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Modeling of Cane Sugar Colorant Removal in Packed-Bed Ion Exchange Columns and an Investigation into Pretreatment Methods

Bruce Malcolm Ellis
Louisiana State University and Agricultural and Mechanical College

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MODELING OF CANE SUGAR COLORANT REMOVAL IN PACKED-BED ION EXCHANGE COLUMNS AND AN INVESTIGATION INTO PRETREATMENT METHODS

A Thesis
Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering in The Department of Chemical Engineering

by
Bruce Ellis
B.S., University of Natal 2002, August, 2004
ACKNOWLEDGEMENTS

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GLOSSARY OF TERMS

AU   Absorbance units
Brix Total dissolved solids (%m/m), measured by refractometry
Breakthrough When the adsorbent can no longer absorb all of a solute species from the feed
BV   Bed volumes
GPC  Gel permeation chromatography
HADP Hexose alkaline degradation products
ICUMSA International Commission for Uniform Methods of Sugar Analysis
Inversion The hydrolysis of sucrose into fructose and glucose
Isotherm Equilibrium expression relating the concentration of a species in solution to that on the resin
Indicator value Quantitative measure of the effect of pH on the color of a component
IV   Indicator value
Mixed Juice Sugar containing liquid from extraction plant
MWCO Molecular weight cut-off.
NTU  Nephelometric turbidity units
Permeate Material below the MWCO, accepted by the ultra-filter membrane
Retentate Material rejected from the ultra-filter membrane
SAC  Strong acid cationic resin
SMB  Simulated moving bed
<table>
<thead>
<tr>
<th>Ultra-filtration</th>
<th>A membrane system that removes small colloids and large particles from solution above a MWCO dictated by the membrane pore size</th>
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<tr>
<td>RI</td>
<td>Refractive index</td>
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<td>WBA</td>
<td>Weak base anionic resin</td>
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### NOMENCLATURE

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<td>Column cross-sectional area</td>
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</tr>
<tr>
<td>C</td>
<td>Concentration in bulk fluid</td>
<td>AU</td>
</tr>
<tr>
<td>C*</td>
<td>Concentration of fluid in equilibrium with adsorbent</td>
<td>AU</td>
</tr>
<tr>
<td>C₀</td>
<td>Feed concentration</td>
<td>AU</td>
</tr>
<tr>
<td>̅C</td>
<td>Dimensionless concentration in bulk fluid</td>
<td>[-]</td>
</tr>
<tr>
<td>̅Cₚₗ</td>
<td>Dimensionless concentration at node m, for time p</td>
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<tr>
<td>̅C₀</td>
<td>Dimensionless inlet concentration</td>
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<tr>
<td>dₚ</td>
<td>Particle diameter</td>
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<tr>
<td>D</td>
<td>Axial dispersion coefficient</td>
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<td>Diffusivity of A in B</td>
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<td>Activation energy</td>
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<td>kₙ(T)</td>
<td>Reaction rate</td>
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<td>Pre-exponential term in Arrhenius expression</td>
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<td>pH dependent adsorption parameter</td>
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<td>Molecular weight of component i</td>
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<tr>
<td>q</td>
<td>Concentration on solid phase</td>
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<td>Q</td>
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<td>Stanton number: St = k'L/uᵢ</td>
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<td>T</td>
<td>Temperature</td>
<td>K</td>
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<td>uᵢ</td>
<td>Interstitial fluid velocity</td>
<td>m/s</td>
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<td>Volume of resin in bed (including voidage)</td>
<td>ml</td>
</tr>
<tr>
<td>Vₙₓₑₙₐₑ</td>
<td>Volume of hexane</td>
<td>ml</td>
</tr>
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<td>Description</td>
<td>Units</td>
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<td>--------</td>
<td>-------------</td>
<td>-------</td>
</tr>
<tr>
<td>$V_{Resin}$</td>
<td>Volume of resin in packed-bed</td>
<td>ml</td>
</tr>
<tr>
<td>$V_T$</td>
<td>Total volume</td>
<td>ml</td>
</tr>
<tr>
<td>$z$</td>
<td>Distance from top of column</td>
<td>m</td>
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<td>Defined variable : $G = \frac{T}{2} S t$</td>
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<td>$H$</td>
<td>Packed-bed void fraction</td>
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<tr>
<td>$J$</td>
<td>Defined variable : $J = \frac{G}{K(pH)}$</td>
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<td>$\eta$</td>
<td>Dimensionless distance</td>
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<td>$\lambda$</td>
<td>Parameter in $K(pH)$</td>
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<td>$\mu$</td>
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<td>$\rho$</td>
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<td>kg/m$^3$</td>
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<tr>
<td>$\tau$</td>
<td>Retention time</td>
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ABSTRACT

Cane sugar colorants have been extensively researched but still little is known about their exact compositions. Rather than distinct compounds, they are a mixture of many compounds. Some it is assumed can be classified into the pseudo components that have been defined using gel permeation chromatography, based on molecular weight. The defining of these components has allowed the colorants to be modeled independently, instead of as one lumped color parameter. The measured colored components were modeled using a linear driving force adsorption model, which could be applied in the design process for optimizing the decolorizing capacity of the resins.

The majority of these colored compounds possess a charge allowing the removal by packed-bed ion exchangers and decolorizing processes such as the White Sugar Mill (WSM) process. The WSM process has the advantage of producing white sugar directly from sugar cane as opposed to producing raw sugar, which required refining to make white sugar. This is done by performing ultra-filtration on juice, before sending the permeate to a continuous ion exchange operation.

One of the disadvantages of the WSM process is the high capital and associated running cost of ultra-filtration. As a result an alternative for this pretreatment has been investigated in the form of a packed carbon bed.

Some advantages to a carbon bed pretreatment, followed by the ion exchange treatment, have been identified, namely the removal of colorants and their precursors as well as inorganic material. The removal by ion exchange of these inorganic materials, which can be deposited on the evaporator tubes reducing heat transfer coefficients, could have huge effects on cleaning costs and operability at the mill. It was found that carbon
beds could increase the overall color removal, and prolong resin life, even without the removal of suspended solids by ultra-filtration.

Preliminary testing was done using hydrogen peroxide as an oxidizing agent in conjunction with a carbon bed pretreatment. Results have shown that this form of treatment could extend the number of bed cycles before regeneration and improve overall colorant removal to the extent that white sugar can be produced directly.
CHAPTER 1. INTRODUCTION

1.1 The White Sugar Mill Process

1.1.1 The Production of White Cane Sugar

The production of white cane sugar is at present a two-step operation. Raw cane is taken to the sugar mills where it is processed and raw sugar is produced. Mills are generally in close proximity to cane growers to minimize transport costs. Processed raw sugar is then sent to a refinery where it is further purified through various stages. The figure below shows the main steps in the production of raw sugar. The cane from the cane yard goes through a series of extractions to remove the sucrose from the cane. The extracted juice is then screened and heated before going to a clarification step to further reduce the suspended solids in the juice. The clear juice from the clarifier is then sent to the evaporation station where the juice is concentrated to approximately 65 brix in a multiple effect evaporator train. The syrup from the final effect is then sent to the crystallization stage of processing. After crystallization, the sugar is separated from the mother liquor in centrifuges. The final products are then raw sugar and molasses, with the raw sugar going to the refinery.

![Figure 1.1: Raw sugar mill flowsheet](image_url)

Key: DJ = Draught Juice; MJ = Mixed Juice; CJ = Clear Juice; Sy = Syrup
Ma = Massecute; RS = Raw Sugar; Mol = Molasses

Figure 1.1: Raw sugar mill flowsheet
At the refinery, the raw sugar goes through an affination stage where the outer layer of impurities is washed from the crystal. The affinated sugar is then re-melted before passing through further clarification, filtration, and then a final decolorization stage. This decolorization is obtained by employing a decolorizing resin, producing a low color liquid termed fine liquor. The fine liquor from the decolorization stage is then crystallized after which the white sugar produced is centrifuged and dried.

### 1.1.2 The White Sugar Mill

The main costs associated with the sugar refinery are the costs in energy and sugar losses during the refining process. Many of these costs could be alleviated by the introduction of direct sugar production at the mill. Raw sugar mills have a cheap fuel source by burning of bagasse and losses during the refining process could be reduced due to the reduction in processing stages.

Tongaat-Hulett Sugar Limited and S.A. Bioproducts Limited are currently in the pilot plant stage in the development of a process that produces white sugar directly in the raw sugar mill (Rossiter, 2002). The process is illustrated in figure 1.2 below.

As can be seen in figure 1.2, membrane filtration technology is employed, using either a 0.1μm stainless steel or a 0.05μm ceramic filtration unit. This is done to remove high molecular weight materials from the feed to the ion exchange units that could foul the resins. The retentate from the filtration unit can either be recycled to the clarifiers or used on a neighboring distillery site. Due to the high costs associated with ultra-filtration, it is desirable to have a high brix flux across the filtration unit. Juice from the first and second effects are blended to obtain a brix passing through the ultra-filtration unit of 20 to 25 brix.
The permeate from the ultra-filtration unit is then refrigerated to approximately 10°C. This is necessary as the permeate will be sent to the first stage of the ion exchange process which involves passing it through a strong acid cation (SAC) resin. At low pH, sucrose breaks down into glucose and fructose by a process called inversion. It has been found that inversion can be limited by controlling the temperature and as a result the syrup is cooled to 10°C.

Central to Tongaat-Hulett’s white sugar milling process is the use of Calgon Carbon Corporations ISEP technology. Similar in concept to a Simulated Moving Bed (SMB), this unit comprises of a number of packed beds placed on a rotating carousel. Instead of using switching valves, as in the SMB, the ISEP unit rotates the carousel beds around a central feed valve.
The two resins, which are used in the first ISEP unit, are the strong acid cation (SAC) and weak base anion (WBA) resins, which remove mostly inorganic compounds (demineralization) and some organic impurities in the sugar solution.

Despite some decolorization, the resulting high purity juice still has significant color that must be removed in the second decolorization ISEP. The necessity of this final step and the resin arrangements is obviously a function of the initial color in the juice. The decolorized juice produced from this process is sufficiently low in color to allow four crystallization stages. The benefits of this process were shown to include (Rossiter, 2002):

i. Increase in yield

ii. Increase in sugar quality

iii. Production of high-grade molasses

iv. No fouling in evaporators and vacuum pans

v. Higher heat transfer coefficients in pans and evaporators

1.1.3 The Proposed White Sugar Mill

Due to the high costs associated with the ultra-filtration stage of the WSM process, the prospect of removing this stage and replacing it with a more cost effective stage is an attractive concept. Carbon beds have been used in downstream processes but not on clarified juice. One of the main advantages is due to the comparative cost effectiveness of a packed carbon bed, a lower brix flux could be used allowing the removal of the inorganic and organic impurities prior to an evaporation stage. This would greatly reduce the fouling the first effects and could have another effect in that it may remove some color precursors that could form in the evaporators.
Carbon beds primarily provide color removal, but can also handle solids, thereby reducing the turbidity. Pulsed beds may be necessary to obtain the required suspended solids removal.

A further consideration is the use of hydrogen peroxide on juice prior to the carbon bed treatment (Bento, 2004) as this could dramatically increase the longevity of the resins and reduce overall losses.

1.2 Research Objectives

The benefits of ion exchange demineralization have been reported with regards to color and ash removal as well improved processing conditions and final product yields (Rossiter, 2002 and Fetcher, 2001). An area of interest to process developers is the ion exchange resins color and ash removal. Modeling of ion exchange color adsorption has been done in a model (Broadhurst, 2002) with each identified colorant classified into pseudo components, which are modeled independently. This was done as there was no complete model of cane sugar colorant (Godshall & Baunsgaard, 2000). If these regressed parameters could be used in a predictive model, optimization of the process could be achieved, allowing the most effective use of the resins. This in turn could reduce the current high loading on the decolorization resin, which has to remove the colorants not removed by the preceding resins, by effectively utilizing the SAC and WBA resins.

Using the same modeling assumptions as Broadhurst (2002), that interaction between components is negligible as the colorants are very dilute, a number of single component models can once again be used to predict the color adsorption onto the resin. By quantifying the colorant concentrations using gel permeation chromatography as an analysis technique, the specific goals in the research can be summarized as:
- Investigate color formation using known colorant formation reactions
- Identify the most appropriate wavelength and pseudo components for colorant behavior modeling using results from color formation tests
- Test the feasibility of using a mixed ion exchange resin bed to remove the need for refrigeration
- Perform column loading experiments
- Determine parameters using a regression algorithm and apply the parameters to a predictive model
- Investigate various pretreatment methods and investigate their feasibility and advantages in the color removal process
CHAPTER 2. BACKGROUND

2.1 Cane Sugar Colorants

2.1.1 Color in the Sugar Industry

The main criterion when determining the quality of processed sugar is the purity, sucrose content and particularly color. The color is what determines the grade of the sugar (e.g. raw or white sugar) and is the main concern of the buyers and consumers of the product. An example of this is at the sugar refiners where brown sugar is processed to make white sugar. A higher color raw sugar will require more refining to obtain the desired grade of white sugar, thereby increasing the associated costs. As a result of this, much research has gone into identifying the different types of colorants and investigating their formation and removal.

2.1.2 Types of Colorant

**Phenolics:** Phenolics are derived to a considerable extent by enzyme action, from flavonoid and cinnamic acid precursors, which naturally occur in the cane. These materials are aromatic and are pH sensitive, so that their absorbance changes considerably with pH. Davis (2001) reports that phenolics are generally uncolored, but are oxidized or react with amines or iron to form colorants during processing operations. He distinguishes flavanoids as polyphenols that exist in the cane plant and are involved in enzymic browning reactions. Bento (2003) further describes these browning reactions as enzymic oxidation of phenolic compounds, by enzyme polyphenol oxidase (PPO). These browning products can also polymerize forming high molecular weight and highly colored compounds. These colorants are formed during extraction, at low brix, medium
temperature and at a mild pH. They are also soluble, when derived from cane, and can thus pass through the process and can be incorporated in crystallization.

Phenolic acids can be esterified normally to polysaccharides (Clark M.A. et al., 1988). By enzymic oxidation these phenols can form colored quinines that can polymerize with other quinones, forming bridges between polysaccharide chains. These high molecular weight materials can travel through the process and result in higher viscosities in liquors, syrups and massecuites.

**Plant Pigments:** Davis (2001) documented this category as comprising of principally flavonoids and phenolics. The color in raw sugar is attributed (by approximately two thirds) to these groups of colorants, after the process reaction as mentioned above. Unreacted plant pigments tend to have low to medium molecular weights (MW<1000) but are highly ionized, particularly at high pH values, yielding high Indicator Values (IV). They are readily removed in the refinery, but also readily included in the sucrose crystal in the refinery. Some plant pigments such as chlorophyll, xanthenes and beta-carotene are insoluble and are removed during clarification (Bento 2003). Bento also characterizes plant pigments as flavonoids and phenolics, describing flavonoids as a group of plant pigments that are soluble and pass through the process without being removed. Their affinity to sugar crystals is explained by some of these compounds having a glycoside in their structure.

**Melanoidins:** These dark, factory produced, materials formed from the reducing reaction of sugar with proteins or amino acids (Maillard reactions). Davis (2001) further defines melanoidins as being produced with the application of heat at high brix and low purity, but can also form with low heat over long periods. They are slightly negatively charged at
neutral pH, but positive under acidic conditions. A sub-division of melanoidins is melanins, produced from phenol-amine reactions. These have a medium MW (>2500) and are difficult to remove in processing. Melanoidins are insensitive to pH and hence have low IVs.

**Caramels**: Degraded sucrose and other carbohydrates at high temps form complex products with some highly colored substances. Affected product may be yellow/brown/black depending on the degree of reaction. MW increases with time and temperature as a result of increasing condensation polymerization (Davis 2001). Due to most refinery operations being performed on hot liquors, caramelization occurs approximately continuously, particularly on heated surfaces such as evaporators.

**Invert degradation products**: Invert products of sucrose are very susceptible to rapid darkening in the high pH region. Like caramels these materials have a moderate pH sensitivity and medium to high MW. Under mildly acidic conditions, a different set of darkening reactions takes place, via 5-hydroxymethyl-2-furaldehyde, to brown polymers. Davis (2001) attributes invert degradation products to mainly the decomposition of fructose, referring to the group collectively as Hexose alkaline degradation products (HADPs). Davis writes that the products of HADP reactions are acidic in nature, which leads to the inversion of sucrose and increase the color formation. The main mechanisms are unknown, but amines are known to be involved (Carpenter and Roberts, 1976).

### 2.1.3 Ion Exchange Mechanisms of Color Removal

A large fraction of colorants contain weakly acidic functional groups, which serve as anionic “handles” for cationic surface removal. Phenolics (unlike carboxyls) are not
appreciably ionized ordinarily but their polarity and hydrophilicity allow ion-dipole or dipole-dipole interactions at polar sites.

When colorant molecules approach an adsorbent, van der Waals or London forces become responsible for adsorption. Aromatic structures, and those containing extensively conjugated double bond systems, can adsorb though hydrophobic bonding, on carbon or on the non-polar matrix of ion exchange resins.

Ion exchange resins are synthetically produced fine beads (0.5-1mm diameter), which consist of high molecular weight polymers with a degree of cross-linking to create a porous structure. Within this porous structure are a large number of immobile, active, cationic or anionic sites, coupled with mobile counter-ions. These sites are capable of exchanging anions or cations respectively from a solution according to the equilibrium constant for the ions. These constants depend upon the temperature and the nature of the ions. Changing the ionic species concentrations can shift the equilibrium.

Anionic (basic) resins are used to remove color and negatively charged constituents whereas cationic (acidic) resins are used to remove predominantly inorganic constituents. The above-designated resins refer to the functional group linked to a hydrophobic matrix. These two functional groups are combined in bone char. Resins can be categorized by the type of monomer used as the backbone, such as the styrene and acrylic types. A third classification is by macrostructure or porosity, that is, a gel (micro-reticular) versus a macro-reticular structure. The former have a higher exchange capacity but are more susceptible to osmotic shock.

Anionic resins can be further categorized into weak and strong basic types. The former is comparable to an insolubilized amine and the latter an insolubilized quaternary
ammonium compound. Resins are used in the chloride form to avoid producing strongly alkaline off-liquors. The colorants are adsorbed at both ionic sites and on the hydrophobic matrix. Divalent and especially polyvalent anions are effectively removed by such treatments. Due to pH effects, complex formations and other considerations, the ionic composition of sugar liquor may differ in important respects from textbook expectations. As with bone char, high ash levels inhibit decolorization.

Better decolorization is achieved above pH 8, where large function phenolic components are ionized, but as previously discussed, this is also conducive to color formation reactions. High density syrups can be treated using ion exchange if high temperatures can overcome viscosities. If the syrup density exceeds that of the resin, the resin may float, but this can be overcome by process equipment design. Resin regeneration can be done with brine, which causes the resin to swell, releasing the adsorbed material. Alkaline brine also additionally elutes acidic colorants removed by ionic rather than matrix adsorption.

Acrylic resins are more rugged and resistant to fouling than styrenic resins, but are less effective in decolorization. This is particularly true for aromatic colorants. These resins are thus commonly used in series, with the acrylic first, adsorbing the large organic loads (phenolics, iron compounds and particulates which are all potential foulers), followed by the styrenic resin. The high efficiency of high molecular weight colorant removal, using these techniques, has been proven using GPC.

Bento (1998) further describes acrylic resins as having a lower selectivity for sugar colorants but, unlike styrenic resins, can be completely regenerated using sodium chloride solutions. The more hydrophilic character of the acrylic resin matrix explains
this. Regeneration of acrylic resins is thus easier than for styrenic resins. The use of dark effluents from styrenic regenerations can even be used to regenerate acrylic resins. The use of an acrylic resin is justified when the color load is high and a low level of decolorization is required. The use of resins in a two-bed system is more economic and gives a more even operation than when only one resin bed is used.

Much of decolorization is not via true ion exchange, making the usual measures of ion exchange capacity not very useful in evaluating the resins. Matrix adsorption also makes it difficult to predict decolorization performance, whereas softening cycle lengths, for example, can be computed on the basis of feed composition.

Cationic resins are useful for softening or removal of di- and polyvalent cations. Weak and strong acidic resins can be visualized as immobilized carboxylic and sulphuric acids respectively. In sugar refining, strong acid resins are commonly used in the sodium form, to avoid strongly acidic effluent liquors. Regeneration is with neutral brine. Weak acid resins may be used in the free acid form, often requiring techniques to inhibit inversion at reduced pHs. In this case, a strong mineral acid without brine is the regenerant. Complete removal of inorganic ions, including monovalent ones, requires use of a strongly acid resin in the hydrogen form, combined with an anionic resin in the hydroxide form, in a mixed bed to avoid extremes in the off-liquor pH. Removal of inorganics, unlike decolorization, is a true ion exchange.

The process chemistry of the cationic ion exchange is described as follows (Ahmed et al 2001):

An ion exchange process is used to remove ash from the high test molasses (HTM). A strong acid cation resin removes sodium, potassium, calcium, magnesium and
other cations and produces hydrogen ions which result in mineral acids being formed. The pH of the solution thus decreases during this step. The ion exchange process is described by the following equation:

\[
RSO_3^-H^- + Na^+Cl^- \rightarrow RSO_3^-Na^+ + H^+Cl^- \quad (2.1)
\]

Where “R” is the resin matrix. Other cations are removed by a similar mechanism. Hydrochloric acid is used for regeneration as it prevents the precipitation of calcium salts in the resin bed due to the high solubility of chloride salts. The hydrochloric acid is diluted to 7% m/m prior to regeneration. An excess of the chemical is normally required to regenerate the resin completely, but this excess is very low in the ISEP® process. The regeneration reaction can be described as follows:

\[
RSO_3^-Na^+ + H^+Cl^- \rightarrow RSO_3^-H^+ + Na^+Cl^- \quad (2.2)
\]

The resin referred to by Ahmed et al, is a styrenic, SAC, macroporous resin. Other regenerants such as ammonia and nitric acid can also be used, which are advantageous but more expensive, as the effluent can be used to produce a fertilizer.

2.1.4 Granular Carbon Mechanism of Colorant Removal

Riffer (2000) describes the mechanisms of granular carbon decolorization in detail. Granular carbon is a very highly porous material with most of the surface area inside the honeycombed interior of the particles. The adsorptive forces are relatively nonspecific.

Although the adsorptive forces on carbonaceous materials are fairly weak, typically less than 20.93 kJ/mol, a large colorant molecule might be bound to a multiplicity of sites. Consequently, most color cannot be washed off at the end of a cycle, and regeneration requires thermal degradation of the adsorbed material.
Colorants have structural features making them suitable for adsorption. Due to having a weakly acidic nature, the acid function provides a means of electrostatic linkage to the adsorbent, a mechanism lacking in neutral sugar. A portion of the colorant fraction is high molecular weight material, formed either via polymerization or by bonding with large molecules, especially polysaccharides. These large complex molecules may contain non-polar regions that are available for hydrophobic bonding. Polymeric dark thermal degradation products have graphitelike structural features that would be expected to have an enhanced affinity towards carbon, which shares a similar structure.

Micropores in the range of 100 to 400 Å, are useful for sugar decolorization due to most colorant molecules having a size considerably smaller than 100 Å, but the relatively large pore-size requirement is a consequence of the colorant diffusion characteristics. The hydrated molecules are bulky and sluggish in the viscous sugar environment. As a result, diffusion is the rate-determining step in decolorization, reducing the flow-rate, and hence increasing the contact time, can improve the performance.

2.2 Quantifying Colorant

Quantifying sugar colorants is a very subjective topic due to the nature of the colored components discussed above. Despite industry standards, many may question the methods used for quantifying color. An example of this is the standard industry method of ICUMSA color. It has been found (Bento, 2003) that up to 50% of raw sugar color is not measured by the ICUMSA method and that if a 1.25μm (instead of a 0.45μm filter) is used an increase of 36% in color is measured. Due to indiscriminate methods of ICUMSA for analyzing color, measuring high and low molecular weight components as one, it is necessary to use other analytical tools such as GPC.
2.2.1 ICUMSA Color

The industrial standard for measuring sugar solution colorants is the International Commission for Uniform Methods of Sugar Analysis (ICUMSA) color method. A sugar juice having passed though a 0.45μm filter, to removal all suspended solids, is corrected to a pH of 7 ± 0.1. Diluting the sample to a known solids concentration, the sample is then analyzed in a spectrophotometer set to 420nm (SASTA laboratory manual). Using the equation:

\[
ICUMSA(420nm) = \frac{[Abs(420\text{nm}) \times 10,000]}{[\text{Conc.} \times \text{Cell} \times \text{Length}]} \tag{2.3}
\]

the color of the solution is calculated with its solution having a color measurement defined as ICUMSA units.

The ICUMSA method, as discussed above, gives an overall indication of the color of the juice. Although this is useful in evaluating the color removal of a process, no information is given as to the types of colorants that have been removed. Knowing more about the types of colorant is useful, as the ICUMSA color of the mother liquor may not define the final product color. An example of this would be a syrup with a high concentration of a colorant with no affinity for the sugar crystal. Although it would give a high ICUMSA color, the final product would not necessarily be of high color as the colorants would not have been occluded in the crystal. Conversely, for a syrup with a low ICUMSA color mother liquor but a high affinity for the sugar crystal, the final product would be of higher color than expected.

2.2.2 Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) uses liquid chromatography to separate samples based on their molecular sizes. The sample is injected into the eluent, or buffer
solution, and is then passed though a packed gel column of precisely controlled pore size. Larger molecules are not able to diffuse into these pores and pass directly through the column, yielding a chromatogram with a molecular weight distribution from the highest to the lowest molecular weights. An absorbance detector capable of measuring ultraviolet and visible light is placed at the end of the column. A refractive index (RI) detector is placed in series with the absorbance detector.

Calibration of the GPC can be done by injecting standards of known molecular weights into the column. It is however important that the standard solutions are similar in molecular size and shape as the samples to analyze, to ensure they exhibit the same behavior. This allows the molecular weight of the samples to be found from the calibration curve and will help in identifying the samples.

GPC has been widely utilized in analysis of sugar solutions by many authors, including Shore et al (1984), Godshall et al (1988, 1992, 2000), Bento et al (1977, 2003), Saska & Oubrahim (1987) and Broadhurst (2002). Due to the distinct separation of the components, GPC is a useful tool in quantifying individual colored component removal as opposed to the overall color reduction.

2.3 Removal of Cane Sugar Colorant

The removal of cane sugar colorants has been done on various scales industrially. The methods most pertinent to our discussion are: membrane filtration; ion exchange resins; packed carbon beds and oxidation reactions.

2.3.1 Membrane Filtration

Membrane filtration is a pressure filtration process whereby the feed is separated by a membrane of precise pore size into its components by size exclusion. Any material
of greater diameter than the pore diameter will be rejected by the filter and pass out as the retentate stream. Material of smaller diameter than the pore will pass through in the permeate stream. The molecular weight of the largest particles to pass through the membrane is termed the molecular weight cut-off (MWCO). Membranes are typically constructed of ceramic, stainless steel or polymeric material and must be able to withstand high cross-membrane pressures. The choice of material is generally a function of the material being filtered although the membrane should be able to withstand the harsh cleaning chemicals to remove the scale and buildup from operation. A combination of factors such as high temperatures, viscosities, presence of fibrous and abrasive particles, all present a challenge for predicting the lifetime and reliability of a membrane system (Kochergin, 2001).

The higher the pressure applied across the membrane, the higher the flux or material passing through into the permeate stream. One way to maintain the flux during operation, with material being deposited on the membrane during filtration, is by increasing the velocity across the membrane as the run progresses. Although it is desirable to have a high operating flux through the system, the pumping requirements and costs are greatly increased.

As discussed above, higher molecular weight and colloidal material can be removed using ultra-filtration. Bento (2003) reported that the calculated ICUMSA color is increased by up to 50% by simply varying the filter aperture from 0.45μm to 1.25μm. After this aperture, color is maintained approximately constant. The effectiveness of ultra-filtration with regards to removing undesirable components, is reported by Steindl (2001). Average performances are shown below:
- Purity rise 0.45 units
- Removal of
  - Turbidity 95%
  - Dextran 98%
  - Starch 70%
  - Total polysaccharides 80%
  - ICUMSA color 25%

A large range of pore sizes is available although no significant color removal is experienced (Crees, 1986; Kochergin, 1997; Patel, 1991) unless the pore size is reduced to below 20,000 MW. The choice of pore size is done based upon the total membrane area (capital cost) and on maximizing the permeate flux (Fechter et al, 2001). The requirements of the permeate will also determine the choice of pore size as in ion exchange and chromatography where a clean feed is required. As such it has been suggested that ultra-filtration be used as a pretreatment, as it generally cannot produce a syrup of high enough quality to directly crystallize white sugar (Steindl, 2001). As a pretreatment, membrane technology may be applied to raw cane sugar mills after the lime defecation and clarification stage, which removes the insoluble solids and some soluble material. The reduced concentration of impurities in clarified juice will allow higher fluxes and increase the run time of the unit between cleaning.

Urquhart et al, (2000) report that filtering clarified juice using a membrane unit allows the production of high pol, low color sugar conforming to the Australian QHP (Queensland High Pol) standard. Another installation allowed the production of VLC (Very Low Color) sugar (Kwok, 1996), and high quality sugar produced with this
technique enabled the removal of the affination and remelt stations at the Crockett refinery in California. Membrane filtration has also been shown to reduce the crystallization time for the boiling of A sugar by 20-30% (Saska, 1997).

A large source of potential loss in an operation utilizing ultra-filtration is in the retentate stream, which contains a large amount of sucrose. This stream cannot be neglected, and as such various methods have been researched for its usefulness.

- Dilution of the retentate, to increase the flux rate in a secondary filtration (Steindl, 2001)
- Clarification of the retentate using a flotation clarifier (Steindl, 2001)
- Recycling of the retentate to the existing settling clarifiers (Rossiter et al, 2002)
- Using the retentate as a feed to a neighboring ethanol facility (Rossiter et al, 2002)

2.3.2 Ion Exchange Resins

Ion exchange resins have been used in sugar refineries since the 1970’s despite their effluent disposal problems. The lower capital and operating costs have made fixed-bed ion-exchangers advantageous to activated carbon and bone char decolorizers (Van der Poel et al, 1998; de Lataillade, 2002).

More recently membrane technology has been investigated on a pilot scale (Rossiter et al, 2002) in a raw sugar mill in South Africa to allow the use of fixed-bed ion-exchangers at the raw sugar mill to manufacture white sugar directly. The removal of large particulates has allowed the use of ion-exchangers, without severe fouling of the
resin beads, allowing the use of a single set of resin for a period longer than the length of an average South African season (about 9 months).

Broadhurst (2002) using gel permeation chromatography to measure individual colored components, derived a model for finding model parameters specifically for ion-exchange resins. This was a more detailed attempt to model the decolorization using ion-exchange resins, than done by Morley (1988), in that it attempted to model colored components individually. The previous model by Morley treated the colorants as a whole, using the ICUMSA method, which gives no indication as to the colorants removed. This can be misleading as colored components removed may not be transferred to the crystal during crystallization giving a false indication of the color of the final sugar.

2.3.3 Packed Carbon Beds

Packed carbon beds are nothing new to the sugar industry, being used as a decolorizing stage in the refining of raw sugar to produce white sugar. Historically, bone charcoal has been the principal color adsorbent, with records of its use dating from the early 1800’s. More recently, granular activated carbon or ion exchange resins have replaced it in new or refurbished refineries (Moodley et al, 1998; Debwe 2001). Powdered activated carbon is also used in some refineries, but more as a polishing adsorbent than as a bulk mainstream decolorizer (Field, 1997).

Granular activated carbons used in sugar refining are comprised of up to 90% carbon and are generally made from a bituminous coal base. The manufacturing process includes an initial carbonization stage in a reducing atmosphere at 600 – 700°C, followed by an activation stage with steam at 900 – 1000°C to develop and open up the pore structure. As with bone charcoal, the capacity to remove color is due to the very high
surface area available in the adsorbent. The carbon surface is non-polar, and the adsorption mechanism is physical adsorption via Van Der Waal’s forces. The carbon manufacturing process produces a higher surface area than bone charcoal, and granular carbons generally have about 10 times the color adsorptive capacity than that of bone charcoal.

Because the carbon surface is non-polar, granular carbons, unlike bone charcoal, have no ash removal capacity. This may present a problem in some applications particularly where high ash raw sugars are being processed. This however makes granular carbons an ideal pretreatment for ion exchange resins where the ash will be taken out in the following stages.

2.3.4 Oxidation Reactions

The use of oxidants as decolorizers in the sugar industry has been reported by many authors, with the use of oxidizing agents such as hydrogen peroxide (Moodley, 1992; Mendoza, 2002; Bento, 2004) and ozone (Davis et al, 1998). Of particular interest is the work by Bento (2004) with hydrogen peroxide being used as a pretreatment method before a resin decolorizing stage. The advantages of this pretreatment were shown to include:

- Resins will be less contaminated
- Resin cycles could be extended 3 or 5 times
- Less effluent (with lower color) will be produced
- Less chemicals and utilities will be consumed
- Less sweet water will be produced
- Effluent treatment costs will be reduced
CHAPTER 3. THEORY

3.1 Axially Dispersed Packed Bed Adsorption Model

This model describes the adsorption of components, within a binary mixture, onto the porous adsorbent particles within a packed bed reactor. To simplify the model, it is assumed that the adsorption process is not rate limiting, in that it occurs very fast relative to the convection and diffusion effects within the bed. As a result, local equilibrium will exist close to the adsorbent beads, allowing the equilibrium to be represented as an adsorption isotherm.

An adsorption isotherm describes the thermodynamic equilibrium of the concentration of one component in a fluid (gas or liquid) and a solid phase. The adsorption isotherm provides fundamental information relating the concentration in the film around the resin to the concentration on the resin bead. The three most common isotherms are, the Linear; Langmuir or Freundlich isotherm.

3.1.1 Fluid Phase

Consider an element of a packed column (Figure 3.2) of length $dz$, constant fluid flow $Q$, concentration $C$ and cross sectional area $A$ with porosity $\varepsilon$.

![Figure 3.2: Differential element of a packed bed adsorption column](image-url)

Figure 3.2: Differential element of a packed bed adsorption column
Neglecting radial effects, an unsteady-state material balance may be performed, yielding:

\[
\frac{Q C_z}{\text{Fluid Flow}} \bigg|_{z} - \frac{Q C_z}{\text{fluid}} \bigg|_{z+\epsilon} + \varepsilon A \left[ -D \frac{\partial C}{\partial z} \right]_{z} - \varepsilon A \left[ -D \frac{\partial C}{\partial z} \right]_{z+\epsilon} = \varepsilon \frac{\partial C}{\partial t} Adz + (1-\varepsilon) \frac{\partial q}{\partial t} Adz \quad (3.1)
\]

With \( q \) being the concentration on the resin surface. Dividing by \( Adz \) and taking the limits,

\[
- u_0 \frac{\partial C}{\partial z} + \varepsilon D \frac{\partial^2 C}{\partial z^2} = \varepsilon \frac{\partial C}{\partial t} + (1-\varepsilon) \frac{\partial q}{\partial t} \quad (3.2)
\]

Where \( u_0 = \frac{Q}{A} \)

The following boundary conditions are required:

i) \( C(z = 0, t) = C_0 \) \quad (3.3)

ii) \( C(z = \infty, t) = 0 \) \quad (3.4)

These first of these spatial conditions is a simple Dirichlet condition that controls the feed concentration to the column making the assumption that the feed concentration is fixed. The second condition arises from an assumption that at a point, infinitely far from the inlet, the concentration is zero. As a result, the column can absorb an infinite amount of solute resulting in a solute free product.

The more common Dankwerts boundary conditions could have been used but due to a calculated Peclet number \( \gg 1 \), the use of the above simplified boundary condition (equation 3.3) is justified. Equation 3.4 is also an appropriate simplified condition as the reactor is long enough to absorb all the colorant.

From the assumption that the column is cleaned and free of contaminants after successive runs, we arrive at the initial condition:
3.1.2 Solid Phase

The solid phase concentration is controlled by the rate at which the solute is removed from the solution. Although there are many complex expressions describing interphase transport, the two most popular expressions are: the bidisperse pore model and the linear driving force (LDF) approximation.

The bidisperse pore model (Ruckenstein, 1971) models the adsorbent particle as a macrosphere comprising of many small microspheres. Spaces between the micro and macrospheres (macropores) allows diffusion of the solute into the particle. The microspheres are also porous allowing further diffusion into the particle. This results in two equations describing the diffusion of the solute into the micro and macropores. Another equation is then required, describing the fluid phase, resulting in a very complex system of three differential equations.

The linear driving force model (LDF) model was formulated by Gleuckauf (1947) and makes the simplification that a single film mass transfer coefficient controls the rate of uptake from the liquid phase. Rice (1982), observed that it is also possible to use the same model even when the intraparticle diffusion cannot be neglected. The film coefficient is simply renamed as an overall effective mass transfer coefficient.

Using the above assumption, the rate of accumulation in the solid phase is equal to the rate of uptake from the liquid phase according to the LDF approximation resulting in the equation:

\[
C(z,t = 0) = 0 \quad (3.5)
\]

\[
(1 - \varepsilon) \frac{\partial q}{\partial t} Adz = k_f \alpha (C - C^*) \varepsilon Adz \quad (3.6)
\]
Where \( q \) is the concentration on the resin surface. Simplifying the above,

\[
(1 - \varepsilon) \frac{\partial q}{\partial t} = k'(C - C^*) \varepsilon \quad (3.7)
\]

From the assumption that perfect regeneration of the resins is possible after successive runs, we obtain the initial condition:

\[
q(z, t = 0) = 0 \quad (3.8)
\]

In accordance with the assumption of a point at infinity having zero concentration, a boundary condition can also be obtained of the form:

\[
q(z = \infty, t) = 0 \quad (3.9)
\]

### 3.2 Plug Flow Adsorption Model

Carberry and Wendel (1963) report that if the bed depth exceeds fifty particle diameters, the axial dispersion term can be neglected. In the experiments performed, the ratio of column length to particle diameter far exceeds this value and so plug flow is likely. Therefore, neglecting the axial dispersion, the governing equations 3.2 and 3.7 are expressed as:

\[
u_i \left( \frac{\partial C}{\partial z} + \frac{\partial C}{\partial t} \right) + \left(1 - \frac{\varepsilon}{\varepsilon} \right) \frac{\partial q}{\partial t} = 0 \quad (3.10)
\]

\[
\left(1 - \frac{\varepsilon}{\varepsilon} \right) \frac{\partial q}{\partial t} = k'(C - C^*) \quad (3.11)
\]

Where \( u_i \), the superficial velocity is defined as,

\[
u_i = \frac{u_0}{\varepsilon}
\]

A linear isotherm will be substituted into 3.9, but unlike the classical substitution for \( q \), it will be substituted for \( C^* \). Morley (1988) reports that the measured,
ICUMSA color isotherm is Langmuir, but is linear under normal column operating conditions. Equation 3.11 is then replaced by:

$$\frac{1 - \varepsilon}{\varepsilon} \frac{\partial q}{\partial t} = k^* \left( C - \frac{q}{K(pH)} \right)$$  \hspace{1cm} (3.12)

It has been shown (Broadhurst, 2002) that $K$, the equilibrium constant is a function of pH. Since pH is a time dependent variable, it makes sense to substitute for $C^*$, as it does not appear in any of the derivative terms. This has the advantage of not requiring the derivative of the pH with respect to time. A number of other authors (Chern et al, 2001; Wu et al., 1999 & Guibal et al, 1994) have experienced pH effects on adsorption isotherms.

### 3.2.1 Non-dimensionalization

The combination of equations 3.10 and 3.12, we can obtain a more concise form by non-dimensionalization. By defining the following dimensionless variables:

$$\eta = \frac{z}{L}; \hspace{1cm} \bar{C} = \frac{C}{C_0}; \hspace{1cm} \bar{q} = \frac{q}{C_0}$$ \hspace{1cm} (3.13)

Upon substitution we obtain,

$$\frac{L}{u_i} \frac{\partial \bar{C}}{\partial \tau} = -\frac{\partial \bar{C}}{\partial \eta} - S_{t}\left( \bar{C} - \frac{\bar{q}}{k(pH)} \right)$$ \hspace{1cm} (3.14)

Where,

$$S_{t} = \frac{k^* L}{u_i}$$ \hspace{1cm} (3.15)

Further defining the variables $\theta$ and $\tau$ as:

$$\tau = \frac{L}{u_i}; \hspace{1cm} \theta = \frac{t}{\tau}$$ \hspace{1cm} (3.16)
Equation 3.14 then reduces to:

\[
\frac{\partial \bar{C}}{\partial \theta} = -\frac{\partial \bar{C}}{\partial \eta} - St\left(\bar{C} - \frac{\bar{q}}{K(pH)}\right) \tag{3.17}
\]

The boundary and initial conditions are essentially unchanged, yielding their new form:

\[
\bar{C}(\eta = 0, \theta) = 1
\]

\[
\bar{C}(\eta = \infty, \theta) = 0
\]

\[
\bar{C}(\eta, \theta = 0) = 0 \tag{3.18}
\]

Similarly, by substitution, we obtain the following solution for 3.12 and its boundary conditions.

\[
\frac{\partial \bar{q}}{\partial \theta} = \left(\frac{\varepsilon}{1 - \varepsilon}\right)St\left(\bar{C} - \frac{\bar{q}}{K(pH)}\right) \tag{3.19}
\]

\[
\bar{q}(\eta, \theta = 0) = 0
\]

\[
\bar{q}(\eta = \infty, \theta) = 0 \tag{3.20}
\]

### 3.2.2 Plug Flow Model Summary

\[
\frac{\partial \bar{C}}{\partial \theta} = -\frac{\partial \bar{C}}{\partial \eta} - St\left(\bar{C} - \frac{\bar{q}}{K(pH)}\right) \tag{3.21}
\]

\[
\frac{\partial \bar{q}}{\partial \theta} = \left(\frac{\varepsilon}{1 - \varepsilon}\right)St\left(\bar{C} - \frac{\bar{q}}{K(pH)}\right) \tag{3.22}
\]

### 3.2.3 Estimation of Stanton Number

The correlation by Wilson and Geankoplis (1966) may be used to estimate the mass transfer of liquids in packed beds. For Reynolds and Schmidt numbers in the range of 0.0016-55 and 165-70,600, respectively:
\[ J_D = \frac{1.09}{e} \text{Re}^{2/5} \] (3.23)

where,

\[ \text{Re} = \frac{d \mu u_0}{\mu}, \quad J_D = \frac{k_c}{u_i} (Sc)^{2/3}, \text{ and } Sc = \frac{\mu}{\rho D_{AB}} \] (3.24)

Using the correlation of Wright (1981) for the viscosity of the sugar solution at 10°C and 25 brix:

\[ \mu = 4.70 \times 10^{-3} \text{ Pa.s} \]

Bubnik et al (1995), reported a correlation that yields a density at the above conditions of:

\[ \rho = 1107 \text{ kg/m}^3 \]

This yields \( \text{Re} = 0.20 \) and \( J_D = 6.89 \).

The colorant diffusivities, for differing molecular weights, can be found using the semi-empirical equation of Polson (1950). This correlation is recommended for biological solutes of molecular weight greater than 1,000:

\[ D_{AB} = \frac{9.40 \times 10^{-15} T(K)}{\mu (M_A)^{1/3}} \] (3.25)

At a temperature of 10°C, the diffusivity and hence the Schmidt number can be calculated. Noting that:

\[ k' = \frac{k_c}{d_p} \] (3.26)

\[ St = \frac{k' c \tau}{d_p} \] (3.27)

The Stanton number for each pseudo component can then be calculated as shown in Table 3.1:
Table 3.1: Literature predictions for Stanton number

<table>
<thead>
<tr>
<th>Component</th>
<th>MW</th>
<th>$D_{AB}$ (m²/s)</th>
<th>Sc</th>
<th>St</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5900</td>
<td>3.13E-11</td>
<td>135474</td>
<td>1.142</td>
</tr>
<tr>
<td>B</td>
<td>3660</td>
<td>3.67E-11</td>
<td>115540</td>
<td>1.270</td>
</tr>
<tr>
<td>C</td>
<td>2530</td>
<td>4.16E-11</td>
<td>102159</td>
<td>1.379</td>
</tr>
<tr>
<td>D</td>
<td>1720</td>
<td>4.73E-11</td>
<td>89828.3</td>
<td>1.502</td>
</tr>
<tr>
<td>E</td>
<td>1180</td>
<td>5.36E-11</td>
<td>79225.4</td>
<td>1.633</td>
</tr>
<tr>
<td>F</td>
<td>720</td>
<td>6.32E-11</td>
<td>67196.7</td>
<td>1.823</td>
</tr>
<tr>
<td>G</td>
<td>380</td>
<td>7.82E-11</td>
<td>54304.0</td>
<td>2.101</td>
</tr>
</tbody>
</table>

It should be noted that the correlation of Polson for the diffusivity of the colorant is recommended for molecular weights greater than 1,000, indicating that the Stanton numbers for pseudo component F and particularly G, are slightly inaccurate.

3.2.4 Estimation of Hydrodynamic Dispersion

Although Carberry and Wendel (1963) report for the packed bed case above that axial dispersion is negligible, this statement can be readily validated by finding the hydrodynamic dispersion and adapting the model to include this term.

First calculating a Peclet number using the expression:

$$Pe = \frac{u_d d_p}{D_{AB}} \quad (3.27)$$

A value of $Pe = 3.41 \times 10^6$ is obtained for the highest molecular weight component, which will have the highest hydrodynamic dispersion. Using this value with a dispersion correlation by Dullien (1979), a dispersion of $D = 1.57 \times 10^{-4}$ m²/s is obtained.

Using the same technique of non-dimensionalizing, the developed model can be altered to include a dispersion term. The final result is given below in equation 3.28.

$$\frac{\partial \bar{C}}{\partial \theta} = -\frac{\partial \bar{C}}{\partial \eta} + \frac{D \tau}{L^2} \frac{\partial^2 \bar{C}}{\partial \eta^2} - \frac{St}{\tau} \left( \bar{C} - \frac{\bar{q}}{K(pH)} \right) \quad (3.28)$$
3.3 Numerical Solution Technique

3.3.1 Finite-Difference Methods

In contrast to an analytical solution, which allows for determination of an unknown variable at any point of interest, a numerical solution enables the determination of the desired variable at only discrete points (Incropera & DeWitt, 2002). This is done by first discretizing the given domain and then applying either an explicit or implicit method to the system of differential equations, with their associated boundary conditions. Once in the appropriate form, the solution can then be obtained using many different mathematical software packages. The software of choice for this solution is MATLAB.

3.3.2 Solving Using MATLAB

In order to solve the above set of equations in MATLAB, equations 3.21 and 3.22 must first be discretized and then put into a matrix form, which can be solved in a MATLAB algorithm. Using the following expressions, we can discretize equations 3.21 and 3.22:

\[
\frac{\partial q}{\partial \theta}_{m,n} = \frac{q^{p+1}_{m,n} - q^p_{m,n}}{\Delta \theta} \quad (3.29)
\]

\[
\frac{\partial \overline{C}}{\partial \eta}_{m,n} = \frac{\overline{C}^{p+1}_{m+1,n} - \overline{C}^p_{m-1,n}}{2\Delta \eta} \quad (3.30)
\]

\[
\frac{\partial \overline{C}}{\partial \theta}_{m,n} = \frac{\overline{C}^{p+1}_{m,n} - \overline{C}^p_{m,n}}{\Delta \theta} \quad (3.31)
\]

Noting the simple one dimensional geometry, substitution into 3.21 yields,

\[
\overline{C}^{p+1}_{m} = \alpha \overline{C}^p_{m-1} + (1-\delta)\overline{C}^p_{m} - \alpha \overline{C}^p_{m+1} + \gamma q^p_{m} \quad (3.32)
\]
Where:

\[ \alpha = \frac{\Delta \theta}{2 \Delta \eta}; \quad \delta = \Delta \theta \cdot St; \quad \gamma = \frac{\delta}{K(pH)} \]

Placing the above equation in a matrix of the form:

\[ AC^{(p+1)} = BC^{(p)} + \gamma \]

We obtain,

\[
\begin{bmatrix}
C_{m}^{p+1} \\
C_{m+1}^{p+1} \\
\vdots \\
C_{n}^{p+1}
\end{bmatrix}
= \begin{bmatrix}
1 - \delta & -\alpha & 0 & 0 & 0 \\
\alpha & 1 - \delta & -\alpha & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 1 - \delta & -\alpha
\end{bmatrix}
\begin{bmatrix}
C_{m}^{p} \\
C_{m+1}^{p} \\
\vdots \\
C_{n}^{p}
\end{bmatrix}
+ \gamma \bar{q}_{m}^{p} \quad (3.33)
\]

Similarly for 3.22,

\[
\bar{q}_{m}^{p+1} = \bar{q}_{m}^{p} \left(1 - \frac{\xi}{K(pH)} \right) + \xi \bar{C}_{m}^{p} \quad (3.34)
\]

With,

\[ \xi = \left(\frac{\varepsilon}{1 - \varepsilon}\right) \delta \]

We obtain the matrix:

\[
\begin{bmatrix}
\bar{q}_{m}^{p+1} \\
\bar{q}_{m+1}^{p+1} \\
\vdots \\
\bar{q}_{n}^{p+1}
\end{bmatrix}
= \begin{bmatrix}
1 - \frac{\xi}{K(pH)} & 0 & 0 & 0 & 0 \\
0 & 1 - \frac{\xi}{K(pH)} & 0 & 0 & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 1 - \frac{\xi}{K(pH)} & -\alpha
\end{bmatrix}
\begin{bmatrix}
\bar{q}_{m}^{p} \\
\bar{q}_{m+1}^{p} \\
\vdots \\
\bar{q}_{n}^{p}
\end{bmatrix}
+ \xi \bar{C}_{m}^{p} \quad (3.35)
\]

The above matrices can then be solved simultaneously, solving for the successive time steps.
CHAPTER 4. MATERIALS AND METHODS

4.1 Experiments

4.1.1 Feed Preparation

Feed preparation, for the ion exchange column runs, were done by passing the syrup through either an ultra-filtration unit, or a packed carbon column. The syrup used during the experiments was syrup from the St. James mill from three consecutive seasons. Smaller volumes of syrup were stored at 9°C when not in use and were filled from 40 gallon drums which were kept in cold storage at -8°C.

4.1.2 Ultra-Filtration

Ultra-filtration was originally done using a PallSep™ 0.45μm Vibrating Membrane Filter (See Figure 4.1) with polymeric membranes. For the later control experiments, a Graver 0.1μm, stainless steel, ultra-filtration unit (Figure 4.2) was used.

Figure 4.1: Pallsep™ 0.45μm Filter

Figure 4.2: Graver 0.1μm Filter
The procedure for ultra filtration using either the Graver or PallSep™ units is as follows:

a. Dilute syrup to approximately 25% brix in feed tank.

b. Heat the feed to approximately 65°C using steam.

c. Open valve from the tank to ensure the pump does not run dry.

d. Start the pump

e. Set desired cross membrane pressure by adjusting the retentate control valve.

f. For the vibrating screen ultra-filtration unit:

   a. Start oscillating motor and set vibration to within recommended operating amplitude

   b. Maintain oscillating motor amplitude during the run to ensure it remains within the operating boundaries

g. When feed runs low, turn off pump. (For vibrating screen, oscillating motor must be switched off prior to the pump)

h. Wash feed tank and system thoroughly with heated water.

i. Fill tank and add bleach.
j. Heat the tank

k. Start filtration system as before

l. When the tank is near empty, commence shutdown procedure.

m. Fill the tank with water, heat, and wash thoroughly

4.1.3 Batch Tests

Batch tests were performed on syrup at various concentrations to try and establish an isotherm for the resin. As the name suggests, isothermal conditions are required and were achieved using jacketed 250ml glass beakers for all the tests. Circulating water at 10°C from a Neslab refrigerated water bath was passed through the jacketed vessels to ensure constant temperature.

Volumes of 150ml ultra-filtered syrup are placed in the beakers and cooled to 10°C. The isotherm will be the color in the resin as a function of the color in solution for various sample times. Thus, by increasing the brix, and hence the concentration in the solution, we can see the different regions of the isotherms. Approximately 15ml of filter-dried resin were used in the batch tests. Once dried, the resin is added to the beaker, starting the first time interval. Magnetic stirrers are also to be placed in the beaker to ensure sufficient contact of the fluid with the resin beads.

Five minute intervals were used for the batch tests and samples were removed using an Eppendorf® adjustable-volume pipettor. Particular attention must be paid when sampling to ensure no resin is removed with the sample.

Although resin equilibrium testing is normally done over a much longer time period (Morley, 1988), to ensure equilibrium is achieved, this is not feasible for these tests. When the H⁺ or OH⁻ ions are released, from the SAC and WBA resin respectively,
the pH of the solution changes significantly. Some of the colored components in the syrup exhibit a very strong pH effect with regard to color and much color can be formed over prolonged time intervals. As a result of this, the testing time was shortened to thirty minutes with sampling every five minutes.

### 4.1.4 Void Fraction Measurement

Void fraction, or voidage, of the resin plays a very important role when calculating interstitial velocities and the nature of the packed bed. As a result of this, the void fraction should be known as accurately as possible. This was done by first putting the resin in a weak salt solution. The purpose of this is to fill the micro-pores within the resin, as it is only the macro-porosity that is of interest, for calculating the voidage. After placing the resin in a salt solution it is washed sparingly with water and oven dried. This is necessary as it is desirable to remove the salt solution from the beads without unsaturating the micro-pores. The dry resin is then placed in a 10ml measuring cylinder and a known volume of hexane is added. This is done to allow the resin to settle more rapidly due to the lower density of hexane and inhibit the salt solution from leaving the micropores. After ensuring that the resin has been properly mixed in the hexane, the voidage of the resin can be calculated using the packed-bed resin volume, the hexane added and the total volume.

### 4.1.5 Carbon Column Pretreatments

A jacketed 25mm OD glass column of 600mm length was used for the carbon pretreatment stage. A feed concentration of approximately 25 Brix was fed to the column, although in practice a much lower brix would be used, as the carbon pretreatment stage would occur before the first effect. At present, the ultra-filtration station is implemented
after the first effect due to the high operating costs requiring it to be run at a higher brix flux. Sampling times were the same for color analysis. For suspended solids and turbidity analysis, a larger sample was taken to satisfy the required sampling size at later time intervals. Regeneration of the carbon column is currently being done by autoclaving, at 121°C and 15 psi for 15 minutes, where in practice a kiln would be used. Although this is not the conventional means of regenerating the carbon it serves to prevent microbial growth and it is then known that even better carbon regeneration and subsequently color removal could be obtained with proper regeneration.

4.1.6 Packed Bed Column Runs

Two resins were investigated in the packed-bed column experiments (Table 4.1) with two separate aliquots of resin being used. Due to the investigation of the pretreatment using a carbon bed, a control to compare the carbon treated syrup was setup. The control consisted of the exact same operating conditions, and runs, with the exception that the control resins were fed ultra-filtered syrup, having been filtered using a 0.1µm ultra-filtration system.

<table>
<thead>
<tr>
<th>Resin</th>
<th>Type</th>
<th>Form</th>
<th>Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rohm &amp; Haas Amberlite 252 RF</td>
<td>Strong acid cation (SAC)</td>
<td>H⁺</td>
<td>Diluted treated syrup</td>
</tr>
<tr>
<td>Rohm &amp; Haas Amberlite IRA 92 RF</td>
<td>Weak base anion (WBA)</td>
<td>OH⁻</td>
<td>Cation product</td>
</tr>
</tbody>
</table>
The before mentioned jacketed columns were connected to VWR Scientific and Neslab circulating baths, for cooling and heating of the jackets, respectively. The SAC was maintained at 10°C for all the runs due to the possibility of inversion. FMI piston pumps were used to keep constant flow rates in and out of the columns. A pump was used at the column entrance and exit to ensure a constant flow rate out of the column throughout the run. The pH of the solution leaving the column was monitored using an Orion pH meter to observe when the column was becoming saturated.

Prior to starting the run, the column is washed using deionized water to ensure that any contaminants, which may have got into the resin since previous runs, are removed. A sample is taken of the column feed and then the run is started. By knowing the bed volume and the flow rate, it can be calculated how long it will take for one bed volume to pass through the column. At this time a sample is taken and the clock is reset to zero with successive samples being collected every five minutes.

For the control experiment, only 0.1μm ultra-filtered syrup was passed through the resins and the resins were kept separate from those with the carbon-pretreated syrup.
Both resins were fed syrup at approximately 25 brix for comparative purposes, in practice the carbon treated process would use juice at a lower brix level.

Samples from the column run were analyzed using GPC. Other tests performed included; ICUMSA color, conductivity and pH. For the case of carbon-pretreated samples, turbidity tests were also performed.

4.1.7 Mixed Bed Column Runs

A jacketed glass column was again used for the mixed bed runs. Different permutations were tried for the mixed bed runs with respect to the anion-cation ratios. Initially a WBA was used in conjunction with a SAC but after the pH could not be neutralized, a SBA was used. SAC to SBA ratios of 1:1; 1:3 and 1:4 were used but a neutral pH could not be obtained for any satisfactory period of time. Regeneration of the mixed bed was done by back-flushing the column and taking advantage of the different densities of the resins. Once adequate separation was obtained, the resins were physically separated and regenerated independently, as for the SAC and WBA regenerations. Although tedious, very good separation was obtained with minimum resin loss during each run. Samples were taken every five minutes with the exception of the initial sample, which was calculated at one bed volume.

4.1.8 Oxidation Reactions

A large glass container is filled with syrup and diluted to approximately 14 brix to perform the oxidation reaction. The container is then placed on a heating plate with a magnetic stirrer and heated to 85°C. This temperature is to be monitored continually with a thermometer to ensure the temperature is kept constant. An increase in temperature could result in further color formation and a decrease could reduce the rate and reduce the
effectiveness of the oxidation reaction. The pH required for the reaction is 8.5 and the reaction time is approximately 30 minutes (Bento, 2004). The recommended dosing of hydrogen peroxide varies from 200ppm (Davis et al, 2000) to 500ppm on solids (Bento, 2004) for a raw melt, but due to the high concentration of colorants in the syrup 1000ppm should be used on the diluted syrup.

Analytical measurements performed on the original diluted syrup and treated syrup should include ICUMSA color, GPC and turbidity measurements to find the overall change during the reaction.

4.1.9 Resin Regeneration

Due to the saturation of the resins during a run, the column must be regenerated at the end of a run prior to successive runs being performed. The SAC resin is regenerated using HCl at approximately 6%. This is done at 25°C by running 6 bed volumes through the resin at approximately 45ml/min. The resin is washed with de-ionized water before and after the acid regeneration. The WBA resin is regenerated using a NaOH solution at 10%. This is followed by an HCl regeneration at 6% and then another NaOH wash. The column is flushed with de-ionized water between the regenerations with NaOH and HCl. All regeneration is done at 80°C and 6 bed volumes are used for each wash. The acid wash is used to the nature of the colorant bonding on the resin. As reported by Bento (1992), the majority of sugar colorants have a negative charge in an alkaline medium and have an amphiphilic nature, having both hydrophilic and hydrophobic parts. These characteristics allow sugar colorants to be fixed to anionic resins by ionic and/or hydrophobic interactions. In the first case the ionic bond is formed by the negative polar part of the colorant and the resin fixed ion. In the second case, the hydrophobic part of
the colorant is forced against the resin matrix by hydrophobic interaction. Weak Van-der-Waal forces then bond the colorant to the resin matrix. The NaOH wash will serve to remove the ionically bonded colorant and then allow the hydrophobic bond to be replaced by an ionic bond. The acid wash serves to remove the hydrophobic bond that is not replaced by an ionic bond after the NaOH wash.

4.1.10 Carbon Regeneration

Carbon regeneration was originally conducted in an autoclave at 121°C and 15 psig for 15 minutes, mainly to sterilize the material and prevent microbial activity on the carbon, that could reduce the decolorizing ability and contaminate the syrup passing through the bed. It later became apparent after successive runs that the decolorizing ability of the carbon bed was decreasing and as a result the carbon was then regenerated in a furnace.

The required temperature for regeneration for a multiple hearth furnace, that was used for regenerating granular carbon from a decolorizing system, (Harrison, 1988) reported temperatures in the hearths incrementing from 504°C to 760°C and then finally to 954°C. Field (1997) also reported temperatures ranging from 700°C – 800°C in the middle hearths and increasing to 900°C in the lower hearths. A lower temperature of 600°C was used, in a Thermolyne furnace, due to there being a small quantity of carbon to be regenerated and the desire to reduce the amount of fines produced. Successive runs showed the regeneration to be adequate, taking the product color down to that of virgin carbon. The furnace takes approximately one hour to heat to the temperature and three hours to return to the starting set point of 200°C.
4.1.11 Color Investigation

Using GPC as an analysis tool, various color formation tests were performed on syrup to try and introduce various colored components. These identified colored components or pseudo components were then assigned a peak number and used in modeling of the colorants. The tests performed upon the syrup were:

- Caramelization
- Alkaline degradation products (ADP)
- Iron effects
- Enzyme effects
- Maillard reactions on molasses and juice

Materials: Syrup, from the St. James mill, was ultra-filtered for the ADP and caramelization tests. For the iron and enzyme effects, juice was prepared using whole stalk cane from St. Gabriel. Maillard tests were performed on both juice and molasses samples.

The juice was prepared in a stainless steel environment using a jacketed, water-cooled, stainless steel Reetz Varigrator™ 7200rpm disintegrator. The whole stalk cane was first cut into approximately four inch pieces and then quartered before being placed in the disintegrator with water. After the disintegrator, the juice was filtered with a large Buchner funnel. Samples taken from the products where also centrifuged to allow them to pass through a 5µm filter, before going into the GPC.

It should be noted that cane-borer larvae were observed in all the cane stalks, but the affected areas were included to provide a representative sample.
Caramelization and ADP: Ultra-filtered syrup was boiled under constant reflux at atmospheric pressure for 30 minutes. Sodium hydroxide was added to the syrup to yield a pH of 8.8 for the ADP reaction prior to heating. Although caramelization and ADP reactions are similar in their thermal mechanisms, ADP forms much darker colorant due to the elevated pH (Godshall, 2000).

Iron and Enzyme Effects: Iron and enzyme effects were investigated on the juice prepared from the cane stalks. Tests were done using acid cleaned and rusty iron samples. Concurrent tests were also performed using autoclaved juice, to destroy any enzymes. Autoclaving was done at 121°C for 10 minutes after the addition of one part mercuric chloride per 5000 parts juice. All samples were maintained at 50°C for 1 hour.

Maillard Reactions: The Maillard reactions are favored by high temperature and brix but low purity (Newell, 1979). This was achieved by heating the molasses to 75°C and maintaining the temperature, using a jacketed flask, for 24 hours. The same procedure was used when performing the Maillard reactions on juice, but the high brix condition was not satisfied.

4.2 Sample Analysis

ICUMSA color: ICUMSA color measurements are done in accordance with the ICUMSA method as described in the SASTA laboratory procedures. ICUMSA color tests were performed, as it is a well-known industry standard for color measurement. The procedure entails neutralizing the sample to a pH of 7 ± 0.1 using NaOH and HCl solutions. This is particularly difficult for deashed solutions as they have little or no buffering capacity. The sample is then diluted to a light color (so as to fall within the 0.1-1.0 absorbance units range) and then filtered at 0.45μm. The absorbance is then measured using a
spectrophotometer at 420nm. The brix value of the sample is determined using a
refractometer. The ICUMSA color is then calculated using the formula:

\[
ICUMSA(420nm) = \frac{[Abs(420\,nm)] \times 10,000}{\text{Conc. (g/ml)} \times \text{Cell Length (mm)}}
\]  

(4.1)

The concentration term is found using Table 8 in the SASTA Laboratory manual relating
brix to concentration. Fitting a curve to the points a quadratic equation is found, where
the concentration is:

\[
\text{Concentration (g/100ml)} = 0.0041 \times \{\text{Brix}\}^2 + 0.9972 \times \{\text{Brix}\}
\]

(4.2)

A correlation coefficient of 0.999 was found for the above expression showing that the
equation is very accurate for the range being investigated.

Turbidity: Turbidity measurements are done using a HACH 2100 Turbidity meter. A
sample vial is filled with the solution to be measured and inserted in the turbidity meter,
which has an internal calibration. The output is in nephelometric turbidity units (NTU’s),
which will be a function of the suspended material, the brix and the color of the solution.

Conductivity: Conductivity measurements are done using a Fischer Acumet conductivity
meter. Conductivity gives an indication of the ash contained in a sample. The
conductivity meter is calibrated using a Potassium solution with known conductivity of
328µS at 20°C.

GPC procedure: The data obtained from the above tests were then analyzed at 280nm,
with occasional analysis at 420nm to check validity of results and be able to reference to
ICUMSA colors.

Samples removed from the products, for GPC analysis, are first neutralized to a
pH of 7, as is done with the ICUMSA color test. This is done due to the strong effect of
pH on color for certain components (Bento, 2003), known as the indicator value (IV).
The samples are then diluted to approximately 7 brix. After dilution, the samples were filtered using a 5\(\mu\)m filter. Juice samples were centrifuged due to the high amounts of suspended particulates.

Filtered samples were placed in sample vials and inserted into the BioRad autosampler. The auto-sampler takes 100\(\mu\)l samples and injects the samples into the mobile phases (1M NaNO\(_3\)). An isocratic pump delivers the injected samples at a rate of 0.5ml/min to the column.

The absorbance detector is in series with the GPC columns and is set to the appropriate wavelength at the start of the run. The absorbance detector analyzes injected samples after passing through the column. The sample then passes though a differential refractometer (DRI) before disposal. Absorbance and RI data is logged simultaneously on the system.

**GPC Deconvolution Procedure:** The chromatograms obtained from the above GPC procedure were deconvoluted using a MATLAB\textsuperscript{®} algorithm developed by Broadhurst (2002). The algorithm followed for the deconvolution of GPC chromatograms is summarized below:

1. Load data from text-file logged by GPC.
2. User specifies baseline.
3. User specifies approximate location of peak maxima.
4. Regression on standard deviations.
5. Regression on retention times, using the regressed standard deviation.
f) Regression on peak maxima, and standard deviation from above retention times.

g) Calculate peak area and correlation coefficient.

Iterate with number of peaks to get optimum fit.
CHAPTER 5. RESULTS AND DISCUSSION

5.1 Color Formation Investigation

Color formation tests were conducted on syrup and juice to try and generate different colored components in order to establish which wavelength would be the best for identifying colorants over the entire molecular weight range. The tests performed were:

- Caramelization
- Alkaline degradation products (ADP)
- Iron effects
- Enzyme effects
- Maillard reactions on molasses and juice

Product samples were removed after these tests and analyzed using GPC. The resulting GPC chromatograms were then deconvoluted using a MATLAB® algorithm developed by Broadhurst (2002), as discussed in Chapter 4. An example of the algorithm output is demonstrated below, showing the seven peaks representing each of the pseudo components identified from the various color formation tests. The choice of seven peaks to represent the colored components was based on the color formation tests mentioned above. It was at these identified regions that significant changes in the absorbance response were witnessed during the color formation trials. It should be noted that the identified pseudo components are not necessarily the only colored components in the solution, but more likely a combination of many components that cannot be individually discerned.
5.2 Wavelength Determination For Analysis

Choosing the appropriate wavelength is necessary for the purpose of quantifying the colorants when using GPC. The magnitude of the absorbance response varies significantly depending on the wavelength used by the absorbance detector for different components. It is this response that is used in modeling the defined pseudo components.

The purpose of the chosen wavelength is not to isolate which wavelength is most suitable for detecting each colorant but rather to provide a wavelength responding reasonably to all colorant groups of interest. As discussed in chapter two, color quantification using standard methods such as the ICUMSA color method have their shortcomings in that they do not differentiate between the different types of colorants.
This method of analysis will provide a comparative means of quantifying color formation and removal over the entire range of molecular weights.

Four wavelengths were considered covering the ultra-violet and visible spectrum. The criteria being considered were; relative magnitudes of signals; catering for all peaks; comparative sensitivity and response to color formation. These criteria are clearly illustrated in figure 5.2 below.

As can be seen in the above figure, 254nm exhibits the greatest response, but too much emphasis is place on one peak or component. The other three wavelengths all catered for the components as required but the response from 420nm and 300nm was not as pronounced as 280nm. Another shortcoming of 420nm is that although it does have all peaks represented, the response for each is so marginal that little resolution is apparent in
the peaks. As the results above dictate, it would appear 280nm is the best wavelength, with the available equipment, for identifying all the components at their various molecular weights.

### 5.3 Pseudo Component Identification

The seven pseudo components identified are shown below in figure 5.3.

![Figure 5.3: GPC chromatogram at 280nm showing pseudo components at their respective retention times](image)

The molecular weights of these components can be related to their retention times using the calibration curve given in figure 5.4. This molecular weight calibration was done using standards of known molecular weights.
It is known that melanoidins, caramels and phenolics are removed by ion exchange (SB Davis 2001), which is apparent in the range of 15 to 20 minutes (10,000 to >1,000 MW range) when comparing the syrup to the final liquor chromatograms (See figure 5.5).

Figure 5.5: GPC Chromatogram at 280nm showing the colorant removal in the ion exchange columns by comparing syrup to the final WBA sample
The GPC chromatogram in Figure 5.6, for differing pH’s, at 420nm allows further differentiation of these three colorants. The effect of pH on the absorbance helps to differentiate between the three components. Component B (between retention times 16.5min and 17.5mins) can be seen to change its magnitude of absorbance significantly in Figure 5.5, which is characteristic of plant pigments, which are normally comprised of flavanoids or phenolics. Although the molecular weights do seem slightly high for phenolics, it should be noted that phenolics can polymerize to form higher molecular weight colored components (Davis, 2001), which could be in the correct range for component B. Davis also reported that Melanoidins have a medium molecular weight (>2500) and are pH insensitive which is true for component A. Caramels are harder to distinguish in that the can have varying molecular weights and color depending on the extent of the caramelization reaction.

Figure 5.6: GPC Chromatogram showing the difference in absorbance for varying magnitude at 420nm
It is documented that ion exchange resins remove color by other mechanisms than pure ion exchange, such as matrix adsorption (Riffer 1987). There is some color removal at approximately 22 minutes, which could be attributed to matrix adsorption. These components would be components other than melanoidins, caramels and phenolics and are hence not removed by pure ion exchange. It is also noted that these components are most effectively removed for low bed volumes, and as the matrix adsorption rate rapidly decreases, it could be by this mechanism that these colorants are removed. It is presumed that the colorants adsorbed into the matrix are HADP’s, which would explain their poor removal by the ion exchange mechanism (Bento, verbal communication) and why they are more difficult to remove from the resin during regeneration.

5.4 Mixed Bed Column Runs

The low pH in the SAC column can cause significant sucrose losses requiring a refrigeration stage to inhibit inversion. The mixed bed column runs were tried in various ratios of weak and strong base anion to cation resins to try and obtain a neutral pH product. By obtaining a neutral pH the refrigeration stage on the SAC could be eliminated, as pH inversion would no longer be a factor. The following figures show the product pH and conductivity from the mixed bed.
Figure 5.7: pH and conductivity readings for a 1:2 SAC to WBA ratio in a mixed bed

Figure 5.8: pH and conductivity readings for a 1:5 SAC to WBA ratio in a mixed bed
Figure 5.9: pH and conductivity readings for a 1:1 SAC to SBA ratio in a mixed bed

The pH variation is clearly seen in the above figures. Another aspect of these figures is the conductivity. It should be noted that the conductivity is generally above 1mS in contrast to the 100-500μS leaving a SAC and WBA in series.

The ICUMSA color values were also significantly higher throughout the runs as can be seen in Figure 5.10. It should be noted that a SAC and WBA runs separately have a final ICUMSA value <1000 for up to 7 bed volumes. It should also be noted that the runs were stopped based on the pH indicating that the resin was saturated. Furthermore, a lower number of bed volumes passed through the column before the run ended, which is another reason this operation would not be feasible due to the low capacity.
The mixed bed results were conclusive in that it doesn’t appear feasible to remove
the refrigeration, and individual column runs, while still maintaining the desired colorant
removal. It was also found that a neutral pH is not possible even with different
permutations with the resin ratios, which is a requirement for the removal of the
refrigeration to inhibit inversion at a reduced pH. The reduction of the deashing ability of
the resin is also undesirable in the mixed bed arrangement. This reduction in deashing
ability could be attributed to the counteraction of the oppositely charged ions within the
bed. This can be seen in figures 5.7 through 5.9 where the conductivity is measured in
milli-Siemens whereas in figures 5.14 and 5.18 for individual column runs, the
conductivity is measured in micro-Siemens leaving the WBA. An interesting observation
is that while trying to obtain a neutral pH, by increasing the anionic resin ratio, the
cationic resin reaches saturation quicker, resulting in the conductivity increasing rapidly
with the pH. This could mean that the ionic charges on the resins are neutralizing each
other. This would explain the reduction in colorant removal, as it is known that colorants are fixed to the resin by ionic and hydrophobic interactions (Bento 1992). By counteracting the ionic charges, this intuitively removes one of the mechanisms for color removal.

5.5 Carbon Bed Filtration

Carbon pre-treatment has been looked at as a possible replacement for the ultrafiltration stage. So as to obtain a representative comparison, two separate aliquots of resin have been used with ultra-filtered syrup being sent to the one set of resins and carbon-filtered syrup to the other. The syrup fed to the one set of resins is ultra-filtered at 0.1μm, which is the control against which the carbon performance will be compared. The packed carbon bed filtration results were in favor of using a packed carbon bed in preference to an ultra-filtration unit as depicted in figures 5.11 though 5.18 below. This is an interesting result as turbidity results and a visual inspection show that far less suspended solids are removed using a packed carbon bed (Table 5.1).

<table>
<thead>
<tr>
<th>Run</th>
<th>Turbidity (NTU)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
</tr>
<tr>
<td>4</td>
<td>67.1</td>
</tr>
<tr>
<td>5</td>
<td>425</td>
</tr>
<tr>
<td>6</td>
<td>40.3</td>
</tr>
<tr>
<td>7</td>
<td>42.7</td>
</tr>
<tr>
<td>8</td>
<td>44.2</td>
</tr>
<tr>
<td>9</td>
<td>136</td>
</tr>
<tr>
<td>10</td>
<td>103</td>
</tr>
</tbody>
</table>

There is a large variation in the turbidity in the above data, this can be explained by the syrup used in the experiment. A large amount of settling occurs while the syrup is in storage, resulting in higher turbidity values towards the bottom of the drum. It can
even be seen in the above values that Run 5 came from the bottom of a drum, with Run 6 then coming from the top of the next drum.

Turbidity measurements were done on the samples taken from the SAC and WBA to find the effects of the ion exchange resins on suspended solids. A lot of variation was seen in the results, with the turbidity increasing and decreasing across the run, resulting in some doubt in the validity of the measurements.

In separate ultra-filtration tests, the following data (Table 5.2) was obtained for varying brix conditions:

**Table 5.2 Turbidity values for ultra-filtration tests**

<table>
<thead>
<tr>
<th>Brix</th>
<th>Turbidity (NTU)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Product</td>
</tr>
<tr>
<td>15</td>
<td>85.6</td>
<td>0.212</td>
</tr>
<tr>
<td>20</td>
<td>92.8</td>
<td>0.261</td>
</tr>
<tr>
<td>25</td>
<td>104</td>
<td>0.345</td>
</tr>
</tbody>
</table>

In the WSM process it is stated that membrane filtration is used to protect the resins from fouling components present in the juice (Fechter et al, 2001). The experiments conducted, however, show that the colorants removed in the packed carbon bed are more of a fouling component that the suspended particles, which could block the pores reducing the total surface area for adsorption. This can be supported by considering the mechanism of adsorption of the resins and granular carbon. Due to the non-polar surface of the carbon, the adsorption is physical adsorption through Van Der Waal’s forces (Field, 1997), as is one of the bonding interactions between the resins and the colorants (Riffer, 1987). This would result in a reduced load on the resins after the carbon pretreatment.
This can be seen in figures 5.11 though 5.18 below, where the ICUMSA colors for the first and final runs using each pretreatment method, for the respective resins, are shown. The ICUMSA colors remain lower for a longer period of time for a carbon pretreatment for both the virgin resin and the used resin in the final run (run 10).

Figure 5.11: Run 1: SAC product ICUMSA colors for carbon and UF pretreatments

Figure 5.12: Run 1: SAC product pH and conductivity for carbon and UF pretreatments
Figure 5.13: Run 1: WBA product ICUMSA colors for carbon and UF pretreatments

Figure 5.14: Run 1: WBA product pH and conductivity for carbon and UF pretreatments
Figure 5.15: Run 10: SAC product ICUMSA colors for carbon and UF pretreatments

Figure 5.16: Run 10: SAC product pH and conductivity for carbon and UF pretreatments
Another refining benefit of using a packed carbon bed as a pretreatment, instead of ultra filtration, is there will be a lower sucrose loss due to there being no retentate stream. Not only is the yield increased, but also there is also no effluent stream to continually dispose of while running the unit, with the exception of sweet water that will be
generated when taking off and putting on columns. Furthermore, due to the lower running cost of a carbon bed, the brix flux will not be as critical allowing the raw juice to be processed without being concentrated and blended after the first evaporator. This will cause less fouling of the first effect evaporator tubes and in turn allow for the evaporators to be run longer before cleaning will be required.

A surprising result that was found during the analysis of the carbon bed filtration runs was the lack of change in absorbance, at 280nm, during the GPC analysis. When experiments were conducted taking samples of the product from the packed carbon bed, a large decrease was seen in the ICUMSA colors (See Figure 5.19), yet a minimal change was experienced according to the GPC chromatogram at 280nm (See Figure 5.20), where successive samples were taken at five-minute intervals. A trend was seen at 420nm (Figure 5.21) on the GPC that was more in agreement with the ICUMSA results, which are also conducted at 420nm.

![Figure 5.19: ICUMSA color vs BV for carbon column run](image)

Figure 5.19: ICUMSA color vs BV for carbon column run
Figure 5.20: GPC Chromatograms of samples taken from carbon column run at 280nm

Figure 5.21: GPC Chromatograms of samples taken from carbon column run at 420nm

These results were not limited to this trial with the same results occurring during successive runs as illustrated below.
Figure 5.22: ICUMSA color vs BV for carbon column run

Figure 5.23: GPC Chromatograms of samples taken from carbon column run at 280nm
This anomaly did appear to improve when syrup from the 2003 season was used. The chromatogram below (Figure 5.25) shows the change in absorbance during a carbon bed run. The initial syrup sample can be seen to be higher than the final sample taken from the bulk product from the carbon bed. Although there is a decrease, the ICUMSA values reported a color reduction of approximately 63%. This could show that the GPC is not sensitive to the components removed by the carbon column or that the specific components are less predominant at 280nm than at 420nm.
Figure 5.25: GPC Chromatograms of syrup and product samples taken from carbon column run at 280nm

A flow-rate of approximately 15 BV/h was used for the carbon experiments to make run times reasonable for the purpose of sampling. A run was performed at half this flow-rate to determine if the carbon bed was operating below its potential decolorizing capacity. It was found that the ICUMSA color showed no significant change by reducing the flow-rate. This is a significant result as it shows that the carbon beds could be used to feed multiple ion exchange beds, which typically operate at lower flow-rates, or a lower installed capacity would be required on the plant.

5.6 Strong-Acid Cation Resin

Typical results from the cation column are shown in figure 5.26. The dimensionless concentration (from the GPC absorbance analysis), pH and conductivity are plotted on the vertical axis. The number of bed volumes having passed through the column are represented on the horizontal axis. The variable of immediate interest is the concentration, representing the intensity of the colorant leaving the packed bed. The
relationship can be clearly seen between the concentration and the pH, with the breakthrough occurring as the pH begins to increase.

Figure 5.26: A typical SAC breakthrough curve (SAC UF-4 G)

The product from the column remains at a low pH and high conductivity until the number of bed volumes having passed through is approximately 13. Initially hydrogen ions (H+) that are attached to the resin are exchanged for the cations in the feed to the column, lowering the pH. This can be explained by equation 5.1 below:

\[ \text{pH} = -\log_{10}[H^+] \]  

(5.1)

The above also then explains the relationship between conductivity and the pH of the solution. The higher the concentration of cations in solution, the more H+ ions are exchanged on the resin, resulting in a lower pH. This exchange will continue until the breakthrough, where the resin’s supply of H+ ions is exhausted resulting in a decrease in the conductivity and an increase in the pH out of the column. After 15 bed volumes, it can be seen that the conductivity falls below its initial concentration and then increases again. This may be caused by a “softening” effect (Broadhurst, 2002), where divalent
cations in solution can exchange with monovalent cations on the resin. This trend appears to be paralleled by the colorant concentration with the colorant increasing past the feed value at the breakthrough and then beginning to fall again afterwards. This increase at the breakthrough point can be explained using the developed theory from Chapter 3.

The two parameters governing the dynamics of the system are the Stanton number (St) and the equilibrium adsorption constant (K). Knowing that a linear isotherm exists, we can see that if K decreases due to a change in pH, then q will be forced to decrease. This decrease in q can be interpreted as colorant being desorbed from the resin, giving a net increase in the color seen at the outlet of the column.

The dependence of K on the pH is assumed to be of the form of the Arrhenius equation (5.2), that describes the dependency of a rate constant on temperature (Fogler, 1999)

\[ k_r (T) = k_0 e^{\frac{E}{RT}} \] (5.2)

Since the pH is defined as a logarithmic function, the above equation can be adapted to give a higher K(pH) than at low a pH condition and decrease exponentially to a constant value for a higher pH. This functionality is given below in equation 5.3 and figure 5.27.

\[ K(pH) = K_0 e^{-\lambda \cdot pH} + K_1 \] (5.3)
Applying the above equations into the model developed in Chapter 3, the following typical result is obtained (Figure 5.28). The model is not perfect with the breakthrough not being accurately described for all the components. This could be attributed to:

- Expression for $K(pH)$ not perfect
- Mass transfer effects will also be affected by the pH i.e. $St(pH)$
The oscillatory result at the beginning of the figure can be attributed to the explicit finite difference solution technique used. The plug flow assumption requires the finite difference method to take points on either side of the plug front, which could cause the oscillations. Adding a dispersion term into the model regression can validate this assumption as can be seen below in figure 5.29.

![Graph](image)

**Figure 5.29: Model showing effect of a dispersion term**

Although a dispersion term may reduce the oscillations in the model, the regressed dispersion term is far higher than any literature values (found in Chapter 3), yielding values > 1x10^{-2}. It was found any values lower in orders of magnitude than 1x10^{-3} have little effect on the model.

The following regressed parameters (Table 5.3) were obtained from the column runs for the pseudo component A. GPC data was not obtained for many of the ultra-filtered runs due to intermittent problems with the auto-sampler. A major problem encountered when dealing with colored sugar solutions is that they deteriorate very quickly, even if stored at low temperatures.
Tables 5.3: SAC Regressed parameters for component A

<table>
<thead>
<tr>
<th>Run</th>
<th>$K_0$</th>
<th>$K_1$</th>
<th>$\lambda$</th>
<th>St</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF 1</td>
<td>9.669</td>
<td>3.695</td>
<td>9.995E-01</td>
<td>0.837</td>
</tr>
<tr>
<td>UF 2</td>
<td>2.930</td>
<td>2.177</td>
<td>1.173E-02</td>
<td>0.853</td>
</tr>
<tr>
<td>UF 4</td>
<td>12.06</td>
<td>2.215</td>
<td>1.229E+00</td>
<td>0.864</td>
</tr>
<tr>
<td>UF 10</td>
<td>2.895</td>
<td>0.161</td>
<td>4.164E-13</td>
<td>0.643</td>
</tr>
<tr>
<td>C 1</td>
<td>3240</td>
<td>3218</td>
<td>2.965E-03</td>
<td>0.695</td>
</tr>
<tr>
<td>C 2</td>
<td>3.769</td>
<td>1.815</td>
<td>1.576E-07</td>
<td>0.851</td>
</tr>
<tr>
<td>C 3</td>
<td>5.063</td>
<td>0.000</td>
<td>3.249E-01</td>
<td>1.160</td>
</tr>
<tr>
<td>C 4</td>
<td>121.3</td>
<td>0.000</td>
<td>1.627E+00</td>
<td>0.769</td>
</tr>
<tr>
<td>C 5</td>
<td>1.137</td>
<td>1.766</td>
<td>4.290E-02</td>
<td>0.833</td>
</tr>
<tr>
<td>C 6</td>
<td>4.173</td>
<td>1.027</td>
<td>1.315E-08</td>
<td>0.820</td>
</tr>
<tr>
<td>C 7</td>
<td>2.628</td>
<td>1.996</td>
<td>5.819E-10</td>
<td>0.824</td>
</tr>
<tr>
<td>C 8</td>
<td>24.55</td>
<td>2.582</td>
<td>1.528E+00</td>
<td>0.761</td>
</tr>
<tr>
<td>C 9</td>
<td>24.69</td>
<td>0.701</td>
<td>2.547E-14</td>
<td>0.826</td>
</tr>
<tr>
<td>C 10</td>
<td>7.539</td>
<td>0.303</td>
<td>1.505E-11</td>
<td>0.920</td>
</tr>
</tbody>
</table>

The Stanton numbers reported from the regression are lower than predicted from literature but are fairly self-consistent. The overall trend of the Stanton numbers (see figure 5.30) shows the expected increase with decreasing molecular weight components for some of the pseudo components, particularly component G.

Figure 5.30: Average Stanton numbers for each component
There are very large variations in the parameters of the equilibrium constant, particularly for the parameter λ. The discrepancies could be explained by the fact that despite the same regeneration techniques being used, the resin is never regenerated to the same degree and does deteriorate over successive runs. This would alter the dynamics of the system. Another factor are imperfections in the model, particularly with the equilibrium expression not perfectly describing the dynamics measured.

Variations in the parameters can also be attributed to experimental errors due to the precise nature of the GPC technique. Should any part of the auto-sampler injection system be hindered due to a blockage, or any contamination, this could influence the amount of the solution injected and hence affect the color coming out of the system.

The Stanton number is the ratio of the effective mass transfer to the interstitial fluid velocity. From the equations 3.23 through 3.27, by substituting into the definition for the Stanton number, we find the Stanton numbers relationship to the superficial velocity by the following expression:

\[ St \propto \frac{1}{u_0^{\frac{5}{3}}} \]  

(5.4)

Thus by decreasing the flow-rate into the packed bed, by a factor of two, the Stanton number should increase by the above proportion. Figure 5.31, below depicts a solution for component A for St = 2.63, which was based on the average regressed Stanton number, for Component A, of approximately 0.83. The regression was also performed on the measured data to find a regressed Stanton number for comparison.
The above figure shows that the relationship based on the correlations by Wilson and Geankoplis (1966) do not hold for the packed bed being analyzed. The effective mass transfer appears to change in similar proportion to the superficial velocity in the above case. This relationship was also found by Broadhurst (2002) where the Stanton number did not change significantly for varying flows, as shown in Table 5.4 below, for his identified pseudo components.

Table 5.4: SAC Stanton number \( St = \frac{k'L}{u_i} \) as a function of superficial velocity (Boadhurst 2002)

<table>
<thead>
<tr>
<th>SAC</th>
<th>6</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>( u_0 ) (m/h)</td>
<td>3.75</td>
<td>4.89</td>
<td>6.21</td>
</tr>
<tr>
<td>C</td>
<td>0.9621</td>
<td>0.9078</td>
<td>0.8535</td>
</tr>
<tr>
<td>D</td>
<td>1.0308</td>
<td>0.9195</td>
<td>1.0431</td>
</tr>
<tr>
<td>E</td>
<td>1.0415</td>
<td>1.1358</td>
<td>1.0079</td>
</tr>
<tr>
<td>F</td>
<td>1.0799</td>
<td>1.4159</td>
<td>0.9710</td>
</tr>
</tbody>
</table>
5.7 Weak-Base Anion Resin

The WBA column runs showed much simpler dynamics than the SAC. A typical breakthrough is shown below in figure 5.32. Starting from a high pH, due to the resin releasing hydroxide ions (OH⁻) into solution, the pH falls as the supply of hydroxide ions is exhausted. Having a feed from the SAC, the final pH after the breakthrough will be very acidic. The conductivity of the WBA is very low, compared to that of that initial feed which is approximately 10mS. This is due to the product having a very low ash content after having passed through the two resins. The conductivity will begin to rise as the resin’s hydroxide ion supply runs out.

![Figure 5.32: A typical WBA breakthrough curve (WBA UF-1 G)](image)

The product color can be seen to remain low but then steadily increases as the pH starts to drop. This can be attributed to adsorption rate decreasing as the pH drops resulting in the increase of color that can be seen in figure 5.32. As a result, a very simple expression was used to describe the equilibrium adsorption constant (equation 5.5). This
expression is based on the fact that colorants have a higher affinity for the WBA resin at a higher pH than at a lower pH, up to a value of 9 or 10. The same regression technique was used to solve this system, as for the SAC, with the exception of two parameters being regressed instead of four.

\[ K(pH) = K_0 \cdot pH \]  \hspace{1cm} (5.5)

The regressed parameters are displayed in Table 5.5. The fluctuation of \( K_0 \) over the runs could be attributed to the run conditions not been identical for all the runs with respect to regeneration, as all the \( K_0 \) values are of the same magnitude. The Stanton numbers are significantly higher than those regressed for the SAC resin. This would indicate that the mass transfer effects are significantly higher for the WBA as the flow-rates were approximately the same for both the resins in the column tests. There is a fairly large difference between the Stanton numbers throughout the runs.

**Table 5.5: WBA Regressed parameters for component C**

<table>
<thead>
<tr>
<th>Run</th>
<th>( K_0 )</th>
<th>( St )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF1</td>
<td>12.85</td>
<td>4.629</td>
<td>0.913</td>
</tr>
<tr>
<td>UF2</td>
<td>8.748</td>
<td>3.397</td>
<td>0.807</td>
</tr>
<tr>
<td>UF4</td>
<td>14.79</td>
<td>4.370</td>
<td>0.735</td>
</tr>
<tr>
<td>UF 10</td>
<td>10.81</td>
<td>3.068</td>
<td>0.947</td>
</tr>
<tr>
<td>Carbon 1</td>
<td>12.80</td>
<td>3.739</td>
<td>0.547</td>
</tr>
<tr>
<td>Carbon 2</td>
<td>6.223</td>
<td>4.979</td>
<td>0.943</td>
</tr>
<tr>
<td>Carbon 3</td>
<td>10.15</td>
<td>4.571</td>
<td>0.957</td>
</tr>
<tr>
<td>Carbon 4</td>
<td>36.91</td>
<td>5.218</td>
<td>0.165</td>
</tr>
<tr>
<td>Carbon 5</td>
<td>7.725</td>
<td>4.574</td>
<td>0.987</td>
</tr>
<tr>
<td>Carbon 6</td>
<td>9.054</td>
<td>4.226</td>
<td>0.793</td>
</tr>
<tr>
<td>Carbon 7</td>
<td>7.979</td>
<td>5.319</td>
<td>0.826</td>
</tr>
<tr>
<td>Carbon 8</td>
<td>7.707</td>
<td>7.584</td>
<td>0.968</td>
</tr>
<tr>
<td>Carbon 9</td>
<td>8.246</td>
<td>2.722</td>
<td>0.973</td>
</tr>
<tr>
<td>Carbon 10</td>
<td>10.02</td>
<td>3.727</td>
<td>0.988</td>
</tr>
</tbody>
</table>

Experimental errors during the WBA column runs affect the results far more than during the SAC, which could attribute to some discrepancies in the results. The intensity
of the colorants leaving the WBA is much lower than that of the SAC so even marginal
dilution or injection changes can have significant effects on the obtained data.

5.8 Oxidation Pretreatment

The use of hydrogen peroxide has often been considered as a possible color
removal agent in sugar refining. Some laboratory tests have been performed at the Sugar
Milling Research Institute (SMRI), and these tests showed that peroxide worked well in
combination with conventional decolorization processes such as carbonatation (Davis et
al, 2000).

It has been suggested that hydrogen peroxide be used in conjunction with
resins to improve the number of cycles possible and reduce the contamination of the resin
(Bento, 2004). As a result of this, it was proposed to use hydrogen peroxide in
conjunction with a packed carbon bed as a pretreatment stage for ion exchange resins.
This could also possibly remove the necessity for a decolorizing resin after the ion
exchange resins, which would further reduce the capital and operating costs as well the
amount of effluent produced by the process.

The following figures show the ICUMSA colors for the diluted syrup used in the
experiment, the product of the hydrogen peroxide reaction, and the SAC and WBA
products.
An interesting observation in figure 5.33 is the small change in color during the oxidation reaction but then a very large change after the carbon bed filtration. This color removal is substantial but to put it in perspective, it can be compared to the color removal
by the other pretreatment methods discussed earlier. Figure 5.35 shows the final ICUMSA color coming out of the WBA column, from which sugar would be crystallized.

Figure 5.35: Final ICUMSA colors leaving WBA for different pretreatment methods

Figure 5.36: Final conductivity measurements leaving WBA for different pretreatment methods
Another important aspect of the resin performance is the deashing ability of the resin. Figure 5.36 above compares the three different pretreatment methods and their final ash content in the form of conductivity.

It should be noted that the resins used in the above experiments were not virgin resins and had been regenerated numerous times prior to the above experiments.

5.9 Regeneration Aids

The main color reducing resin was found to be the WBA resin, with much of the color reduction in the SAC appeared to be due to the pH effects on the colorants. The WBA also visually appears to go through the most changes between being a virgin resin and a regenerated resin, darkening substantially upon its first use. As a result of this, further emphasis was placed on the regeneration of the WBA into extending its longevity. The WBA resin was originally regenerated using a NaOH solution at 10%, with the resin being flushed with de-ionized water before and after. This regeneration step was still conducted with the exception that an HCl regeneration was done after the first NaOH wash, using a 6% HCL solution, and then another NaOH wash. The column is flushed with de-ionized water between the regenerations with NaOH and HCl. Approximately 6 bed volumes are used for each regenerant and water wash. Although no quantification of the regeneration was performed, the amount of colorant leaving the resin was visually noted to be substantially greater when changing regenerants as opposed to using only NaOH.

The acid wash is used due to the nature of the colorant bonding on the resin. As reported by Bento (1992), the majority of sugar colorants have a negative charge in an alkaline medium and have an amphiphilic nature, having both hydrophilic and...
hydrophobic parts. These characteristics allow sugar colorants to be fixed to anionic resins by ionic and/or hydrophobic interactions. In the first case the ionic bond is formed by the negative polar part of the colorant and the resin fixed ion. In the second case, the hydrophobic part of the colorant is forced against the resin matrix by hydrophobic interaction. Weak Van-der-Waal forces then bond the colorant to the resin matrix. The NaOH wash will serve to remove the ionically bonded colorant and then allow the hydrophobic bond to be replaced by an ionic bond. The acid wash serves to remove the hydrophobic bond that is not replaced by an ionic bond after the NaOH wash.

Using a packed carbon bed as a pretreatment requires the regeneration of the carbon to remove the organic particles that get deposited on the carbon. Originally, regeneration of the carbon column was done by autoclaving, at 121°C and 15 psi for 15 minutes. Although this is not the conventional means of regenerating the carbon it served to prevent microbial growth and it was known that the results underestimate what will be achieved in practice. Improved regeneration, and subsequently color removal, could be obtained with higher temperature regeneration.

After performing numerous runs with regeneration by autoclaving, the performance decrease of the carbon packed bed can be seen with the increase of ICUMSA color of the syrup leaving the bed. As a result the carbon was then regenerated in a furnace and the figure below illustrates the comparative effectiveness using ICUMSA color to quantify the results.
Figure 5.37: Graph showing extent of carbon regeneration for different regeneration techniques

The series ‘Sample 1 (Autoclaved)’ in the above figure, was carbon that had already been used in previous runs and as a result the ICUMSA color of its product can be seen to be noticeably higher than the first point on ‘Sample 2 (Autoclaved)’, which is a point for a virgin run using carbon. The extent of the furnace regeneration can be seen in the series ‘Sample 3 (Regenerated in furnace)’, as the first point was made using the carbon from the last run of Sample 2 and regenerating it in the furnace. The color of the product is close enough in color than that of a virgin carbon run, which could either be attributed to measurement inaccuracies, contamination of the virgin carbon or an increase in surface area of the carbon granules from heat sintering.
CHAPTER 6. CONCLUSIONS

6.1 GPC as an Analytical Tool

The suitability of using GPC as a colorant measuring tool is apparent when seeing the resolution attainable when looking at individual colorants as opposed to lumping the colorants as a whole in the ICUMSA method. This is particularly true when analyzing the components in the ultra-violet spectrum where more significant responses were experienced. The ability to see how different treatments affect the defined pseudo components is very advantageous and provides a much better understanding of the color removal and formation. The defining of pseudo components also allow the colorants to be modeled individually which could help in the designing of a process to ensure that the colorants more susceptible to be included during crystallization are removed.

The discrepancy that was experienced with the use of GPC as an analytical tool in the analysis of carbon as a pretreatment method does raise the question of the overall applicability of the UV spectrum for colorant analysis. The use of the UV spectrum in opposition to visible light can still be justified in certain circumstances. In the instances where it does appear to suitably describe the colorant removal, the resolution and partitioning is far superior to that of other wavelengths.

For modeling the identified pseudo components, the color formation tests showed 280nm to be a more suitable wavelength than previous suggestions of 420nm. The absorbance response was much greater and the resolution of the peaks for the identified components is far superior to that at 420nm.
6.2 Validity of the Plug-Flow Model

The validity of the plug flow model was justified by the calculation of the Peclet number. Froment and Bischoff (1990) recommend a Peclet number based on a particle diameter of between 1 and 2mm. Multiplying the calculated Peclet number by the length to diameter ratio yields a very large particle based Peclet number. The Peclet number also appears in its inverse form in equation 3.2, making the axial dispersion term very small.

Based on the above conclusion it can be seen that the plug-flow model is a good choice for modeling the color adsorption process.

6.3 SAC Resin

The SAC resins dynamics were found to be difficult to describe mathematically. This can be attributed to the strong pH dependence of the colorants with respect to their affinity for the resin. The area of particular interest was the “softening” region of the resin where colorants were desorbed back into the solution. This particular region will be the most fundamental when it comes to optimizing a process as it would be beneficial to operate the column as close to this region as possible, without exceeding it. Exceeding this region would be very undesirable with the colorant concentration going higher than that of the feed condition. The greatest decolorizing would then be attainable by operating prior to this region, with the resin being regenerated at this desorption stage.

The adapted Arrhenius equation appeared to adequately describe the dynamics of the system when regressing the data, despite large fluctuations in the regressed parameters fitted to the equilibrium constant. For predictive purposes the Stanton number did not change as significantly as predicted by the literature for a decreased flow-rate.
This could be attributed to the literature underestimating the change in the mass transfer coefficient when applied to this system.

6.4 WBA Resin

The weak base anion demonstrated simpler dynamics than those of the SAC, allowing a much simpler expression for the equilibrium adsorption constant to be used. The mass transfer coefficient was found to be much higher than that of the SAC.

The WBA showed greater affinities for the sugar colorant than that of the SAC, with the majority of the decolorization occurring during the WBA run. The WBA also appeared to have greater affinity towards the lower molecular weight components, with the SAC affecting the higher molecular weight components. This would indicate that the WBA resin is a good resin to be used after the SAC resin.

The GPC technique was found to be very sensitive during the WBA test runs, due to the low colorant intensity leaving the WBA. As a result, fluctuations in data points can be attributed to small errors, such as dilution or injection errors, that would not have been as significant for higher color solutions, as in the case of the SAC.

6.5 Pretreatment Methods

6.5.1 Ultra-Filtration

The ability of ultra-filtration to remove suspended material and other high molecular weight impurities is well documented, but due to its high capital and maintenance costs the feasibility of a process involving ultra-filtration is uncertain. Many operating factors in a sugar mill can contribute to low performance on the membrane, or catastrophic failure, owing to the nature of the material that is processed. The inherent instability, with respect to biological losses and degradation, of the feed material is
another factor when considering ultra-filtration. Significant sugar losses may be experienced not only in effluent streams, but if solutions are stored for more than one or two hours. This is due to bacterial or other mechanisms of degradation that will occur unless a sufficiently high or low temperature is maintained. The fact that the permeate is usually sterile does not mean that sucrose will remain safe in the feed loop or tanks. Potential for color formation is another factor that is related to excessive storage (Kochergin, 2001).

A major cost saving, such as the direct white sugar production when using ultra-filtration as a pretreatment, could make ultra-filtration economically attractive but in the advent of another cheaper pretreatment that is as effective, if not more, ultra-filtration would not be the unit operation of choice.

6.5.2 Packed Carbon Bed

The use of a granular carbon in a packed bed as a first step in the juice purification process has shown to have some promising results. Work done comparing ultra-filtered syrup at 0.1 μm (as a control) to the product from a packed carbon bed showed lower color for longer periods of time using the packed carbon bed as pretreatment. This result was consistent through successive runs with a larger color difference between the ultra-filtered run and packed carbon bed run being apparent. This would suggest that the colorants removed by the packed carbon bed are more detrimental to the resins than the colorants and high molecular weight material removed by ultra-filtration.
The deashing ability of the resin remained fairly constant when comparing the packed carbon bed to the ultra-filtered syrup, with the conductivity of the two pretreated solutions being very similar.

From a process perspective the packed carbon bed is advantageous, reducing the capital and operating costs through the elimination of the membrane filter. The elimination of the final decolorization resin used in the WSM process may also be possible depending on the arrangements of the ion exchange beds after the initial pretreatment. Further testing on a larger scale and for longer run times will need to be conducted to verify this possibility.

6.5.3 Oxidation Reactions

The use of oxidation with hydrogen peroxide as a pretreatment method in conjunction with a packed carbon bed appears an attractive operation. Preliminary data shows higher color removal for prolonged column runs, which could result in lower operating costs due to increased resin run times. The possibility of removing the decolorizing resin currently employed in processes such as the WSM could also drastically reduce operating costs and effluent production.

There are many factors that need to be considered, such as the dosing and reaction time required for varying syrups but the benefits of increased cycle numbers and reduction of resin contamination could produce a very lucrative process.

6.6 Future Research Directions

The results obtained during the course of this research show a large amount of scope for research in various pretreatment methods for ion exchange resins. Of particular interest is the combination of the carbon column and oxidation reactions prior to the ion
exchange columns. More runs need to be done in order to further validate the findings of this project and to investigate the longevity of the resins in comparison to the more traditional ultra-filtration pretreatment.

A better expression for the equilibrium constant describing the dynamics of the system needs to be investigated. This will allow for improved modeling of the column and provide a more robust model that can be applied to optimizing an ion exchange process.
REFERENCES


Bento, L.S.M. (2003); *Technological Color Control Of Sugar Products*, A.V.H meeting, Reims, France 2003


APPENDIX A. SAMPLE CALCULATIONS

A.1 ICUMSA Color

a) Calibrate pH meter

b) Using ~0.5N NaOH and HCl, correct pH to 7 ± 0.1

c) Dilute sample to register between 0.1 and 1 AU on the spectrophotometer at 420nm

d) Measure absorbance on spectrophotometer at 420nm.

\[ A = 0.2441 \text{ AU} \quad \text{Absorbance} \]
\[ L = 10\text{mm} \quad \text{Cuvette length} \]

e) Measure brix of sample using refractometer.

\[ b = 7.92 \% \quad \text{Brix of sample} \]

f) Convert brix to a concentration using the bellow correlation:

\[ \text{Concentration (g/100ml)} = 0.0041 \times \text{Brix}^2 + 0.9972 \times \text{Brix} \]
\[ = 8.16 \text{ (g/100ml)} \]
\[ = 0.0816 \text{ g/ml} \]

g) Calculate ICUMSA color:

\[ ICUMSA(420nm) = \frac{[Abs(420nm)] \times 10,000}{[Conc.(g/ml)] \times [Cell _ Length(mm)]} \]
\[ = \frac{0.2441 \times 10,000}{0.0816 \times 10} \]
\[ = 2990 \]
A.2 GPC Chromatogram Analysis

This program was written by Broadhurst (2002) to generate the values of the chromatogram at the determined times intervals. This is also required to ensure that should there be any shift in retention times, it will be accounted for.

a) Load data from text-file logged by GPC.

b) User specifies baseline.

c) User specifies approximate location of peak maxima.

d) Regression on standard deviations.

e) Regression on retention times, using the regressed standard deviation.

f) Regression on peak maxima, and standard deviation from above retention times.

g) Calculate peak area and correlation coefficient.

A.3 Void Fraction Calculation

The packed bed void fraction to be used in the calculations for each resin is described by equation A.1 below:

\[ \varepsilon = \frac{V_{\text{void}} \, (\text{m}^3)}{V_{\text{bed}} \, (\text{m}^3)} \]  

(A.1)

The above equation needs to be expressed in terms of measurable quantities.

\[ \varepsilon = \frac{V_{\text{void}}}{V_{\text{bed}}} = \frac{V_{\text{bed}} - V_{\text{resin}}}{V_{\text{bed}}} = 1 - \frac{V_T - V_{\text{hexane}}}{V_{\text{bed}}} \]  

(A.2)

Where the above measurable quantities are,

\[ V_{\text{Hexane}} = \text{Volume of hexane added (ml)} \]

\[ V_T = \text{Total volume in measuring cylinder (ml)} \]
\[ V_{\text{Bed}} = \text{Volume of resin bed (ml)} \]

After saturating the micro pores with a salt solution, the above measured values for the cationic resin are:

\[ V_{\text{Hexane}} = 7 \text{ ml} \]
\[ V_T = 8.5 \text{ ml} \]
\[ V_{\text{Bed}} = 2.8 \text{ ml} \]

Calculating the voidage using A.2:

\[ \varepsilon = 1 - \frac{8.5 - 7}{2.8} = 0.464 \]

**A.4 Hydrogen Peroxide Dosing**

a) Measure brix of syrup

\[ b = 15.49 \% \]

b) Required dosage 1000ppm = 0.001 kg/kg

c) Calculate density at this temperature and brix using the correlation A.3 (Bubnik et al, 1995):

\[ \rho_{\text{Syrup}} = 1000 \left( 1 + \frac{b(b+200)}{54000} \right) \times \left( 1 - 0.036 \frac{T(\degree C) - 20}{160 - T(\degree C)} \right) \]

\[ = 1000 \left( 1 + \frac{15.49(15.49+200)}{54000} \right) \times \left( 1 - 0.036 \frac{85 - 20}{160 - 85} \right) \]

\[ = 1028.69 \text{ kg/m}^3 \]

d) Using a known volume of syrup, calculate the mass of syrup, then the dissolved solids using the brix.

\[ V_{\text{Syrup}} = 9 \text{ L} \]

\[ = 0.009 \text{ m}^3 \]
\[ m_{\text{Syrup}} = 9.258 \text{ kg} \]
\[ m_{\text{Brix}} = 1.434 \text{ kg} \]

e) Using the required dosage, find the mass of H\text{2}O\text{2} to be added, and then the volume, knowing that H\text{2}O\text{2} at 30% has a density of 1100 kg/m\text{3}.

\[ m_{\text{H}_2\text{O}_2} = 0.001434 \text{ kg} \]
\[ = 1.434 \text{ g} \]
\[ V_{\text{H}_2\text{O}_2} = 4.346 \text{ cm}^3 \]

**A.5 Packed-Bed Parameter Regression**

The parameter regression is done using a MATLAB non-linear curve-fitting using a least squares algorithm. The model input parameters will be the pH, the time steps, boundary and initial conditions and the associated discretized governing equations. The equations are then solved giving the concentration breakthrough curve at the outlet. The solver routine then minimizes the sum-of-squares by varying the model parameters using the Sequential Quadratic Programming (SQP) technique.

**A.5.1 Regression Algorithm**

a) Define input vectors:

\[ \theta \quad - \quad \text{Dimensionless time} \]
\[ \bar{C}_{\text{meas}} (\eta = 1) \quad - \quad \text{Measure outlet concentration} \]
\[ \text{pH}(\theta) \quad - \quad \text{Measured pH} \]

b) Define first guess of model parameters

\[ \text{St} \quad - \quad \text{First guess for Stanton number} \]
\[ K_0, K_1, \lambda \quad - \quad \text{Equilibrium parameters} \]
Due to the non-dimensionalization of the equations, the inlet concentration is set to unity.

c) The minimization can be represented as:

\[
\min_{St, K_0, K_1, \lambda} \frac{1}{2} \sum_j \left[ F(St, K_0, K_1, \lambda, pH, \theta_j) - \overline{C}_{\text{meas}}(\theta_j) \right]^2 \quad (A.4)
\]

The function \( F(St, K_0, K_1, \lambda, pH, \theta) \) is calculated in a separate MATLAB algorithm.

d) The result is then plotted again the measured data and the correlation coefficient \( (R^2) \) is then calculated.

**A.5.2 R^2 Calculation**

A non-linear \( R^2 \) is calculated as follows:

a) A matrix of correlation coefficients is calculated between the measured and calculated concentration values using the syntax:

\[
s = \text{corrcoef}(ydata, y)
\]

b) The product of the correlation coefficients is then calculated and then squared using the MATLAB function for calculating the product of array elements

\[
R^2 = \text{prod} \left( \text{prod} \left( \text{corrcoef}(ydata, y) \right) \right)
\]

**A.5.3 MATLAB Algorithm**

a) Define constants

b) Define distance step size

c) Define time step size

d) Define initial and boundary conditions

e) Input expression for \( K(pH, \theta) \):
\[ k(pH, \theta) = K_0 e^{-k_{pH}(\theta)} + K_1 \quad (A.5) \]

Since pH is a function of \( \theta \), an expression of the form below was used with the unknown parameters been regressed using solver to fit the data.

\[ pH = a(1 + c e^{b \theta}) \quad (A.6) \]

f) The discretized matrix shown in Chapter 3 is then setup.

g) The two governing equations are then solved simultaneously with the solution for the balance on the solid phase (equation 3.22) providing the unknown for the next time step on the balance from the fluid phase (equation 3.21).

h) The time is stepped until the required number of bed volumes has passed through the column.

i) The solution for the final node, for each time step, is stored in a vector and then displayed as the breakthrough at the end of the computation.
APPENDIX B. MIXED BED RESULTS

Various permutations were tried for the mixed bed runs, such as mixing a strong acid cationic resin with a weak base anionic resin or a strong base anionic resin. The ratios of the cationic resins to anionic resins were also varied.

Figure B.1: ICUMSA values for 1:2 SAC:WBA ratio

Figure B.2: pH and conductivity vs BV for 1:2 SAC:WBA ratio
Figure B.3: ICUMSA values for 1:1 SAC:SBA ratio

Figure B.4: pH and conductivity vs BV for 1:1 SAC:SBA ratio
Figure B.5: ICUMSA values for 1:3 SAC:SBA ratio

Figure B.6: pH and conductivity vs BV for 1:3 SAC:SBA ratio
Figure B.7: ICUMSA values for 1:4 SAC:SBA ratio

Figure B.8: pH and conductivity vs BV for 1:4 SAC:SBA ratio
APPENDIX C. SAC RESIN COLUMN TEST RESULTS

Twenty SAC runs were performed with ten of these having ultra-filtered feed. The other ten runs all had a carbon bed pretreatment prior to the SAC column.

Table C.1: SAC UF-1 Regression summary

<table>
<thead>
<tr>
<th>Component</th>
<th>$K_0$</th>
<th>$K_1$</th>
<th>$\lambda$</th>
<th>St</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>9.67</td>
<td>3.695</td>
<td>9.99E-01</td>
<td>0.837</td>
<td>0.986</td>
</tr>
<tr>
<td>B</td>
<td>2.03</td>
<td>1.869</td>
<td>1.13E-01</td>
<td>0.793</td>
<td>0.976</td>
</tr>
<tr>
<td>C</td>
<td>4.80</td>
<td>0.873</td>
<td>3.66E-06</td>
<td>0.838</td>
<td>0.980</td>
</tr>
<tr>
<td>D</td>
<td>5.25</td>
<td>1.124</td>
<td>1.78E-09</td>
<td>0.918</td>
<td>0.982</td>
</tr>
<tr>
<td>E</td>
<td>9.07</td>
<td>0.493</td>
<td>3.30E-07</td>
<td>0.802</td>
<td>0.961</td>
</tr>
<tr>
<td>F</td>
<td>3.73</td>
<td>0.124</td>
<td>3.15E-09</td>
<td>0.745</td>
<td>0.957</td>
</tr>
<tr>
<td>G</td>
<td>24.50</td>
<td>3.602</td>
<td>1.40E+00</td>
<td>0.890</td>
<td>0.984</td>
</tr>
</tbody>
</table>

Figure C.1: SAC UF-1 Product ICUMSA color
Figure C.2: SAC UF-1 Product color component A

Figure C.3: SAC UF-1 Product color component B
Figure C.4: SAC UF-1 Product color component C

Figure C.5: SAC UF-1 Product color component D
Figure C.6: SAC UF-1 Product color component E

Figure C.7: SAC UF-1 Product color component F
Figure C.8: SAC UF-1 Product color component G

Table C.2: SAC UF-2 Regression summary

<table>
<thead>
<tr>
<th>Component</th>
<th>$K_0$</th>
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<th>$\lambda$</th>
<th>St</th>
<th>$R^2$</th>
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</thead>
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<tr>
<td>A</td>
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<td>1.17E-02</td>
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<tr>
<td>B</td>
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<td>0.707</td>
<td>4.47E-10</td>
<td>0.780</td>
<td>0.986</td>
</tr>
<tr>
<td>C</td>
<td>5.11</td>
<td>0.937</td>
<td>1.28E-11</td>
<td>0.836</td>
<td>0.988</td>
</tr>
<tr>
<td>D</td>
<td>17.22</td>
<td>3.974</td>
<td>1.39E+00</td>
<td>0.835</td>
<td>0.992</td>
</tr>
<tr>
<td>E</td>
<td>5.57</td>
<td>1.805</td>
<td>5.18E-02</td>
<td>0.804</td>
<td>0.956</td>
</tr>
<tr>
<td>F</td>
<td>4.34</td>
<td>0.181</td>
<td>2.07E-09</td>
<td>0.768</td>
<td>0.976</td>
</tr>
<tr>
<td>G</td>
<td>39.97</td>
<td>5.023</td>
<td>1.48E+00</td>
<td>1.082</td>
<td>0.972</td>
</tr>
</tbody>
</table>
Figure C.9: SAC UF-2 Product ICUMSA color

Figure C.10: SAC UF-2 Product color component A
Figure C.11: SAC UF-2 Product color component B

Figure C.12: SAC UF-2 Product color component C
Figure C.13: SAC UF-2 Product color component D

Figure C.14: SAC UF-2 Product color component E
Figure C.15: SAC UF-2 Product color component F

Figure C.16: SAC UF-2 Product color component G
Figure C.17: SAC UF-3 Product ICUMSA color

Figure C.18: SAC UF-3 Product pH and conductivity
Table C.3: SAC UF-4 Regression summary

<table>
<thead>
<tr>
<th>Component</th>
<th>$K_0$</th>
<th>$K_1$</th>
<th>$\lambda$</th>
<th>St</th>
<th>$R^2$</th>
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<td>A</td>
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<td>1.23E+00</td>
<td>0.864</td>
<td>0.985</td>
</tr>
<tr>
<td>B</td>
<td>3.24</td>
<td>0.000</td>
<td>3.46E-01</td>
<td>0.781</td>
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</tr>
<tr>
<td>C</td>
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<td>1.134</td>
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<td>0.000</td>
<td>3.26E-01</td>
<td>0.765</td>
<td>0.965</td>
</tr>
<tr>
<td>G</td>
<td>7.40</td>
<td>0.984</td>
<td>8.73E-03</td>
<td>1.364</td>
<td>0.905</td>
</tr>
</tbody>
</table>

Figure C.19: SAC UF-4 Product ICUMSA color
Figure C.20: SAC UF-4 Product color component A

Figure C.21: SAC UF-4 Product color component B
Figure C.22: SAC UF-4 Product color component C

Figure C.23: SAC UF-4 Product color component D
Figure C.24: SAC UF-4 Product color component E

Figure C.25: SAC UF-4 Product color component F
Figure C.26: SAC UF-4 Product color component G

Figure C.27: SAC UF-5 Product ICUMSA color
Figure C.28: SAC UF-5 Product pH and conductivity

Figure C.29: SAC UF-6 Product ICUMSA color
Figure C.30: SAC UF-6 Product pH and conductivity

Figure C.31: SAC UF-7 Product ICUMSA color
Figure C.32: SAC UF-7 Product pH and conductivity

Figure C.33: SAC UF-8 Product ICUMSA color
Figure C.34: SAC UF-8 Product pH and conductivity

Figure C.35: SAC UF-9 Product ICUMSA color
Figure C.36: SAC UF-9 Product pH and conductivity

Table C.4: SAC UF-10 Regression summary

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<td>0.916</td>
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<td>4.55E-01</td>
<td>1.060</td>
<td>0.966</td>
</tr>
<tr>
<td>C</td>
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<td>0.000</td>
<td>4.26E-01</td>
<td>1.964</td>
<td>0.860</td>
</tr>
<tr>
<td>D</td>
<td>5.80</td>
<td>0.639</td>
<td>7.43E-01</td>
<td>0.972</td>
<td>0.976</td>
</tr>
<tr>
<td>E</td>
<td>4.21</td>
<td>0.993</td>
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<tr>
<td>F</td>
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<td>4.29E-01</td>
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<td>G</td>
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<td>4.74E-01</td>
<td>1.659</td>
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Figure C.37: SAC UF-10 Product ICUMSA color

Figure C.38: SAC UF-10 Product color component A
Figure C.39: SAC UF-10 Product color component B

Figure C.40: SAC UF-10 Product color component C
Figure C.41: SAC UF-10 Product color component D

Figure C.42: SAC UF-10 Product color component E
Figure C.43: SAC UF-10 Product color component F

Figure C.44: SAC UF-10 Product color component G
Table C.5: SAC Carbon-1 Regression summary

<table>
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<th>$\lambda$</th>
<th>$St$</th>
<th>$R^2$</th>
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<td>A</td>
<td>21345</td>
<td>21348.710</td>
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<td>0.695</td>
<td>0.502</td>
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<tr>
<td>B</td>
<td>7269</td>
<td>7288.679</td>
<td>6.79E-03</td>
<td>0.794</td>
<td>0.403</td>
</tr>
<tr>
<td>C</td>
<td>77040</td>
<td>77057.384</td>
<td>3.88E-07</td>
<td>0.792</td>
<td>0.467</td>
</tr>
<tr>
<td>D</td>
<td>2287</td>
<td>2272.010</td>
<td>2.33E-03</td>
<td>0.684</td>
<td>0.496</td>
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<tr>
<td>E</td>
<td>12961</td>
<td>12949.162</td>
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<td>0.849</td>
<td>0.474</td>
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<td>F</td>
<td>5875</td>
<td>5866.255</td>
<td>1.20E-02</td>
<td>0.785</td>
<td>0.318</td>
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<tr>
<td>G</td>
<td>2863</td>
<td>2837.291</td>
<td>1.96E-06</td>
<td>0.954</td>
<td>0.664</td>
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</table>

Figure C.45: SAC Carbon-1 Product ICUMSA color
Figure C.46: SAC Carbon-1 Product color component A

Figure C.47: SAC Carbon-1 Product color component B
Figure C.48: SAC Carbon-1 Product color component C

Figure C.49: SAC Carbon-1 Product color component D
Figure C.50: SAC Carbon-1 Product color component E

Figure C.51: SAC Carbon-1 Product color component F
Figure C.52: SAC Carbon-1 Product color component G

Table C.6: SAC Carbon-2 Regression summary

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<tr>
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<th>$\lambda$</th>
<th>St</th>
<th>$R^2$</th>
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</thead>
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<td>1.815</td>
<td>1.58E-07</td>
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<td>0.976</td>
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<tr>
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<td>0.177</td>
<td>6.34E-12</td>
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<td>0.975</td>
</tr>
<tr>
<td>C</td>
<td>6.24</td>
<td>1.017</td>
<td>2.47E-09</td>
<td>0.828</td>
<td>0.977</td>
</tr>
<tr>
<td>D</td>
<td>6.79</td>
<td>0.096</td>
<td>3.64E-11</td>
<td>0.860</td>
<td>0.974</td>
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<tr>
<td>E</td>
<td>63.92</td>
<td>8.422</td>
<td>1.04E+00</td>
<td>0.792</td>
<td>0.867</td>
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<tr>
<td>F</td>
<td>4.08</td>
<td>0.030</td>
<td>9.36E-14</td>
<td>0.771</td>
<td>0.914</td>
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<tr>
<td>G</td>
<td>6.42</td>
<td>0.861</td>
<td>2.98E-03</td>
<td>1.363</td>
<td>0.834</td>
</tr>
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</table>
Figure C.53: SAC Carbon-2 Product ICUMSA color

Figure C.54: SAC Carbon-2 Product color component A
Figure C.55: SAC Carbon-2 Product color component B

Figure C.56: SAC Carbon-2 Product color component C
Figure C.57: SAC Carbon-2 Product color component D

Figure C.58: SAC Carbon-2 Product color component E
Figure C.59: SAC Carbon-2 Product color component F

Figure C.60: SAC Carbon-2 Product color component G
Table C.7: SAC Carbon-3 Regression summary

<table>
<thead>
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<th>Component</th>
<th>$K_0$</th>
<th>$K_1$</th>
<th>$\lambda$</th>
<th>St</th>
<th>$R_2$</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>5.06</td>
<td>2.79E-14</td>
<td>3.25E-01</td>
<td>1.157</td>
<td>0.752</td>
</tr>
<tr>
<td>B</td>
<td>4.23</td>
<td>2.23E-14</td>
<td>3.36E-01</td>
<td>0.762</td>
<td>0.900</td>
</tr>
<tr>
<td>C</td>
<td>4.22</td>
<td>2.23E-14</td>
<td>3.37E-01</td>
<td>0.758</td>
<td>0.906</td>
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<tr>
<td>D</td>
<td>4.61</td>
<td>2.23E-14</td>
<td>3.15E-01</td>
<td>1.025</td>
<td>0.854</td>
</tr>
<tr>
<td>E</td>
<td>4.89</td>
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<td>3.33E-01</td>
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<td>0.890</td>
</tr>
<tr>
<td>F</td>
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<td>4.44E-14</td>
<td>3.43E-01</td>
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<td>1.20E+00</td>
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Figure C.61: SAC Carbon-3 Product ICUMSA color
Figure C.62: SAC Carbon-3 Product color component A

Figure C.63: SAC Carbon-3 Product color component B
Figure C.64: SAC Carbon-3 Product color component C

Figure C.65: SAC Carbon-3 Product color component D
Figure C.66: SAC Carbon-3 Product color component E

Figure C.67: SAC Carbon-3 Product color component F
Figure C.68: SAC Carbon-3 Product color component G

Table C.8: SAC Carbon-4 Regression summary

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<th>$\lambda$</th>
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<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>121.28</td>
<td>0.000</td>
<td>1.63E+00</td>
<td>0.769</td>
<td>0.887</td>
</tr>
<tr>
<td>B</td>
<td>24.33</td>
<td>1.223</td>
<td>1.34E+00</td>
<td>0.709</td>
<td>0.951</td>
</tr>
<tr>
<td>C</td>
<td>9.45</td>
<td>0.104</td>
<td>6.47E-01</td>
<td>0.858</td>
<td>0.963</td>
</tr>
<tr>
<td>D</td>
<td>20.46</td>
<td>0.007</td>
<td>1.00E+00</td>
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<td>0.982</td>
</tr>
<tr>
<td>E</td>
<td>28.24</td>
<td>0.000</td>
<td>9.24E-01</td>
<td>0.759</td>
<td>0.962</td>
</tr>
<tr>
<td>F</td>
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<td>0.622</td>
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<td>0.717</td>
<td>0.975</td>
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<tr>
<td>G</td>
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<td>2.62E+00</td>
<td>1.498</td>
<td>0.927</td>
</tr>
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</table>
Figure C.69: SAC Carbon-4 Product ICUMSA color

Figure C.70: SAC Carbon-4 Product color component A
Figure C.71: SAC Carbon-4 Product color component B

Figure C.72: SAC Carbon-4 Product color component C
Figure C.73: SAC Carbon-4 Product color component D

Figure C.74: SAC Carbon-4 Product color component E
Figure C.75: SAC Carbon-4 Product color component F

Figure C.76: SAC Carbon-4 Product color component G
Table C.9: SAC Carbon-5 Regression summary

<table>
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<th>$\lambda$</th>
<th>$St$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.14</td>
<td>1.766</td>
<td>4.29E-02</td>
<td>0.833</td>
<td>0.968</td>
</tr>
<tr>
<td>B</td>
<td>3.56</td>
<td>0.000</td>
<td>2.25E-01</td>
<td>0.735</td>
<td>0.979</td>
</tr>
<tr>
<td>C</td>
<td>8.88</td>
<td>0.051</td>
<td>5.30E-09</td>
<td>0.772</td>
<td>0.976</td>
</tr>
<tr>
<td>D</td>
<td>6.10</td>
<td>0.109</td>
<td>2.38E-13</td>
<td>0.816</td>
<td>0.971</td>
</tr>
<tr>
<td>E</td>
<td>10.48</td>
<td>0.000</td>
<td>2.23E-14</td>
<td>0.858</td>
<td>0.949</td>
</tr>
<tr>
<td>F</td>
<td>2.68</td>
<td>0.204</td>
<td>1.50E-01</td>
<td>0.703</td>
<td>0.970</td>
</tr>
<tr>
<td>G</td>
<td>9.90</td>
<td>0.374</td>
<td>2.87E-11</td>
<td>1.539</td>
<td>0.933</td>
</tr>
</tbody>
</table>

Figure C.77: SAC Carbon-5 Product ICUMSA color
Figure C.78: SAC Carbon-5 Product color component A

Figure C.79: SAC Carbon-5 Product color component B
Figure C.80: SAC Carbon-5 Product color component C

Figure C.81: SAC Carbon-5 Product color component D
Figure C.82: SAC Carbon-5 Product color component E

Figure C.83: SAC Carbon-5 Product color component F
Figure C.84: SAC Carbon-5 Product color component G

Table C.10: SAC Carbon-6 Regression summary

<table>
<thead>
<tr>
<th>Component</th>
<th>$K_0$</th>
<th>$K_1$</th>
<th>$\lambda$</th>
<th>$St$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4.17</td>
<td>1.027</td>
<td>1.32E-08</td>
<td>0.820</td>
<td>0.988</td>
</tr>
<tr>
<td>B</td>
<td>2.74</td>
<td>0.500</td>
<td>2.29E-02</td>
<td>0.738</td>
<td>0.980</td>
</tr>
<tr>
<td>C</td>
<td>13.52</td>
<td>0.019</td>
<td>3.50E-10</td>
<td>0.862</td>
<td>0.981</td>
</tr>
<tr>
<td>D</td>
<td>6.28</td>
<td>1.263</td>
<td>2.43E-13</td>
<td>0.899</td>
<td>0.991</td>
</tr>
<tr>
<td>E</td>
<td>7.90</td>
<td>0.000</td>
<td>4.42E-01</td>
<td>1.020</td>
<td>0.923</td>
</tr>
<tr>
<td>F</td>
<td>9.87</td>
<td>0.000</td>
<td>2.22E-14</td>
<td>0.683</td>
<td>0.939</td>
</tr>
<tr>
<td>G</td>
<td>9.34</td>
<td>0.751</td>
<td>2.07E-07</td>
<td>1.025</td>
<td>0.983</td>
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</table>
Figure C.85: SAC Carbon-6 Product ICUMSA color

Figure C.86: SAC Carbon-6 Product color component A
Figure C.87: SAC Carbon-6 Product color component B

Figure C.88: SAC Carbon-6 Product color component C
Figure C.89: SAC Carbon-6 Product color component D

Figure C.90: SAC Carbon-6 Product color component E
Figure C.91: SAC Carbon-6 Product color component F

Figure C.92: SAC Carbon-6 Product color component G
### Table C.11: SAC Carbon-7 Regression summary

<table>
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<th>$R^2$</th>
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</thead>
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<tr>
<td>A</td>
<td>2.63</td>
<td>1.996</td>
<td>5.82E-10</td>
<td>0.824</td>
<td>0.962</td>
</tr>
<tr>
<td>B</td>
<td>2.91</td>
<td>1.451</td>
<td>1.17E-09</td>
<td>0.732</td>
<td>0.973</td>
</tr>
<tr>
<td>C</td>
<td>3.30</td>
<td>1.583</td>
<td>1.42E-13</td>
<td>0.825</td>
<td>0.970</td>
</tr>
<tr>
<td>D</td>
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<td>1.078</td>
<td>4.47E-08</td>
<td>0.847</td>
<td>0.969</td>
</tr>
<tr>
<td>E</td>
<td>8.40</td>
<td>0.133</td>
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<td>0.789</td>
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<tr>
<td>F</td>
<td>2.53</td>
<td>1.385</td>
<td>1.37E-09</td>
<td>0.703</td>
<td>0.962</td>
</tr>
<tr>
<td>G</td>
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<td>0.002</td>
<td>6.88E-12</td>
<td>0.916</td>
<td>0.912</td>
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### Figure C.93: SAC Carbon-7 Product ICUMSA color
Figure C.94: SAC Carbon-7 Product color component A

Figure C.95: SAC Carbon-7 Product color component B
Figure C.96: SAC Carbon-7 Product color component C

Figure C.97: SAC Carbon-7 Product color component D
Figure C.98: SAC Carbon-7 Product color component E

Figure C.99: SAC Carbon-7 Product color component F
Figure C.100: SAC Carbon-7 Product color component G

Table C.12: SAC Carbon-8 Regression summary

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<th>$\lambda$</th>
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<th>$R^2$</th>
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<td>A</td>
<td>24.55</td>
<td>2.582</td>
<td>1.53E+00</td>
<td>0.761</td>
<td>0.988</td>
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<tr>
<td>B</td>
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<td>0.359</td>
<td>1.10E-02</td>
<td>0.787</td>
<td>0.980</td>
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<tr>
<td>C</td>
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<td>2.800</td>
<td>1.35E+00</td>
<td>0.773</td>
<td>0.987</td>
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<tr>
<td>D</td>
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<td>1.318</td>
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<td>0.847</td>
<td>0.986</td>
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<tr>
<td>E</td>
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<td>3.598</td>
<td>1.67E+00</td>
<td>0.827</td>
<td>0.992</td>
</tr>
<tr>
<td>F</td>
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<td>0.346</td>
<td>1.76E-02</td>
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<td>0.972</td>
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<td>G</td>
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<td>0.409</td>
<td>7.25E-03</td>
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Figure C.101: SAC Carbon-8 Product ICUMSA color

Figure C.102: SAC Carbon-8 Product color component A
Figure C.103: SAC Carbon-8 Product color component B

Figure C.104: SAC Carbon-8 Product color component C
Figure C.105: SAC Carbon-8 Product color component D

Figure C.106: SAC Carbon-8 Product color component E
Figure C.107: SAC Carbon-8 Product color component F

Figure C.108: SAC Carbon-8 Product color component G
Table C.13: SAC Carbon-9 Regression summary

<table>
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<th>$\lambda$</th>
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<th>$R^2$</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>24.69</td>
<td>0.701</td>
<td>2.55E-14</td>
<td>0.826</td>
<td>0.978</td>
</tr>
<tr>
<td>B</td>
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<td>0.025</td>
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<td>0.712</td>
<td>0.967</td>
</tr>
<tr>
<td>C</td>
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<td>3.46E-01</td>
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<td>0.990</td>
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<tr>
<td>F</td>
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<td>0.008</td>
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<td>0.693</td>
<td>0.973</td>
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<td>2.746</td>
<td>8.93E-01</td>
<td>1.013</td>
<td>0.994</td>
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Figure C.109: SAC Carbon-9 Product ICUMSA color
Figure C.110: SAC Carbon-9 Product color component A

Figure C.111: SAC Carbon-9 Product color component B
Figure C.112: SAC Carbon-9 Product color component C

Figure C.113: SAC Carbon-9 Product color component D
Figure C.114: SAC Carbon-9 Product color component E

Figure C.115: SAC Carbon-9 Product color component F
Figure C.116: SAC Carbon-9 Product color component G

Table C.14: SAC Carbon-10 Regression summary

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<th>$\lambda_2$</th>
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<td>A</td>
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<td>0.990</td>
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<tr>
<td>B</td>
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<td>0.172</td>
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<td>0.973</td>
</tr>
<tr>
<td>C</td>
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<td>0.730</td>
<td>0.972</td>
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<td>0.843</td>
<td>0.988</td>
</tr>
<tr>
<td>E</td>
<td>12.88</td>
<td>0.149</td>
<td>2.22E-14</td>
<td>0.858</td>
<td>0.980</td>
</tr>
<tr>
<td>F</td>
<td>4.35</td>
<td>1.635</td>
<td>9.69E-10</td>
<td>0.660</td>
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<td>G</td>
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<td>2.463</td>
<td>9.83E-01</td>
<td>0.814</td>
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</table>
Figure C.117: SAC Carbon-10 Product ICUMSA color

Figure C.118: SAC Carbon-10 Product color component A
Figure C.119: SAC Carbon-10 Product color component B

Figure C.120: SAC Carbon-10 Product color component C
Figure C.121: SAC Carbon-10 Product color component D

Figure C.122: SAC Carbon-10 Product color component E
Figure C.123: SAC Carbon-10 Product color component F

Figure C.124: SAC Carbon-10 Product color component G
The product from the SAC resin tests was used as the feed for the WBA column tests, resulting in twenty WBA runs.

Table D.1: WBA UF-1 Regression summary

<table>
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<tr>
<th>Component</th>
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<tbody>
<tr>
<td>A</td>
<td>2272</td>
<td>4.089</td>
<td>0.752</td>
</tr>
<tr>
<td>B</td>
<td>29.03</td>
<td>5.540</td>
<td>0.879</td>
</tr>
<tr>
<td>C</td>
<td>12.85</td>
<td>4.629</td>
<td>0.913</td>
</tr>
<tr>
<td>D</td>
<td>4.82</td>
<td>2.847</td>
<td>0.879</td>
</tr>
<tr>
<td>E</td>
<td>4.96</td>
<td>2.484</td>
<td>0.808</td>
</tr>
<tr>
<td>F</td>
<td>12.97</td>
<td>4.560</td>
<td>0.876</td>
</tr>
<tr>
<td>G</td>
<td>4.32</td>
<td>3.028</td>
<td>0.888</td>
</tr>
</tbody>
</table>

Figure D.1: WBA UF-1 Product ICUMSA color
Figure D.2: WBA UF-1 Product color component A

Figure D.3: WBA UF-1 Product color component B
Figure D.4: WBA UF-1 Product color component C

Figure D.5: WBA UF-1 Product color component D
Figure D.6: WBA UF-1 Product color component E

Figure D.7: WBA UF-1 Product color component F
Figure D.8: WBA UF-1 Product color component G

Table D.2: WBA UF-2 Regression summary

<table>
<thead>
<tr>
<th>Component</th>
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</tr>
<tr>
<td>B</td>
<td>10.79</td>
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<td>0.709</td>
</tr>
<tr>
<td>C</td>
<td>8.75</td>
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<td>D</td>
<td>3.70</td>
<td>2.574</td>
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<tr>
<td>E</td>
<td>3.45</td>
<td>2.954</td>
<td>0.963</td>
</tr>
<tr>
<td>F</td>
<td>4.09</td>
<td>4.074</td>
<td>0.985</td>
</tr>
<tr>
<td>G</td>
<td>3.75</td>
<td>2.213</td>
<td>0.917</td>
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</table>
Figure D.9: WBA UF-2 Product ICUMSA color

Figure D.10: WBA UF-2 Product color component A
Figure D.11: WBA UF-2 Product color component B

Figure D.12: WBA UF-2 Product color component C
Figure D.13: WBA UF-2 Product color component D

Figure D.14: WBA UF-2 Product color component E
Figure D.15: WBA UF-2 Product color component F

Figure D.16: WBA UF-2 Product color component G
Figure D.17: WBA UF-3 Product ICUMSA color

Figure D.18: WBA UF-3 Product pH and conductivity
Table D.3: WBA UF-4 Regression summary

<table>
<thead>
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<th>$R^2$</th>
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<tbody>
<tr>
<td>A</td>
<td>14.64</td>
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</tr>
<tr>
<td>B</td>
<td>14.68</td>
<td>4.314</td>
<td>0.640</td>
</tr>
<tr>
<td>C</td>
<td>14.79</td>
<td>4.370</td>
<td>0.735</td>
</tr>
<tr>
<td>D</td>
<td>7.28</td>
<td>2.623</td>
<td>0.890</td>
</tr>
<tr>
<td>E</td>
<td>5.23</td>
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</tr>
<tr>
<td>F</td>
<td>5.17</td>
<td>3.259</td>
<td>0.938</td>
</tr>
<tr>
<td>G</td>
<td>4.04</td>
<td>1.981</td>
<td>0.920</td>
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</table>

Figure D.19: WBA UF-4 Product ICUMSA color
Figure D.20: WBA UF-4 Product color component A

Figure D.21: WBA UF-4 Product color component B
Figure D.22: WBA UF-4 Product color component C

Figure D.23: WBA UF-4 Product color component D
Figure D.24: WBA UF-4 Product color component E

Figure D.25: WBA UF-4 Product color component F
Figure D.26: WBA UF-4 Product color component G

Figure D.27: WBA UF-5 Product ICUMSA color
Figure D.28: WBA UF-5 Product pH and conductivity

Figure D.29: WBA UF-6 Product ICUMSA color
Figure D.30: WBA UF-6 Product pH and conductivity

Figure D.31: WBA UF-7 Product ICUMSA color
Figure D.32: WBA UF-7 Product pH and conductivity

Figure D.33: WBA UF-8 Product ICUMSA color
Figure D.34: WBA UF-8 Product pH and conductivity

Figure D.35: WBA UF-9 Product ICUMSA color
Figure D.36: WBA UF-9 Product pH and conductivity

Table D.4: WBA UF-10 Regression summary

<table>
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<th>Component</th>
<th>$K_0$</th>
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<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>8.59</td>
<td>2.617</td>
<td>0.967</td>
</tr>
<tr>
<td>B</td>
<td>7.21</td>
<td>3.538</td>
<td>0.978</td>
</tr>
<tr>
<td>C</td>
<td>10.8</td>
<td>3.068</td>
<td>0.947</td>
</tr>
<tr>
<td>D</td>
<td>7.92</td>
<td>2.347</td>
<td>0.924</td>
</tr>
<tr>
<td>E</td>
<td>6.60</td>
<td>2.207</td>
<td>0.917</td>
</tr>
<tr>
<td>F</td>
<td>7.26</td>
<td>2.849</td>
<td>0.945</td>
</tr>
<tr>
<td>G</td>
<td>8.14</td>
<td>2.220</td>
<td>0.879</td>
</tr>
</tbody>
</table>
Figure D.37: WBA UF-10 Product ICUMSA color

Figure D.38: WBA UF-10 Product color component A
Figure D.39: WBA UF-10 Product color component B

Figure D.40: WBA UF-10 Product color component C
Figure D.41: WBA UF-10 Product color component D

Figure D.42: WBA UF-10 Product color component E
Figure D.43: WBA UF-10 Product color component F

Figure D.44: WBA UF-10 Product color component G
Table D.5: WBA Carbon-1 Regression summary

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</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>22.59</td>
<td>2.996</td>
<td>0.326</td>
</tr>
<tr>
<td>B</td>
<td>62.36</td>
<td>3.961</td>
<td>0.295</td>
</tr>
<tr>
<td>C</td>
<td>12.80</td>
<td>3.739</td>
<td>0.547</td>
</tr>
<tr>
<td>D</td>
<td>2271</td>
<td>4.089</td>
<td>0.752</td>
</tr>
<tr>
<td>E</td>
<td>6.71</td>
<td>2.622</td>
<td>0.849</td>
</tr>
<tr>
<td>F</td>
<td>20.71</td>
<td>4.438</td>
<td>0.830</td>
</tr>
<tr>
<td>G</td>
<td>5.93</td>
<td>2.495</td>
<td>0.780</td>
</tr>
</tbody>
</table>

Figure D.45: WBA Carbon-1 Product ICUMSA color
Figure D.46: WBA Carbon-1 Product color component A

Figure D.47: WBA Carbon-1 Product color component B
Figure D.48: WBA Carbon-1 Product color component C

Figure D.49: WBA Carbon-1 Product color component D
Figure D.50: WBA Carbon-1 Product color component E

Figure D.51: WBA Carbon-1 Product color component F
Figure D.52: WBA Carbon-1 Product color component G

Table D.6: WBA Carbon-2 Regression summary

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<th>St</th>
<th>$R^2$</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>19.56</td>
<td>6.146</td>
<td>0.737</td>
</tr>
<tr>
<td>B</td>
<td>12.64</td>
<td>6.390</td>
<td>0.982</td>
</tr>
<tr>
<td>C</td>
<td>6.22</td>
<td>4.979</td>
<td>0.943</td>
</tr>
<tr>
<td>D</td>
<td>3.93</td>
<td>3.486</td>
<td>0.901</td>
</tr>
<tr>
<td>E</td>
<td>4.98</td>
<td>3.576</td>
<td>0.856</td>
</tr>
<tr>
<td>F</td>
<td>9.95</td>
<td>5.236</td>
<td>0.885</td>
</tr>
<tr>
<td>G</td>
<td>3.73</td>
<td>3.445</td>
<td>0.839</td>
</tr>
</tbody>
</table>
Figure D.53: WBA Carbon-2 Product ICUMSA color

Figure D.54: WBA Carbon-2 Product color component A
Figure D.55: WBA Carbon-2 Product color component B

Figure D.56: WBA Carbon-2 Product color component C
Figure D.57: WBA Carbon-2 Product color component D

Figure D.58: WBA Carbon-2 Product color component E
Figure D.59: WBA Carbon-2 Product color component F

Figure D.60: WBA Carbon-2 Product color component G
Table D.7: WBA Carbon-3 Regression summary

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<th>$R^2$</th>
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<tbody>
<tr>
<td>A</td>
<td>7.14</td>
<td>5.427</td>
<td>0.931</td>
</tr>
<tr>
<td>B</td>
<td>19.86</td>
<td>4.992</td>
<td>0.797</td>
</tr>
<tr>
<td>C</td>
<td>17.92</td>
<td>4.451</td>
<td>0.970</td>
</tr>
<tr>
<td>D</td>
<td>6.42</td>
<td>2.696</td>
<td>0.917</td>
</tr>
<tr>
<td>E</td>
<td>7.22</td>
<td>2.158</td>
<td>0.858</td>
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<tr>
<td>F</td>
<td>10.15</td>
<td>4.571</td>
<td>0.957</td>
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<tr>
<td>G</td>
<td>5.87</td>
<td>2.216</td>
<td>0.795</td>
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Figure D.61: WBA Carbon-3 Product ICUMSA color
Figure D.62: WBA Carbon-3 Product color component A

Figure D.63: WBA Carbon-3 Product color component B
Figure D.64: WBA Carbon-3 Product color component C

Figure D.65: WBA Carbon-3 Product color component D
Figure D.66: WBA Carbon-3 Product color component E

Figure D.67: WBA Carbon-3 Product color component F
Figure D.68: WBA Carbon-3 Product color component G

Table D.8: WBA Carbon-4 Regression summary

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<th>St</th>
<th>$R^2$</th>
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<tbody>
<tr>
<td>A</td>
<td>1947</td>
<td>4.813</td>
<td>0.047</td>
</tr>
<tr>
<td>B</td>
<td>1997</td>
<td>5.962</td>
<td>0.048</td>
</tr>
<tr>
<td>C</td>
<td>36.90</td>
<td>5.218</td>
<td>0.165</td>
</tr>
<tr>
<td>D</td>
<td>22.48</td>
<td>4.510</td>
<td>0.247</td>
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<tr>
<td>E</td>
<td>32.88</td>
<td>4.375</td>
<td>0.247</td>
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<tr>
<td>F</td>
<td>80.34</td>
<td>5.336</td>
<td>0.336</td>
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<tr>
<td>G</td>
<td>22270</td>
<td>2.555</td>
<td>0.116</td>
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Figure D.69: WBA Carbon-4 Product ICUMSA color

Figure D.70: WBA Carbon-4 Product color component A
Figure D.71: WBA Carbon-4 Product color component B

Figure D.72: WBA Carbon-4 Product color component C
Figure D.73: WBA Carbon-4 Product color component D

Figure D.74: WBA Carbon-4 Product color component E
Figure D.75: WBA Carbon-4 Product color component F

Figure D.76: WBA Carbon-4 Product color component G
Table D.9: WBA Carbon-5 Regression summary

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<tr>
<td>A</td>
<td>6.91</td>
<td>5.163</td>
<td>0.997</td>
</tr>
<tr>
<td>B</td>
<td>7.53</td>
<td>6.436</td>
<td>0.994</td>
</tr>
<tr>
<td>C</td>
<td>7.73</td>
<td>4.574</td>
<td>0.987</td>
</tr>
<tr>
<td>D</td>
<td>5.11</td>
<td>2.724</td>
<td>0.998</td>
</tr>
<tr>
<td>E</td>
<td>4.06</td>
<td>3.252</td>
<td>0.987</td>
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<tr>
<td>F</td>
<td>5.33</td>
<td>5.340</td>
<td>0.990</td>
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<tr>
<td>G</td>
<td>2.59</td>
<td>2.055</td>
<td>0.990</td>
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Figure D.77: WBA Carbon-5 Product ICUMSA color
Figure D.78: WBA Carbon-5 Product color component A

Figure D.79: WBA Carbon-5 Product color component B
Figure D.80: WBA Carbon-5 Product color component C

Figure D.81: WBA Carbon-5 Product color component D
Figure D.82: WBA Carbon-5 Product color component E

Figure D.83: WBA Carbon-5 Product color component F
Figure D.84: WBA Carbon-5 Product color component G

Table D.10: WBA Carbon-6 Regression summary

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<tbody>
<tr>
<td>A</td>
<td>23.43</td>
<td>5.520</td>
<td>0.641</td>
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<tr>
<td>B</td>
<td>15.69</td>
<td>5.534</td>
<td>0.828</td>
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<tr>
<td>C</td>
<td>9.05</td>
<td>4.226</td>
<td>0.793</td>
</tr>
<tr>
<td>D</td>
<td>9.88</td>
<td>4.280</td>
<td>0.809</td>
</tr>
<tr>
<td>E</td>
<td>17.98</td>
<td>6.188</td>
<td>0.881</td>
</tr>
<tr>
<td>F</td>
<td>41.58</td>
<td>7.855</td>
<td>0.155</td>
</tr>
<tr>
<td>G</td>
<td>6.87</td>
<td>4.896</td>
<td>0.641</td>
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</table>
Figure D.85: WBA Carbon-6 Product ICUMSA color

Figure D.86: WBA Carbon-6 Product color component A
Figure D.87: WBA Carbon-6 Product color component B

Figure D.88: WBA Carbon-6 Product color component C
Figure D.89: WBA Carbon-6 Product color component D

Figure D.90: WBA Carbon-6 Product color component E
Figure D.91: WBA Carbon-6 Product color component F

Figure D.92: WBA Carbon-6 Product color component G
Table D.11: WBA Carbon-7 Regression summary

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<td>A</td>
<td>25.52</td>
<td>4.227</td>
<td>0.390</td>
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<tr>
<td>B</td>
<td>9.99</td>
<td>7.488</td>
<td>0.708</td>
</tr>
<tr>
<td>C</td>
<td>7.98</td>
<td>5.319</td>
<td>0.826</td>
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<td>D</td>
<td>4.97</td>
<td>4.716</td>
<td>0.937</td>
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<td>E</td>
<td>7.04</td>
<td>3.738</td>
<td>0.893</td>
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<td>F</td>
<td>15.58</td>
<td>5.077</td>
<td>0.875</td>
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<td>G</td>
<td>3.86</td>
<td>7.673</td>
<td>0.799</td>
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Figure D.93: WBA Carbon-7 Product ICUMSA color
Figure D.94: WBA Carbon-7 Product color component A

Figure D.95: WBA Carbon-7 Product color component B
Figure D.96: WBA Carbon-7 Product color component C

Figure D.97: WBA Carbon-7 Product color component D
Figure D.98: WBA Carbon-7 Product color component E

Figure D.99: WBA Carbon-7 Product color component F
Figure D.100: WBA Carbon-7 Product color component G

Table D.12: WBA Carbon-8 Regression summary

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<tr>
<td>B</td>
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<td>0.912</td>
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<td>C</td>
<td>7.71</td>
<td>7.584</td>
<td>0.968</td>
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<td>D</td>
<td>4.44</td>
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<td>E</td>
<td>4.79</td>
<td>6.254</td>
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<td>F</td>
<td>8.52</td>
<td>7.990</td>
<td>0.986</td>
</tr>
<tr>
<td>G</td>
<td>2.85</td>
<td>20.81</td>
<td>0.978</td>
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Figure D.101: WBA Carbon-8 Product ICUMSA color

Figure D.102: WBA Carbon-8 Product color component A
Figure D.103: WBA Carbon-8 Product color component B

Figure D.104: WBA Carbon-8 Product color component C
Figure D.105: WBA Carbon-8 Product color component D

Figure D.106: WBA Carbon-8 Product color component E
Figure D.107: WBA Carbon-8 Product color component F

Figure D.108: WBA Carbon-8 Product color component G
Table D.13: WBA Carbon-9 Regression summary

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<td>0.983</td>
</tr>
<tr>
<td>B</td>
<td>6.53</td>
<td>3.195</td>
<td>0.992</td>
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<tr>
<td>C</td>
<td>8.25</td>
<td>2.722</td>
<td>0.973</td>
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<td>D</td>
<td>5.99</td>
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<td>E</td>
<td>5.01</td>
<td>2.110</td>
<td>0.970</td>
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<tr>
<td>F</td>
<td>6.85</td>
<td>2.655</td>
<td>0.965</td>
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<tr>
<td>G</td>
<td>5.59</td>
<td>1.972</td>
<td>0.887</td>
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</table>

Figure D.109: WBA Carbon-9 Product ICUMSA color
Figure D.110: WBA Carbon-9 Product color component A

Figure D.111: WBA Carbon-9 Product color component B
Figure D.112: WBA Carbon-9 Product color component C

Figure D.113: WBA Carbon-9 Product color component D
Figure D.114: WBA Carbon-9 Product color component E

Figure D.115: WBA Carbon-9 Product color component F
Figure D.116: WBA Carbon-9 Product color component G

Table D.14: WBA Carbon-10 Regression summary

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<th>$R^2$</th>
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<tbody>
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<td>A</td>
<td>13.17</td>
<td>2.548</td>
<td>0.962</td>
</tr>
<tr>
<td>B</td>
<td>8.84</td>
<td>4.333</td>
<td>0.990</td>
</tr>
<tr>
<td>C</td>
<td>10.02</td>
<td>3.727</td>
<td>0.988</td>
</tr>
<tr>
<td>D</td>
<td>8.86</td>
<td>2.644</td>
<td>0.946</td>
</tr>
<tr>
<td>E</td>
<td>7.44</td>
<td>2.339</td>
<td>0.919</td>
</tr>
<tr>
<td>F</td>
<td>8.06</td>
<td>3.176</td>
<td>0.961</td>
</tr>
<tr>
<td>G</td>
<td>5.27</td>
<td>2.551</td>
<td>0.845</td>
</tr>
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</table>
Figure D.117: WBA Carbon-10 Product ICUMSA color

Figure D.118: WBA Carbon-10 Product color component A
Figure D.119: WBA Carbon-10 Product color component B

Figure D.120: WBA Carbon-10 Product color component C
Figure D.121: WBA Carbon-10 Product color component D

Figure D.122: WBA Carbon-10 Product color component E
Figure D.123: WBA Carbon-10 Product color component F

Figure D.124: WBA Carbon-10 Product color component G
APPENDIX E. MATLAB CODE

E.1 Model Parameter Regression

clear all

% Ion Exchange Parameter Regression
% Bruce Ellis
% 06/12/2004

X = BV data

Y = Concentration data
ydata = [0.790683092 0.863997209 0.868720435 0.93997185 0.928800345 0.983493547 0.99242185 1.045250708 1.097179263 1.130219587 1.200026726 1.183675388];

% Initial guesses
lambda = 0.1;
K0 = 30;
K1 = 1;
ST = 0.9;

% Starting guess
x0 = [K0,K1,lambda,ST];
lb = [0,0,0,0];

% Least squares non-linear regression
[x,resnorm] = lsqcurvefit(@reg_linear_4par,x0,xdata,ydata,lb);

%y'  
x'  
k0 = x(1);
k1 = x(2);
lambda = x(3);
ST = x(4);
D = 0;
ui = 0.218645963;
epsilon = 0.464;
h = 0.1;          % Step size (m)
% Step size (m)
% Time step
alpha = beta/(2*h);
% Time step
delta = beta*ST;
et = (epsilon/(1-epsilon))*delta;
L = 1;           % Column length (m)
% Column length (m)
n = round(L/h);  % Number of points
Count = 0;
t = beta*Count*(L/ui);
BV_rate = 0.327263635;
BV = t*BV_rate;
a = 1.586589767;
b = 0.125880603;
c = 0.002282669;
pH = a*(1+c*(exp(b*t)));
K = k0*exp(-lambda*pH) + k1;

q_diff = 1000;

Ci = 1;
q0 = 0;
for m = 1:(n-1);
  C(m,1) = 0;
  q(m,1) = 0;
  C(n,1) = 0;
  q(n,1) = 0;
  R(1,1) = alpha;
end

while BV < 20
  Count = Count + 1
  for m = 2:(n-1);
    % Setting up of matrix
    R(1,1) = 
           \( \frac{(D*beta)}{(ui*L*(h^2))} + \frac{(beta/(2*h))}{C[i]} \);
    R(m,1) = 0;
    R(n,1) = 0;
    t = beta*Count*(L/ui);
    BV_rate = 0.327263635;
    BV = t*BV_rate;
    pH = a*(1+c*(exp(b*t)));
    K = k0*exp(-lambda*pH) + k1;
    gamma = (St*beta/K);
    B(m,m) = 
            [1-\( \frac{(2*D*beta)}{(ui*L*(h^2))} \) - (St*beta)];
    B(m,m+1) = \( \frac{(D*beta)}{(ui*L*(h^2))} - \frac{(beta/(2*h))} \);
    B(m,m-1) = \( \frac{(D*beta)}{(ui*L*(h^2))} + \frac{(beta/(2*h))} \);
    B(1,1) = 
           [1-\( \frac{(2*D*beta)}{(ui*L*(h^2))} \) - (St*beta)];
    B(1,2) = \( \frac{(D*beta)}{(ui*L*(h^2))} - \frac{(beta/(2*h))} \);
    B(n,n) = [1-\( \frac{(2*D*beta)}{(ui*L*(h^2))} \) - (St*beta)];
    B(n,n-1) = \( \frac{(D*beta)}{(ui*L*(h^2))} + \frac{(beta/(2*h))} \);
  end
  C_new = [B*C] + (gamma.*q) + R;
  C = C_new;
  for i = 1:n-1
    X(1,1) = \[(-eta/K) + 1\];
    X(i+1,i+1) = \[(-eta/K) + 1\];
  end
  q_new = X*q + eta.*C;
  q_diff = q_new(1,1)-q(1,1);
  q = q_new;
  H(Count,1) = C(n,1);
  H(Count,2) = BV;
end

tlist1 = H(:,2);
data = H(:,1);

% Round to 2 dp

tlist = roundoff(tlist1,2);
data2 = roundoff(xdata,2);

xdata = data2;
z = length(xdata);
for i = 1:z
  j = find(tlist==xdata(i));
  y(i) = data(j);
figure(1)
plot(tlist1, data, 'b');
hold on;
legend('Concentration of A', 0);
xlabel('BV');
ylabel('Concentration')

figure(1)
plot(xdata, ydata, 'r');
hold on;
legend('Concentration of A', 0);
xlabel('BV');
ylabel('Concentration')

% Determine correlation coefficient
for i = 1:length(xdata)
    j = find(tlist == xdata(i));
    y(i) = data(j);
end

% Called regression function
% Bruce Ellis
% 04/20/2004

function F = reg_linear(x, xdata)

% Shows initial guesses

disp(x)

k0 = x(1);
k1 = x(2);
lambda = x(3);
St = x(4);

k0 = x(1);
k1 = x(2);
lambda = x(3);
St = x(4);

D = 0;
ui = 0.218645963;
epsilon = 0.464;
h = 0.1;
beta = 0.008;
alpha = beta/(2*h);
delta = beta*St;
eta = (epsilon/(1-epsilon))*delta;
L = 1;
n = round(L/h);
Count = 0;
t = beta*Count*(L/ ui);

BV_rate = 0.327263635;
BV = t^BV_rate;
a = 1.586589767;
b = 0.125880603;
c = 0.002282669;
PH = a*(1+1+exp(b*t));
K = k0*exp(-lambda*PH)+k1;
Ci = 1;
q0 = 0;
for m = 1:(n-1);
C(m,1) = 0;
q(m,1) = 0;
C(n,1) = 0;
q(n,1) = 0;
R(1,1) = alpha;
end
while BV < 20
Count = Count + 1
for m = 2:(n-1); % Setting up of matrix
R(1,1) = \(((D*beta)/(ui*L*(h^2))+(beta/(2*h)))*Ci\);  
R(m,1) = 0;
R(n,1) = 0;
t = beta*Count*(L/ui);
BV_rate = 0.327263635;
BV = t*BV_rate;
pH = a*(1+c*(exp(b*t)));
K = k0*exp(-lambda*pH) + k1;
gamma = (St*beta/K);
B(m,m) = \[1-((2*D*beta)/(ui*L*(h^2)))-(St*beta)\];
B(m,m+1) = \[((D*beta)/(ui*L*(h^2))-(beta/(2*h)))\];
B(m,m-1) = \[((D*beta)/(ui*L*(h^2))+(beta/(2*h)))\];
B(1,1) = \[1-((2*D*beta)/(ui*L*(h^2)))-(St*beta)\];
B(1,2) = \[((D*beta)/(ui*L*(h^2))-(beta/(2*h)))\];
B(n,n) = \[1-((2*D*beta)/(ui*L*(h^2)))-(St*beta)\];
B(n,n-1) = \[((D*beta)/(ui*L*(h^2))+(beta/(2*h)))\];
end
C_new = \[B*C\]+(gamma.*q)+R;  
C = C_new;
for i = 1:n-1
X(1,1) = \[-eta/K+1\];
X(i+1,i+1) = \[-eta/K+1\];
end
q_new = X*q + eta.*C;
q_diff = q_new(1,1)-q(1,1);
q = q_new;
H(Count,1) = C(n,1);
H(Count,2) = BV;
end
tlist1 = H(:,2);
data = H(:,1);
%Round to 2 dp
ndata = roundoff(xdata,2);
for i = 1:z
\[ j = \text{find}(tlist==xdata(i)); \]
\[ y(i) = data(j); \]
end

\[ F = y \]

% Called rounding function
% Rounds a scalar, matrix or vector to a specified number of decimal places
% Format is roundoff(number,decimal_places)

function y = roundoff(number,decimal_places)


\[ \text{INeg},\text{JNeg} = \text{find}(\text{number}<0); \]
% Negative numbers
if ~isempty(INeg)
    \[ \text{IndNeg} = \text{sub2ind(size(number)},\text{INeg},\text{JNeg}); \]
    \[ \text{Number} = \text{abs}(\text{number}); \]
else
    \[ \text{Number} = \text{number}; \]
end

\[ \text{decimals} = 10.^{\text{decimal_places}}; \]
\[ y1 = \text{fix}(\text{decimals} * \text{Number} + 0.5)./\text{decimals}; \]
if ~isempty(INeg)
    \[ y1(\text{IndNeg}) = -y1(\text{IndNeg}); \]
end
\[ y = y1; \]

E.2 Model Solution

% Predictive Model
% Bruce Ellis
% 05-15-04

clear all
close all
cle

\[ \text{St} = 0.8367633; \]
% From regression
\[ \text{ui} = 0.218645963; \]
\[ \text{epsilon} = 0.464; \]
\[ \text{lambda} = 0.99949996; \]
% From regression
\[ \text{k0} = 9.6688762; \]
% From regression
\[ \text{k1} = 3.6949121; \]
% From regression
\[ h = 0.1; \]
% Step size (m)
\[ D = 0; \]
% Dispersion term that can be included
\[ \beta = 0.01; \]
% Time step
\[ \alpha = \beta/(2*\text{h}); \]
\[ \delta = \beta*\text{St}; \]
\[ \eta = (\text{epsilon}/(1-\text{epsilon}))*\delta; \]
\[ \text{L} = 1; \]
\[ \text{n} = \text{round}(\text{L}/\text{h}); \]
% Number of points
\[ \text{Count} = 0; \]
\[ t = \beta*\text{Count}*(\text{L}/\text{ui}); \]
\[ \text{BV\_rate} = 0.327263635; \]
\[ \text{BV} = t*\text{BV\_rate}; \]
\[ a = 1.5865859767; \]
\[ b = 0.125880603; \]
\[ c = 0.002282669; \]
\[ \text{pH} = a*(1+c*(\exp(b*t))); \]
\[ \text{K} = \text{k0}*\exp(-\text{lambda}\times\text{pH}) + \text{k1}; \]
% BC and IC

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Ci = 1;
q0 = 0;

for m = 1:(n-1);
C(m,1) = 0;
q(m,1) = 0;
C(n,1) = 0;
q(n,1) = 0;
R(1,1) = alpha;
end

while BV < 20
Count = Count + 1

for m = 2:(n-1);  % Setting up of matrix
R(1,1) = \(((D*beta)/(ui*L*(h^2))+(beta/(2*h)))*Ci\);
R(m,1) = 0;
R(n,1) = 0;
t = beta*Count*(L/ui);
BV_rate = 0.327263635;
BV = t*BV_rate;
pH = a*(1+c*(exp(b*t)));
K = k0*exp(-lambda*pH) + k1;
gamma = (St*beta/K);
B(m,m) = \[1-((2*D*beta)/(ui*L*(h^2)))-(St*beta)\];
B(m,m+1) = \(((D*beta)/(ui*L*(h^2))-(beta/(2*h)))\);
B(m,m-1) = \(((D*beta)/(ui*L*(h^2))+(beta/(2*h)))\);
B(1,1) = \[1-((2*D*beta)/(ui*L*(h^2)))-(St*beta)\];
B(1,2) = \(((D*beta)/(ui*L*(h^2))-(beta/(2*h)))\);
B(n,n) = \[1-((2*D*beta)/(ui*L*(h^2)))-(St*beta)\];
B(n,n-1) = \(((D*beta)/(ui*L*(h^2)))+(beta/(2*h)))\);
end

C_new = \[B*C\]+(gamma.*q)+R;
C = C_new;

for i = 1:n-1
X(1,1) = \[-eta/K+1\];
X(i+1,i+1) = \[-eta/K+1\];
end

q_new = X*q + eta.*C;
q = q_new;
H(Count,1) = C(n,1);
H(Count,2) = BV;
end

figure(1)
plot(H(:,2),H(:,1),'b');
hold on;
legend('Concentration of A',0);
xlabel('BV');
ylabel('Concentration')

ydata = [0.790683092 0.863997209 0.93997185 0.928800345 0.983493547
0.99242185 1.045250708 1.097179263 1.130219587 1.200026726
1.183675388];
xdata = [1.2775110582.874399881 4.471288703 6.068177526 7.664066348
9.261955171 10.85884399 12.45443282 14.05262164 15.64951046
17.24639928 18.84328811];
E.3 GPC-Abs Deconvolution

% GPC - Refractive Index
% HA Broadhurst (2002)
% Edited by BM Ellis
% Audubon Sugar Institute

clear all
close all

samples = [1,2,3,4];
NoF = length(samples);
count = 0;
t_peak = [15,17,19];

for file = samples

% Load Data
name = strcat('d:\',num2str(file),'_280.txt');
data = load(name,'-ascii');
N = max(size(data));
OK = 1;
count = count + 1;
while isempty(OK)==0

t = data(1:N,1);
r = data(1:N,2);
delta = mean(diff(t))/2;
clear tb yb tr nr smax stdev r_calc
close all
figure(1)
set(1,'Position',[5 5 1015 695])
plot(t,r)
grid on
title('Zoom to best view to set baseline')
zoom on
pause
title('Set baseline')
[tb,yb] = ginput(2);
n1 = find(t>tb(1)-delta & t<tb(1)+delta);
n2 = find(t>tb(2)-delta & t<tb(2)+delta);
m = mean(r(n1:n2));
r  = r-m;
plot(t,r);
grid on

% Sugar Peak - Non Existent
x_sug = [1,1,0];

% End of Chromatogram
title('Zoom to end of chromatogram')
zoom on
pause
zoom off

[tr,yr] = zoomin(x_sug,x_sug); % zoom in

end
% Peak Detection
N_peak = length(t);  
for i = 1:N_peak  
n_pe(i) = find(t>t_peak(i)-delta & t<t_peak(i)+ delta);  
end  
figure(1)  
set(1,'Position',[5 5 1015 695])  
plot(t,r,'b-',t_peak,r(n_pe),'rx')  
grid on  
title('Click on maxima - press enter when done')  
[tr, yr] = ginput;  
Np = length(tr);  
for i = 1:Np  
nr(i) = find(t>tr(i)-delta & t<tr(i)+delta);  
end  
plot(t,r)  
nr = nr(1:Np);  
tr = tr(1:Np);  
smax = r(nr);  
stdev = ones(1,Np).*0.2;  

% Set Regression Options
options = optimset('lsqcurvefit');
opnew = optimset(options,...
'Display','iter'....
'LargeScale','on');

% Least squares non-linear regression - Standard Deviation
x0 = sdev;
[x,resnorm] = lsqcurvefit(@normals,x0,t,r,[],optnew,tr,smax,x_sug);
stdev = x;  

% First derivative for times
x0 = tr;
lb = ones(1,Np).*10;
ub = ones(1,Np).*25;
[x,resnorm] = lsqcurvefit(@normals2,x0,t,r,lb,ub,optnew,stdev,smax,x_sug);
tr = x;  

% Time Domain
x0 = horzcat(stdev,smax);
lb = zeros(1,Np*2);
[x,resnorm] = lsqcurvefit(@normals3a,x0,t,r,[],optnew,tr,x_sug);
stddev = x(1:Np);
smax = x(Np+1:2*Np);  

% Derivative - standard and times
%x0 = horzcat(stdev,tr);

%[x,resnorm] = lsqcurvefit(@normals7,x0,dt,dr,[],optnew,smax,x_sug,delta);
%sx0 = x(1:Np);
%tr = x(Np+1:2*Np);

stds = horzcat(stdev,x_sug(2));  
smax = horzcat(smax,x_sug(3));  
tr = horzcat(tr,x_sug(1));  
figure(1)  
set(1,'Position',[5 5 1015 695])  
R_calc = 0;  
for i = 1:Np+1  
r_calc(:,i) = normal([tr(i),stds(i),smax(i)],t);
R_calc = R_calc + r_calc(:,i);  
end  
cor = corrcoef(r(751:length(r)),R_calc(751:length(r)));  
R2 = cor(1,2)*cor(2,1);  
subplot(1,2,1);  
plot(t,R_calc,t,r,t,r-R_calc)  
xlabel('Retention time (min)')  
ylabel('Absorbance')  
legend('Calculated','Actual','Residual')  
grid on  
subplot(1,2,2);  
plot(t,r,r_calc)  
xlabel('Retention time (min)')  
ylabel('Absorbance')  
title(strcat('GPC UV ',num2str(file),'nm',Date,' - R^2 = ',num2str(R2)))  
P = questdlg('Do you want to print the chromatograms?'...  
'print','Yes','No ','No ');  
if P == 'Yes'  
orient landscape  
print  
end  
S = questdlg('Do you want to save the chromatograms?'...  
'Save','Yes','No ','No ');  
if S == 'Yes'  
orient landscape  
pause  
end  
response = questdlg('Are you happy with the deconvolution'...  
'Integration','Yes','No','Yes');  
if strcmp(response,'Yes')  
OK = [];  
orient landscape  
end  
end  
for i=length(stdev)+1:10  
stdev(i) = 0;  
tr(i) = 0;  
smax(i) = 0;  
end  
standard(count,:) = horzcat(file,stdev);  
RT(count,:) = horzcat(file,tr);  
Maximum(count,:) = horzcat(file,smax);  
t_peak = tr;  
end  
RIa = peak_area(RT(2:8,:),smax(2:8,:),std(2:8,:),t);
VITA

Bruce Malcolm Ellis was born in East London, South Africa, on October 18, 1979. He attended school at Selborne before moving to Durban where he graduated from high school, at Kloof High School in 1997. After high school, he attended the University of Natal in Durban, South Africa, where he obtained a Bachelor of Science degree in chemical engineering. After graduating in December 2001, he worked for ECOSERV (an environmental consulting company) for 6 months, at which point Audubon Sugar Institute, in conjunction with Calgon Carbon, offered him an assistantship to study for the degree of Master of Science in Chemical Engineering at the Audubon Sugar Institute, Louisiana State University.