Understanding activated carbon reactivation and low-temperature regeneration technology

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Abstract

Activated carbon is one of the mainstay technologies for the decolorization of raw sugar to produce refined sugar products. This paper discusses issues relevant to the application of granular activated carbon in the sugar refining industries. The topics covered include evaluating the performance of recycled adsorbents, the evolution of activated carbon properties during initial activation and reactivation, and a review of analytical methods for measuring adsorption properties. The second half of the paper explores a new lower temperature process being developed for the regeneration of spent sugar decolorization activated carbon. In particular, the features and performance of this regeneration approach are evaluated against “high-temperature reactivation”, which is the dominant practice in the sugar industry today. The paper concludes with a discussion of the energy requirements and capital costs of low-temperature regeneration and high-temperature reactivation.

Introduction

The essence of sugar refining involves removing the non-sucrose impurities, which include both particulates and soluble contaminants, followed by crystallization of product from the mother liquor. While solid-liquid separation processes such as filtration and clarification remove the largest mass of impurities, the final purification is done by physical adsorption on a carbon-based material. Historically, bone char provided this final purification. Modern industrial options now include granular activated carbon, powdered activated carbon and ion exchange resin-based processes.

As summarized in the 11th edition of the Cane Sugar Handbook:

Decolorization is the key process in refining sugar. Of all the differences between raw and refined sugar, color is the one property that is immediately obvious and can be easily measured. ....

When a sugar chemist says “color” he means “colorant”, the material causing the color. ....

The decolorization process actually removes more than color because colorants interact with color precursors, colloidal materials, organic non-sugars, and ash-forming inorganic constituents so they are taken out with the color. (Carpenter, 1985)

While it often goes under-appreciated, decolorization actually encompasses the removal of spurious odor and taste compounds, in addition to visible color. Decolorization renders the granulated sucrose stable for long-term storage and reliably reproducible in a wide variety of food and cooking applications.

As noted above, the ultimate purification step in sugar refining is physical adsorption of the color bodies onto a carbon-based adsorbent, typically activated carbon or ion exchange resin. Physical adsorption implies that the color bodies transfer from the bulk solu-
tion into the internal surfaces of the adsorbent, but the color bodies remain chemically unchanged. While the effect of the adsorbent on the sugar solutions is conceptually straightforward, in that unwanted compounds are removed from the aqueous sucrose solution, the impacts and consequences of the adsorption step on the adsorbent are considerably more complex.

Once the adsorbent has accumulated its capacity for adsorbable compounds, it is termed “spent” and must be replaced with fresh adsorbent. Exiting the adsorption process, after sweetening-off, any spent adsorbent consists mainly of the original adsorbent and the accumulated color bodies.

One option for spent adsorbent is disposal after a single adsorption cycle. This is the typical industrial practice when using powdered activated carbon. While powdered activated carbon is probably the least expensive adsorbent to purchase on a unit-weight basis, disposal after a single decolorizing cycle generally results in higher operating costs than other adsorption media that can be regenerated and reused. Furthermore, the spent powdered media with color bodies represents a continuing environmental concern, since the color bodies are subject to biological degradation, which can lead to odor issues and water contamination concerns.

For granular activated carbon and ion exchange resins, regeneration and reuse is the industrial norm. It should be noted that regeneration speaks to the impact on the adsorbent – recovering some or all of the adsorption capacity – and does not specify the impact on the previously adsorbed color bodies.

In the case of ion exchange resins, the regeneration process desorbs the color bodies into another aqueous solution – and the disposal of this “spent regenerant” solution must be addressed. Depending on the local circumstances, the outlet may be a POTW (Publicly Owned Treatment Works), a dedicated on-site treatment capability or discharge untreated into receiving waters. While the last practice may be exceptionally cost-effective, the deterioration of the local waterways is often undeniable and unacceptable over the long term.

When granular activated carbon is utilized for color removal, the subsequent regeneration process typically results in the destruction of the color bodies. The most prevalent industrial practice is termed “high-temperature reactivation” and is usually performed in multiple hearth furnaces or rotary kilns. The process is called “reactivation” because the regeneration conditions mirror the original conditions utilized during the manufacture of the virgin activated carbon in the “activation” step.

Another option for the regeneration of spent granular activated carbon is termed “low-temperature regeneration” also referred to as “CarbOxLT” in the literature. This approach is a recently developed option that appears to have significant advantages over traditional “high-temperature reactivation” and these features will be explored later in this paper.

In order to explore the technical and operational considerations involved in the regeneration of spent granular activated carbon, it is necessary to develop a framework for evaluating the performance of a regenerable and reusable adsorbent. After establishing this framework for the current practice in the real world application of sugar decolorization, the performance advantages of low-temperature regeneration over high-temperature reactivation will be discussed.

**Understanding and evaluating the performance of recycled adsorbents**

Before delving into the specific differences in the regeneration options, it is useful to understand the interactions that occur between the effectiveness of the regeneration process and the make up rate of virgin activated carbon. The current industrial practice is to add virgin carbon to “make up” the amount of carbon in circulation to a constant volume, in order to keep the adsorbers full during the decolorization process. Hence, there is a tendency to consider the rate of
virgin carbon addition to be a measure of the total losses that occur during the regeneration process.

Unfortunately, this is misleading. Another significant loss during regeneration is the loss of adsorption capacity per unit volume of carbon. This loss is much harder to evaluate and generally is not measured during the routine operation of a carbon adsorption system. However, if this capacity loss were not occurring, then the “pool” of circulating carbon would have the same adsorption capacity per unit volume as virgin activated carbon – which is simply not observed in actual practice.

The circulating carbon pool generally exhibits 50% to 75% of virgin activated carbon capacity – based on testing of samples of industrial pool carbons. This loss of capacity phenomenon is not well documented in the literature, although it is discussed by Hutchins (1973) in an article comparing the performance of bituminous coal carbons to lignite carbons.

The capacity loss per cycle for an individual carbon particle depends on many variables, as discussed by Hutchins (1973). However, since the pool carbon consists of carbons added as make up over many cycles, the overall effect is a relatively constant loss of adsorption capacity per adsorption-regeneration cycle (due to the averaging of the different age carbons present).

This behavior can be modeled for a given circulating pool of activated carbon. One first assumes a prescribed loss of adsorption capacity per regeneration cycle. Then, one reduces the amount of material per cycle by the make up rate and then adds back of the same amount of virgin carbon. Repeating the process calculates the evolution of the adsorption capacity of the pool carbon for each regeneration cycle. By numerically calculating the effect of a large number of iterations, the steady-state properties of the pool carbon can be calculated. The results of such a simulation are shown in Figure 1.

Figure 1 shows some very interesting trends. For the hypothetical “perfect” regeneration, where the regenerated carbon is returned to virgin carbon adsorption capacity or a capacity loss of 0% per cycle, the pool capacity remains at 100% of virgin, independent of make up rate. For any significant capacity losses, 2% per cycle or more, the pool capacity is significantly less than virgin and very sensitive to make up rate. For any non-zero capacity loss per cycle, the greater the make up, the greater the pool capacity, since the make up carbon is virgin carbon with 100% capacity.

One real world situation that demonstrates how sensitive the pool capacity is to the combination of capacity loss and make up rate is the case of under-reactivation in the multiple hearth due to insufficient steam. The effect is to regenerate with a higher capacity loss, since char is left in the carbon (as will be discussed later), but reduces the amount of make up carbon necessary. For the case of low steaming rates, it is possible to have 6% capacity loss per cycle and 4% make up rate. In contrast, higher steaming rates would likely produce 4% capacity loss per cycle, but require 6% make up rates.

As shown on Figure 1, the lower steaming rate and associated 6% per regeneration capacity loss results in a pool capacity of only 40% of virgin carbon capacity; whereas the higher steaming rate results in 60% of virgin capacity. Thus, the higher steaming rate yields regenerated carbon with 50% higher adsorption capacity per adsorption cycle, which directly translates into the amount of sugar refined before the carbon becomes spent and must be regenerated.

One straightforward but computationally complex exercise is to optimize the performance of the pool carbon based on the incremental cost of reactivation, make up carbon, and operating costs for the adsorption cycle. Such an analysis is unique to each individual industrial site, since the operating costs are site specific, but yields great insight into the preferred operating practices of both the adsorbers and the reactivation facilities. It is not unrealistic to identify a 25% reduction in direct operating costs of the combined systems based on revising the operating set-points of an existing high-temperature reactivation facility.

**Figure 2a. Molecular structure of 0% burnoff activated carbon**

Calined Carbon - 0.80 g./cc AD
< 200 Iodine No.

Graphite Plate
Interbonding of plates
Aliphatic dislocation (imperfection) of plate

Exploring the high temperature reactivation process

The most prevalent sugar industry practice for regenerating spent granular activated carbon is termed “high-temperature reactivation” and is usually performed in multiple hearth furnaces or rotary kilns. As discussed, the granular activated carbon adsorbent is recycled to “extinction”. As such, the activated carbon “pool” consists of a small percentage of virgin make up carbon, typically 3 to 5% per cycle, and recycled regenerated carbon. Thus, the key to understanding the properties of the pool carbon lies in understanding the impact of reactivation on the spent activated carbon.
The effect of activation on the internal structure of virgin activated carbon

Reactivation shares operating conditions and equipment with the “activation” process originally used to manufacture the virgin adsorbent. As such, there is merit to briefly reviewing how the activation conditions create activated carbon.

Activated carbon manufacturing involves conditioning a carbon-rich starting material to remove the non-carbon atoms through a series of steps involving drying, devolatilization and calcining. The feed to the activation step is the calcined raw material, meaning that the starting material has been heated above 800°C in an oxygen-free environment. These conditions drive off all volatiles, including residual oxygen and hydrogen, and produce graphite plates that form the internal structure of the activated carbon particles.

The key difference between the calcining step and the activation step is the presence of an oxidizing gas, either steam or carbon dioxide. The most popular choice is steam, which undergoes the “water gas” reaction with carbon to produce hydrogen and carbon monoxide. On a molecular level, the oxidizing gas produces a gradual and uniform removal of the graphitic backbone as the activation process progresses.

Figures 2a (Greenbank, 2002) shows the starting calcined raw material and Figure 2b shows the effect of “activating”, where the internal adsorption sites are modified by the activation process. Four main trends are occurring simultaneously as internal carbon atoms are removed from the individual particle: the particle density is decreasing; the volume of adsorption sites is increasing; the energy of...
the individual adsorption sites is decreasing; and the yield of product, on a weight basis, is decreasing.

One way of envisioning this progression is shown in Figure 3 (Greenbank, 2002), where the effect of the activation process in an individual graphite plate is depicted. Since the graphite plate is the structural backbone of the carbon particle, there is a limit to the reduction of the plate width – which is the mechanical failure of the particle. This concern will reappear during the discussion of high-temperature reactivation that follows.

The effect of reactivation on the internal structure of spent carbon

Figure 4a (Greenbank, 2002) depicts the internal graphite plates within a micropore region of coal-based activated carbon. Figure 4b depicts the same region flooded with adsorbed compounds. The goal of the regeneration is to reverse the process of adsorption and return the carbon to the virgin structure, to the extent that is possible.

Unfortunately, there is no such thing as the “perfect regeneration” for applications like sugar decolorization. This conclusion is driven by the characteristics of the adsorbed color bodies, which range from sucrose size molecules to large molecular weight polysaccharides, as discussed by Godshall (1999). Furthermore, these colorants are deposited within the activated carbon by diffusion from a liquid medium. Thus, when the spent carbon is dried out for regeneration, the colorants desiccate and bind more tightly to the internal surfaces of the carbon. In this form, the only option for removal is to decompose them in-situ by chemical reactions.

As noted, the conditions utilized for high-temperature reactiva-

![Figure 4a. Molecular structure of coal-based carbon](image)

![Figure 4b. Loaded activated carbon - 10,000,000 x magnification](image)
tion parallel those used for the original activation of the virgin carbon. However, the starting material is spent carbon, which differs from the starting material for activated carbon by the presence of the adsorbed color bodies. As the spent carbon is heated in the absence of oxygen, the effect on the graphitic backbone of the carbon is negligible, since the original manufacturing process encountered these conditions previously. The impact on the adsorbed color bodies is a different story – they dehydrate, devolatilize and form a residual material that is called “char”.

Char, which results from the thermal decomposition of the adsorbed color bodies, and the graphitic backbone of the activated carbon itself are chemically identical but physically very different. Because of this chemical equivalence, char reacts similarly to the graphitic plates of the activated carbon itself under the gasification conditions, which is basically the same “water gas” reactions previously encountered during the activation process. As such, during reactivation, both the char and the graphitic backbone of the carbon are gasified.

The sequence of adsorption, followed by devolatilization to form a residue in the carbon pores, calcination to convert the residue to char, and reactivation to create reactivated carbon is worth exploring, especially when repeated multiple times. The reader is referred to reference 10 for a more expanded discussion of the evolution of activated carbon over multiple high temperature regenerations. Basically, the original internal structure, as depicted in Figure 5a, is evolved with each adsorption-calcining-reactivation cycle.

**Figure 5a. Molecular structure of 0% char in virgin carbon**

| 0.55 g./cc. AD | 0.39 cc./g. Adsorption Pore volume |
|  | Iodine No. = 850 | Molasses No. = 220 |

**Figure 5b. Fifth cycle reactivated carbon with 42% char**

| 0.55 g./cc. AD (Total Particle) | 0.29 cc./g. Adsorption Pore volume |
|  | Iodine No. = 660 | Molasses No. = 400 |
The cumulative effect of the multiple reactivations can be seen by comparing Figure 5a (Greenbank, 2002), showing the virgin carbon internal structure, with Figure 5b, the internal structure after five reactivation cycles. While the reactivated material continues to possess adsorption capacity, the energy levels of the adsorption sites have decreased. Figure 6a (Greenbank, 2002) shows the estimated adsorption sites and corresponding energy levels for the virgin carbon and Figure 6b provides the same exercise for the five fold reactivated material. The effect of the multiple reactivations is to create new low-energy sites by the removal of graphitic backbone and to plug high-energy sites with char.

The progressive conversion of adsorption capacity into accumulating char and monotonic erosion of the graphitic backbone of the carbon particle does have an ending, but not a happy one. Figure 7 (Greenbank, 2002) shows the fate of the particle, which is a shattering of the particle into fines when the graphite plate width reaches some minimal size. Comparing Figure 7 with Figure 3, it is apparent that the effect of reactivation on plate width is virtually identical to the effect of additional activation. The difference is that the reactivation process also deposits char in the internal pores of the carbon, reducing useable adsorption capacity. One way of envisioning 0.55 AD (apparent density) carbon after five high-temperature reactivations is to superimpose 0.22 grams per cubic centimeter of accumulated char over a virgin carbon backbone of 0.33 AD.

Measuring the distribution of adsorption energies

Granular activated carbon is a unique material that combines intrinsic properties of naturally occurring starting materials and aggressive activation conditions to create a micro-porous graphitic lattice that possesses exceptional adsorption properties. The adsorption properties are largely due to the polarizability of the localized graphitic structures, which results in “London dispersion forces” that facilitate pure physical adsorption within the internal surface area of the activated carbon.

As a conceptual starting point, envision the internal structure of activated carbon filled with an adsorbed vapor. Figure 6a depicts a small internal region of activated carbon for the case of butane adsorption from a stream of pure butane at room temperature. Under such conditions, much of the micropore structure is flooded with liquid-like adsorbed butane, but some regions have much higher adsorption forces attracting an individual adsorbed butane molecule. This broad range of adsorption sites forms a distribution of adsorption energies.

The challenge is to measure the distribution of adsorption energies within a given sample of activated carbon under conditions that provide meaningful insight to the industrial application one is striving to understand. If possible, activated carbon is characterized by adsorption from the gas phase, since activated carbon reaches equi-
Decolorization by activated carbon, as practiced in sugar refining, is really a very complicated competitive adsorption of the color bodies from a solution also containing very high concentrations of sucrose and other simple sugars. For the purposes of understanding this new low-temperature regeneration technology, several analytical procedures have been utilized that measure adsorption properties of the activated carbon for known vapors under controlled conditions. These methods are used to compare one carbon against another, with virgin activated carbon representing one logical reference point. By using these methods and testing multiple carbons subjected to various regeneration and reactivation conditions, insight into the effects of reactivation and regeneration on spent activated carbon can be accumulated.

When one does map the entire adsorption potential distribution for a given sample of activated carbon, a distribution such as shown in Figure 8 (McLaughlin, 2004a) is generated. Figure 8 shows the relative amount of adsorption capacity at a given adsorption force for Calgon’s CPG activated carbon product, which is a benchmark carbon in the sugar industry. Given that the heat of vaporization of butane is about 4 kcais per mole at room temperature (17 kJ/mole), the heat of adsorption for the highest energy sites in activated carbon is roughly four times the heat of vaporization for butane. As such, adsorption in activated carbon can be viewed as “facilitated condensation”, where the London dispersion forces shift the equilibrium from the bulk vapor phase to a condensed liquid phase in the pores of the carbon.

Because of the difficulty in measuring the entire adsorption force distribution, many analytical tests measure one or two intermediate adsorption energy levels and quantifying the volume of adsorption capacity above those energy thresholds. One such test is the Butane working capacity test, ASTM D5228. This method takes a dried sample of carbon at 25°C and measures the weight gain upon being equilibrated in pure butane at one atmosphere, as depicted in Figures 4b and 6a. The weight gain is termed “Butane Activity”. The sample is then purged with 1000 bed volumes of dry air over 40 minutes and the residual weight gain is measured and termed “Butane Retentivity”. The difference is termed the “Butane working capacity”.

De facto, the Butane Activity measures total adsorption capacity above a relatively low adsorption energy threshold and Butane Retentivity measures the capacity of those adsorption sites above an energy level that represents roughly one third to one half of virgin activated carbon capacity. The total adsorption capacity measured by Butane Activity is worth knowing and correlates well with historical measures of activated carbon capacity, such as Carbon Tetrachloride Activity (ASTM D3467). Unfortunately, a significant portion of the capacity measured by the Butane Activity is too low in adsorption energy to be of any practical value in an actual industrial adsorp-

![Figure 6b. Adsorption sites on 5th cycle reactivated carbon distribution of adsorption forces for butane](image)

librium with gas phase concentrations very quickly, facilitating rapid execution of the analytical procedure.

The butane working capacity analytical method can be performed with any challenge gas, not just butane. Challenge gas is the historical term for a test vapor that the carbon is “challenged” to adsorb. Less easily adsorbed gases provide measures of higher adsorption energy thresholds. Two convenient alternatives to butane are propane and R134a (1,1,1,2 tetrafluoroethane, the HFC replacement for automobiles). These alternatives tend to quantify activated carbon capacities at equilibrium with the pure vapor (the “Activity” measure) with adsorption energies that are sufficient to be of utility in industrial applications.

Figure 8 shows the estimated adsorption energy thresholds for butane activity and retentivity, as well as the corresponding thresholds for the same assay performed with propane. Figure 9 (McLaughlin, 2004a) shows the adsorption capacity distributions for a number of popular industrial carbons, using esoteric historical units that appear in the literature. One can convert the x-axis of Figure 9 by matching the energy thresholds with Figure 8. Note that the y-axis of Figure 9 is scaled in volume of adsorbed butane per 100 grams of carbon, but the densities of the individual carbons are not the same. As such, the volumetric capacity (volume adsorbed per volume of carbon) will be influenced by the apparent density of the bulk carbon.

While it may be tempting to conclude that all carbons look the same, based on Figure 9, it should be noted that small differences on a semi-log plots often represent significant performance differences in the real world. In addition, the curve labeled “React”, signingigy a high-temperature reactivated carbon, is discernibly below the other curves in the lower adsorption potential range. This indicates lower total adsorption capacity, as measured at the propane activity threshold. This phenomenon is commonly observed in actual adsorption applications with reactivated carbons.

In summary, the adsorption capacity of either virgin or regenerated activated carbon can be assayed to determine the available adsorption capacity. The measurement can consist of either one or two sin-
gle point measurements, which quantify the total adsorption capacity above a specific adsorption energy threshold, or the entire “characteristic curve”, which maps the entire distribution of adsorption capacity as a function of adsorption potential.

**Introduction to the low-temperature regeneration (CarbOxLT) alternative for spent carbon**

The phenomenon of low-temperature oxidation of activated carbon in a source of molecular oxygen, typically air, is not new. A body of work performed at the University of Alicante (Gonzalez-Vilchez et al. (1979), Rodriguez-Reinoso et. al. (1984)) in Spain about 25 years ago explored the evolution of previously activated virgin carbon in air at 350°C. As noted in the Discussion section of the 1979 paper:

> At high percentages burn-off and as a consequence of the weight loss, the adsorptive properties of the active carbons is diminished but they can still be considered good active carbons even when the weight loss is about 50%. This could be important from the industrial point of view, since these carbons could stand temperatures up to 350°C for long periods of time (several days) with no other inconvenience than their reduction in weight.

Additional papers (Martin-Martinez et. al. (1984), Linares-Solano et. al. (1984)) further characterized the adsorption characteristics of the activated carbons as air at 350°C was used to modify the internal adsorption sites over a range of up to 70% weight loss or “burn-off”. After these four papers, the researchers seemed to drop this line of inquiry and additional work by this group is not reported in the literature.

What had not been previously demonstrated about the oxidation of activated carbon by air is the effect on other oxidizable organics present with the activated carbon. This will now be explored.

**Characterizing the CarbOxLT regeneration using propane working capacity**

While the background rate of oxidation for virgin activated carbon is slow, as discussed by Gonzalez-Vilchez et al. (1979), the rate of oxidation of spent activated carbon, under similar conditions, is significantly more rapid. As such, when spent activated carbon is exposed to the CarbOxLT conditions, the adsorbed organics oxidize faster than the activated carbon backbone and the adsorbed organics are selectively removed from the pores of the activated carbon. The net effect is the recovery of a significant portion of the adsorption capacity of the original virgin activated carbon.

The incremental regeneration of spent activated carbon is demonstrated in the following study. A sample of spent virgin activated carbon, heavily loaded with sugar refining color bodies, was regenerated over a total of about 24 hours at progressively higher temperatures. The results of the propane working capacity assay, performed at each temperature plateau, are shown in Figure 10.

As can be seen in Figure 10, at each progressively higher regeneration temperature, incremental recovery of adsorption capacity is measured (Note: the sum of Propane Retentivity and Working Capacity equals the Propane Activity).

Figure 11 shows a comparison of high-temperature reactivation and low-temperature regeneration, performed on the same batch of spent carbon used for Figure 10. Figure 11 includes the properties of dried spent carbon and spent carbon that has been calcined (heated to 850°C in a dry nitrogen atmosphere – which reduces any adsorbed compounds to char). Virgin carbon values for propane activity, propane retentivity and density are used to normalize the data shown in Figure 11, hence all virgin carbon properties are shown as 100%.

As can be seen in Figure 11, the dried spent carbon shows a significant increase in density and loss of propane capacity compared to the virgin carbon. Calcining the spent carbon recovers the majority of the propane capacity loss, but also converts the remaining adsorbed material into non-volatile char, which would accumulate over repeated adsorption-calcining cycles.

Calcining followed by steaming simulates the high-temperature reactivation process, since the steam removes the char by the water gas reaction. This allows the density of the reactivated carbon to be returned to near virgin carbon density, yet the propane capacities are still significantly decreased from the original virgin carbon levels.

Finally, the results for the low-temperature regeneration are shown on the far right of Figure 11. The data shown in Figure 11 is for a different regeneration of the same spent carbon as Figure 10 and the second regeneration results were slightly better than before. However, while the regenerated carbon has less adsorption capacity than the starting virgin activated carbon, the propane capacity decrease for the low-temperature regeneration is roughly one half that experienced with high-temperature reactivation.

Since the actual industrial practice is to regenerate and recycle...
carbon adsorbents to “extinction”, the cumulative effect of multiple loading and regeneration cycles is important. A laboratory study was performed to simulate the evolution of “pool” carbon properties. The details of this laboratory study are discussed in McLaughlin (2004).

In summary, the laboratory study utilized virgin activated carbon (Norit GAC1240, another typical sugar decolorizing carbon) and simulated the adsorption step, under laboratory conditions, by equilibrating the carbon with a controlled ratio of industrial molasses. During the equilibration step, the color bodies from the molasses adsorbed into the activated carbon, which was then “sweetened-off” with water rinses and regenerated. The sequence was repeated several times, without the addition of any make-up virgin carbon, in order to establish the trend over multiple adsorption-regeneration cycles.

Figure 12a shows the propane activity trend of multiple adsorption-regeneration cycles for virgin GAC, low-temperature regenerated carbon, high-temperature reactivated carbon and activated carbon that was regenerated by calcining alone. The regeneration of spent carbon by calcining alone reduces the adsorbed organics to char, which does recover some adsorption capacity. However, the char accumulates in the regenerated activated carbon and progressively consumes adsorption capacity. As such, calcining alone does represent the reasonable “worst-case” regeneration, just as restoring the spent carbon to virgin activated carbon properties represents a reasonable “best-case”.

As shown in Figure 12a, the calcining alone of spent carbon results in a progressive loss of adsorption capacity, as measured by the uptake of propane in the “Propane Activity” assay discussed previously. High-temperature reactivation is basically just calcining followed by the “water gas” reaction. As can be seen, the steep loss of propane activity previously seen with calcining alone is avoided, although the capacity of the high-temperature reactivated carbon still declines a significant amount with each adsorption-reactivation cycle.

Figure 12a also shows the trend for low-temperature regeneration. For each adsorption-regeneration cycle, the low-temperature method was used to return the bulk density of the regenerated carbon to near-virgin carbon levels. Low-temperature regeneration results in a noticeably slower rate of adsorption capacity loss, as measured by propane activity, than high-temperature reactivation. However, the loss of capacity compared to virgin activated carbon is still discernible. As such, low-temperature regeneration is not a “perfect regeneration”, but rather a distinguishable improvement over the current industrial practice of high-temperature reactivation.

Figure 12b shows the same comparison for the three regeneration techniques using propane retentivity as the measure of the condition of the regenerated carbons. The overall trends are similar to the trends demonstrated by the propane activity assay, but the differences between the various regeneration methods are considerably less pronounced. It is believed that these high-energy pores are difficult to recover by any regeneration technique, since the pores are subject to both plugging by residual char and deterioration by chemical attack on the graphitic plates forming the pore.

While it cannot be demonstrated from the data presented, it is anticipated that low-temperature regeneration conditions should result in significantly less attack on the graphitic backbone of the activated carbon as compared to high-temperature reactivation. The milder conditions should reduce the generation of fines during carbon transport, which has been attributed to the mechanical weakening of the carbon particles during high-temperature reactivation. As such, for a circulating pool of activated carbon, the make up rate with virgin activated carbon is anticipated to be less for low-temperature regeneration than would be required for a similar system using high-temperature reactivation.

In summary, based on measurements of density, it has been demonstrated that the low-temperature regeneration technology is capable of controlling the bulk density of the regenerated carbon pool at near virgin carbon levels. In addition, based on measurements of propane activity and retentivity, the low-temperature regeneration...
consistently recovers a greater portion of the adsorption capacity as compared to the same spent carbons being subjected to high-temperature reactivation.

However, referring to Figures 8 and 9, it is clear that the entire “characteristic curve” of a given activated carbon cannot be unequivocally inferred by just two data points measured by propane activity and retentivity. Based on the data presented here, it could be conceivable that the low-temperature regeneration is recovering pore capacity at levels just above the thresholds measured by the propane assay. If the high-temperature reactivation were recovering a broader distribution of adsorption potentials, it is possible that the total adsorption capacities, measured at the thresholds of the propane assay, could still be lower than the low-temperature regenerated adsorbent.
To explore this issue, a series of studies were performed and reported in McLaughlin and Clarke (2004). Those experiments demonstrated that the low temperature regeneration impacts the entire spectrum of adsorption pores uniformly and recreates essentially the same broad distribution of micropores as seen in virgin and reactivated carbon samples.

Comparing the energy requirements of spent carbon reuse options

One can easily appreciate how the make up rate per cycle of additional activated carbon impacts on the cost of operating a carbon regeneration system, since the cost of purchasing the make up virgin carbon quantifies the cost. However, make up carbon costs rarely dominate the overall cost of operation of a carbon system, except in the case of “use once and discard” processes, such as with powdered activated carbon. There are other costs that are less obvious, which range from direct fuel costs for the regeneration equipment to depreciation of the capital investment of the regeneration capability.

Zanitsch and Lynch (1978) published an article years ago that does a good job of delineating the economics of operating a high-temperature reactivation system. Unfortunately, since the article dates from the late 1970’s, the utility and capital costs are not accurate for today’s industrial climate. However, the overall structure of the economic analysis is sound and comprehensive.

Relative to the high-temperature reactivation technology, the low-temperature regeneration approach has two significant advantages that impact on the economics of operation. The first advantage relates to direct operating costs, specifically the fuel requirements. As discussed by Zanitsch and Lynch, the fuel consumption for high-temperature reactivation is several thousand Btu per pound of carbon processed (Note: 1 Btu per pound equals 2.326 kJ per kilogram). If an afterburner is required to destroy the volatiles generated during the charring of the adsorbates, the fuel requirement may well double. The high fuel consumption and resulting cost are a direct result of operating at high temperatures and using the “water-gas” reaction, which is endothermic – even at 850°C.

Figure 13 shows the enthalpy increase or the energy input to heat the spent activated carbon up to the reaction temperatures for low-temperature regeneration and high-temperature reactivation. In Figure 13, the enthalpies of all the components of the spent carbon (retained liquid water, the granular activated carbon and gases such as nitrogen and oxygen) are set to zero at room temperature (25°C). The steam curve in Figure 13 is elevated relative to the water curve by the heat of vaporization required to boil the water, since somewhere in the industrial complex, cold make-up water was supplied to the boilers that generate the steam for the reactivation process. Thus, Figure 13 shows the heat requirement to reach the reaction temperatures. To calculate the heat duty, one starts with the incoming spent carbon and raises the temperature of the individual constituents to the required reaction temperature, including energy requirements to vaporize any liquid water present.

As a rule of thumb, drained carbon retains about one kg of liquid water for each kg of dry granular carbon. The enthalpy requirements of adsorbed compounds are estimated by partitioning the compounds into liquid water, based on the amount of available H2O, and treating the rest of the adsorbed material as carbon or GAC. Thus, sucrose, C12H22O11, would be treated as eleven water molecules and twelve carbon atoms, or 58 weight percent water and 42 weight percent GAC. If supplemental air or steam is supplied to the reaction, the enthalpy required to raise the starting material (ambient air or make up water to the boiler) to the reaction conditions can be estimated using Figure 13.

While heat balances are a tedious accounting exercise, it is possible to calculate the adiabatic energy requirement to heat the reactants

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Figure 11. Comparison of regeneration options

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to the reaction temperatures. However, one can appreciate by looking at Figure 13 that the energy input to raise one kg of moist spent carbon to CarbOxLT temperatures is clearly less than to reach the high-temperature reactivation zone. Furthermore, high-temperature reactivation requires one-third to one-half kg of steam per kg of dry reactivated carbon to react with the char (and carbon backbone), which is a significant heat input at the high temperatures required. To make matters worse, the water-gas shift reactions are endothermic to the tune of about 11,000 kJ per kg of carbon removed, so additional heat is required or the entire reacting mass cools as the water-gas shift reaction proceeds.

In addition to lower heat requirements to reach reaction condi-

**Figure 12a. Propane activity trend over multiple loading cycles**

**Figure 12b. Propane retentivity trend over multiple loading cycles**
tions, low-temperature regeneration is exothermic and can use the heat generated by the oxidation of the adsorbed organics to supply the bulk of the necessary heat to raise the reacting mass to the desired regeneration temperature. Since sucrose has a heat of combustion of roughly 16,000 kJ per kg and since most adsorbed compounds are very similar to sucrose in their ratio of carbon to non-carbon atoms, the heat of combustion of most adsorbed organics in sugar decolorization is similar to that of sucrose.

When one does the heat balances, one finds that wet spent activated carbon, containing one kg of retained water and 0.2 kg of adsorbed color bodies per kg of dry carbon, reacts under CarbOxLT conditions as an “autogenous” reaction – where the heat of combustion matches the heat requirement to heat the incoming spent carbon to the reaction temperature, including vaporizing the retained water. Above 20 weight percent color bodies, a level that includes virtually all spent decolorizing carbons, the fuel value of the color bodies being destroyed supplies the energy requirement for the low-temperature regeneration process. As such, the direct fuel costs for the low-temperature regeneration process are estimated at less than one-quarter of the fuel costs for high-temperature reactivation.

Estimating the capital investment requirements of spent carbon reuse options

Estimating direct energy costs is much easier than estimating capital costs to install either regeneration technology. Capital costs are more dependent on individual installation features, due to variations in labor costs and local requirements for ancillary processes, such as air pollution abatement equipment. Furthermore, since there have not yet been any full scale implementations of the low-temperature regeneration process, it is hard to develop a credible estimate to compare the comparable capital costs for multiple hearths used by the high-temperature reactivation process. However, it is possible to put the two technologies in perspective.

The cost of the high-temperature reactivation process is sparsely documented in the literature. Adams and Clark (1989) estimates US$3,650,000 for a 4.54 million kg per year regeneration capacity. Zanitsch and Lynch (1978) estimates US$2,700,000 for a 13,600 kg per day reactivation rate, of which US$770,000 is purchased equipment and US$1.93 million is “Installation” costs. McDonough (2004) provided an estimate for US$980,000 for just the multiple hearth unit capable of 4.54 million kg per year of reactivated carbon. Thus, it looks like the cost of the multiple hearth capability does not come cheap, which can be confirmed by asking almost anyone who owns one.

While the exact cost of an equivalent regeneration capacity using the low-temperature technology has yet to be been demonstrated, it is expected to be significantly less than the high-temperature process for one simple reason: operating temperatures and the corresponding acceptable materials of construction. High-temperature reactivation requires refractory lined equipment and exotic alloys due to the high operating temperatures, 800 to 1000°C. Low-temperature regeneration operates at temperatures of less than 400°C, which allows for carbon and stainless steels without linings to be used for equipment fabrication. Thus, due to dramatically different operating temperatures, not only are the initial construction capital costs significantly reduced, but the operational flexibility and reliability is greatly improved over refractory-lined designs.

There is a concern that the low-temperature process is five to ten times slower than high-temperature reactivation, so the low-temperature equipment may have to be correspondingly larger to provide for sufficient reaction time. It turns out that the low-temperature equipment is anticipated to be of similar size, due to the different “volumetric efficiency” of the two technologies. Multiple hearth furnaces are only about 10% full of carbon, due to the activated carbon being contained on a series of shelves, called hearths, in layers that average

![Figure 13. Enthalpy requirements to heat reactants to elevated temperatures](image-url)
only about 10 cm deep. In contrast, the low-temperature process utilizes free-flowing “dense beds” of carbon, meaning that the reactor volume is more completely filled with carbon, which is mixed to control the temperature of the reacting mass and avoid hot spots.

There are additional unanswered concerns relating to the construction and operation of a full-scale low-temperature regeneration facility, which fall in the general category of “fear of the not-yet-known”. However, as Mick Greenbank of Calgon has noted:

*The only unanswered question is with reliability and maintenance, but that cannot be proven till the first systems are installed. However I would be surprised if the CarbOxLT regeneration systems were not more reliable than existing high-temperature reactivation technology.* (Greenbank, personal communication)

In summary, it appears that the adopters of the low-temperature regeneration technology may save a significant amount of money when building the facility and will save a significant amount of money while operating the facility. At that point, it comes down to the individual organization’s engineering capabilities, tolerance for risk, and propensity for saving money.

**Summarizing the low-temperature regeneration process**

While both low-temperature regeneration, (CarbOxLT) and high-temperature reactivation allow the recycling of spent activated carbon adsorbent, they are really two entirely different approaches to the same application.

The core technical differences between the current high-temperature reactivation process and the low temperature regeneration technology comes down to time, temperature, and reaction conditions. The high temperature reaction conditions first convert all the adsorbed organics into residual char in the carbon pores. Then, the high temperature process uses steam to react with the char (and the activated carbon itself). This reaction occurs above 850°C and adsorbs heat (endothermic). The high temperature reaction is controlled by adding heat to maintain a temperature setpoint and metering the steam supply.

The low temperature reaction occurs at between 150 and 350°C, reacts oxygen (from air) directly with the adsorbed organics, and generates heat (endothermic). The reaction is also relatively slow, since the temperature is controlled to prevent the development of hot spots. The low-temperature reaction is controlled primarily by removing heat to control at a temperature setpoint and, to a lesser extent, by metering the air input.

Another important difference is the dominant vapor atmosphere present within each process. The low-temperature process has excess oxygen present at all times and the predominant off-gases are carbon dioxide and water vapor, with lesser amounts of carbon monoxide. In contrast, high-temperature reactivation uses the water-gas shift reaction and generates an atmosphere containing principally carbon monoxide and hydrogen. These compounds require subsequent destruction, typically with an afterburner. In addition, due to the presence of hydrogen, there are safety concerns and the risks of further reactions with reactive vapors present in the furnace off-gas, such as the formation of hydrogen cyanide.

In closing, it is acknowledged that the actual specifics of a low-temperature regeneration operation will not be known until one or more full-scale units are constructed and operated for a period of time. However, it is clear that the low-temperature regeneration process enjoys several pivotal technical advantages over the high-temperature reactivation technology currently utilized by sugar refining operations worldwide.

**References**


Greenbank, M (2002). Slide from a course titled “Selecting the best activated carbon for a specific application”, presented in September 2002, while in the employment of PACS, a specially activated carbon service firm located in the greater Pittsburgh area.


