMPTION
	(IU)	(Bags / day)
Process with regular PAC	47	120
Process with HPA	36	70

Conclusion

This report conducted an investigation of all decolourization systems which include capital cost, operational cost, de-colourization effectiveness, process flexibility and environmental impact. The choice of a particular decolourization system is also dependent on local energy, financial and environment requirements. The HPA system has succeeded because of the new technology of patented adsorbents which has, increased plant efficiency and flexibility, and provided a low cost decolourization system for producing refined sugar of the highest quality. Recent work in the USA has also shown that fine liquor from activated carbon processes is far less likely to form acid beverage floc or transfer residual enzyme to the final sugar.

References

1. Anon, (2005) Brimac Bone Char. p5
2. Quigley, R (2014) Imperial Sugar, Personal Communication.
3. Davis, S. B. (2001). The Chemistry of Colour Removal. Proceedings of the 75th South African Sugar Technologists Association p332.
4. Donado, C.A. (2013) High Performance Adsorbents for Liquid Sugar Manufacture. CarboUA Internal Report, pp 2-3.
5. Donado, C.A. (2014) CarboUA. Personal Communication.
6. Anon. (2009) Cane Sugar Refining with Ion Exchange Resins. The Purolite Company pp 9.
7. Ahring, G. Emeis, R. (2011) Paper # 1038. Comparison of two different techniques for sugar liquor decolourization in a raw sugar refinery. Proceedings of the Sugar Industry Technologists Inc.
8. Merle, J.P. (1990) Color and Ash Removal through Carbon Adsorbents. Proceeding of the Sugar industry Technologist Inc.
9. Pennington, N.L. Patterson, R.S. (1961) Test use of Granular Carbon at C&H Sugar Refinery. Proceedings of the Sugar Industry Technologists Inc.
10. Rousset, F. J, Bhatt (2011) Conversion from Bone Char to Ion-Exchange Decolorization at the Lantic Sugar Montreal Refinery. Proceedings of the Sugar Industry Technologists Inc.
11. K. Shrivastava, A.K. Babu, R. Jain, D. and Rao, DSC. (2013)Spent Brine Recovery from Ion Exchange Effluent: The Environmentally Friendly De-colourization Option. Proceedings of the Sugar Industry Technologists Inc.
12. Cedano, C (2012) Direct Filtration of Clarified Liquor for Enhanced Process Throughput and Significant Chemical Reduction. Case Study in Central Romana Sugar. Proceeding of the CUA Refining Seminar in Thailand.