SUGARCANE JUICE EXTRACTION AND PRESERVATION, AND LONG-TERM LIME PRETREATMENT OF BAGASSE

A Dissertation

by

CESAR BENIGNO GRANDA COTLEAR

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2004

Major Subject: Chemical Engineering

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Approved as to style and content by:

Mark T. Holtzapple (Co-Chair of Committee)	Richard R. Davison (Co-Chair of Committee)
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ABSTRACT

Sugarcane Juice Extraction and Preservation, and Long-term Lime Pretreatment of Bagasse. (December 2004)

Cesar Benigno Granda Cotlear, B.S., Texas A&M University

Co-Chairs of Advisory Committee: Dr. Mark T. Holtzapple
Dr. Richard R. Davison

New technologies, such as an efficient vapor-compression evaporator, a stationary lime kiln (SLK), and the MixAlco process, compelled us to re-evaluate methods for producing sugar from cane. These technologies allow more water and lime to be used, and they add more value to bagasse.

Extracting and preserving the sugars, and lime pretreating the bagasse to enhance biodigestibility, all at the same time in a pile, was demonstrated to be unfeasible; therefore, sugar extraction must occur before lime treating the bagasse.

Sugar extraction should occur countercurrently by lixiviation, where liquid moves in stages opposite to the soaked bagasse (*megasse*), which is conveyed by screw-press conveyors that gently squeeze the fiber in each stage, improving extraction. The performance of a pilot-scale screw-press conveyor was tested for dewatering capabilities and power consumption. The unoptimized equipment decreased *megasse* moisture from 96 to 89%. Simulation of the process suggested that eight stages are necessary to achieve 98% recovery from typical sugarcane. The cumulative power for the screw-press conveyor system was 17.0±2.1 hp·h/ton dry fiber.

Thin raw juice preserved with lime for several months showed no sucrose degradation and no quality deterioration, except for reducing sugar destruction. The lime loading needed for 1-year preservation is 0.20 g $Ca(OH)_2$/g sucrose. Shorter times require less lime.

After preservation, the juice was carbonated and filtered, and the resulting sludge pelletized. Due to their high organic content, the pellets were too weak for calcination

temperatures used in the SLK. The organics must be decreased prior to pelletization and sodium must be supplemented as a binding agent.

Long-term lime pretreatment of bagasse showed two delignification phases: bulk (rapid) and residual (slow). These were modeled by two simultaneous first-order reactions. Treatments with air purging and higher temperatures (50 – 57^{o}C) delignified more effectively, especially during the residual phase, thus yielding higher cellulase-enzyme digestibilities after 2 – 8 weeks of treatment. At temperatures > 60^{o}C, pure oxygen purging is preferred.

Fresh bagasse was of better quality than old bagasse. Treatment with NaOH yielded a larger bulk delignification phase than $Ca(OH)_2$.

Long-term lime pulping of bagasse was unsuitable for copy-quality paper, but it was appropriate for strawboard and other filler applications.

To God, whom I love and trust above all things.
To my parents, who with their love,
patience and encouragement have always kept me
from giving up. I am here because of them.
My accomplishments are theirs.
To my loving wife, Anita, for all her love and support.

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I want to thank also the rest of my committee, Dr. Richard Davison, Dr. Sam Mannan, and Dr. Cady Engler, for all the advice and help they provided during my preliminary examination as well as during the process of completing this dissertation and final examination.

Special thanks go to Terrabon and Altex Technologies for funding these projects. I also wish to thank the people of Terrabon and Gooseneck Co., Jim Lampley, Jim McAdams, Don Angonia, Manuel Gonzalez, and José Robles for all their invaluable help.

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Finally, I want to thank my entire research group, Sehoon Kim, Guillermo Coward-Kelly, Cateryna Aiello, Vincent Chang, Frank Agbogbo, Susan Domke, Richard Jepson, Piyarat Thanakoses (Jeab), Sally Chang, Maria Elena Almendarez, Xu Li, Li Zhu (Julie), Jonathan O'Dwyer, Zhihong Fu, Hung-wen Yeh, Rocio Sierra, Maxine Jones, all the undergraduate student workers and my laboratory facility neighbors Monjur Hossen from the Food Science Department, Marc Barron, Ernesto Hernandez, Carl Vavra, Duane Wagner, Temur Yunusov and Scott McKenzie from the Food Protein R&D Center, who in one way or another always lent me a helping hand.

TABLE OF CONTENTS

CHAPTER Page

Page

LIST OF FIGURES

Page

Page

Page

Page

Page

Page

Page

Page

Page

Page

LIST OF TABLES

Page

Page

CHAPTER I

INTRODUCTION

I.1 Rationale

In any industry, new technologies can improve processes; therefore, it may be necessary to re-design conventional practices to benefit from the innovations. Sugarcane processing for the production of table sugar (sucrose) is no exception.

We have been compelled to revise some process units employed in the sugarcane industry because of following three new technologies:

1) A very efficient vapor-compression evaporator.
2) An efficient stationary lime kiln.
3) The MixAlco Process.

I.1.1 Vapor Compression Evaporator

A vapor-compression evaporator (Figure 1.1) is being developed at Texas A&M University (Dr. Mark Holtzapple, Chemical Engineering Dept., College Station TX 77843-3122, 979-845-9708). The vapor compressor can be a jet ejector, a mechanical compressor, or both. Studies are being conducted to improve the efficiency of the evaporator and compressor. Preliminary calculations suggest that efficiencies should be between 10 and 30 effects (ratio of latent heat of vaporization to the fuel energy input). The energy-efficiency advantages are obvious; conventional evaporators employ four or five (at most) effects.

This dissertation follows the style of Bioresource Technology.

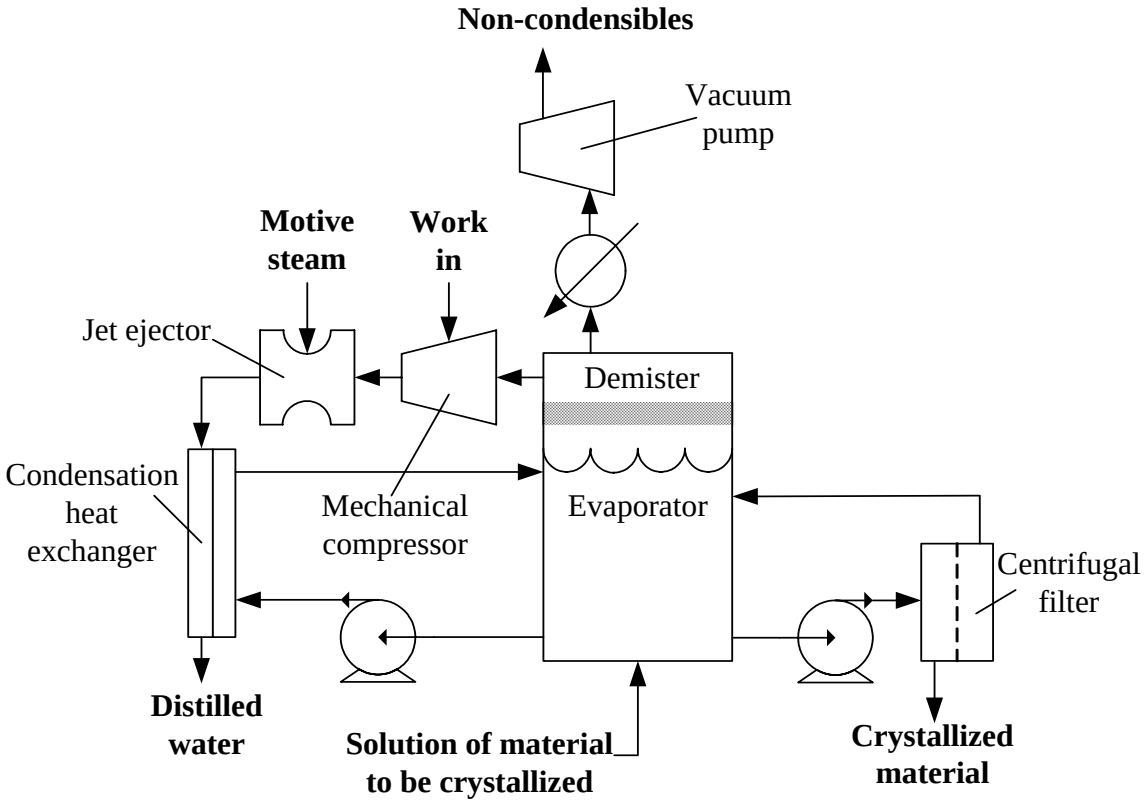


Figure 1.1 Vapor-compression evaporator showing both jet ejector and mechanical compressor. Each may be employed individually or they may be employed in a tandem, as shown.

I.1.2 Stationary Lime Kiln

Processes that employ lime often have calcium carbonate as a by-product. Using a lime kiln, the recovered calcium carbonate can be transformed back into calcium oxide to be used in the process. Unfortunately, conventional lime kilns are very energy inefficient. Altex Technologies Corporation (Dr. John T. Kelly, 244 Sobrante Way, Sunnyvale CA 94086, 408-328-8302, www.altextech.com) has developed an efficient lime kiln process, which consists of pelletizing finely divided calcium carbonate and loading the pellets into a well-insulated stationary reactor. Hot gas at calcination temperatures is then blown through the reactor, transforming the calcium carbonate pellets into calcium oxide. Altex Technologies indicates that this process can decrease

the cost of lime by about 56% compared to conventionally obtained calcium oxide (Namazian, 2004).

I.1.3 The MixAlco Process

The MixAlco process converts biomass into a mixture of alcohols. The biomass is pretreated with lime to increase digestibility. The lime-treated biomass is then fermented by a mixed culture of carboxylic-acid-producing microorganisms. The pH is controlled by adding calcium carbonate. The product from this fermentation is a mixture of carboxylate salts, which are thermally converted to ketones and hydrogenated to a mixture of alcohols (Figure 1.2). This process produces both fuels and chemicals (Holtzapple et al., 1999).

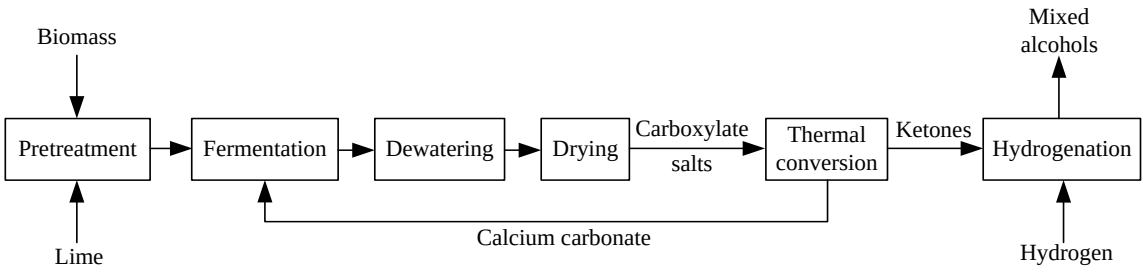


Figure 1.2 Overview of MixAlco process (adapted from Holtzapple et al., 1999).

I.2 Description of Conventional Sugarcane Processing

The processing of sugarcane to produce crystallized sugar occurs by different methods; however, the basic process remains unchanged (Chen and Chou, 1993; Hugot, 1986; Valdes Delgado and de Armas Casanova, 2001). The following is the general procedure:

1) Cane harvesting.
2) Cane shredding and preparation.

3) Extraction of juice either by squeezing with roller mills or by diffusion, which leaves the sugarcane pulp by-product, known as bagasse.
4) Clarification of the juice, which may occur by two common methods:
    a) By *defecation*, which consists of liming to a neutral pH, adding a flocculant, and heating to about 100^{o}C to cause a precipitate that is then filtered out.
    b) By *carbonatation*, which is done by liming to a high pH (~11) then heating to about 55^{o}C, followed by two or more carbonations and filtrations until the pH is brought to neutral either by adding more carbon dioxide or with sulfur dioxide, which is a process known as *sulphitation*.
5) Concentration of the juice by evaporation.
6) Crystallization of raw or white sugars.

Figures 1.3 and 1.4 show the two different methods of sugar production from cane. White sugars can be obtained directly from cane in the same sugar house, a process known as *plantation white sugar* or *direct white sugar*, especially when carbonatation is employed as the clarification method. Nonetheless, in most countries, raw sugars are first produced which are then sold to sugar refineries (Valdes Delgado and de Armas Casanova, 2001). In the refinery (Figure 1.5), raw sugar crystals are affinated (washed), re-dissolved, purified, clarified, and decolorized. Lime is also an additive in this process. The refined syrup is then heated, concentrated by evaporation and crystallized to obtain refined white sugars (Chen and Chou, 1993; Valdes Delgado and de Armas Casanova, 2001).

I.2.1 Sugarcane Juice Extraction

Conventional sugar extraction from sugarcane is performed using roller mills or diffusion. In milling, shredded cane passes between hydraulically loaded, grooved, cylindrical rolls arranged in series. As the crushing/squeezing occurs, juice is expelled. An individual roller mill has three, four, or five rolls in a housing. A tandem of four, five or six roller mills constitute a *train*, as shown in Figure 1.6 (Payne, 1991).

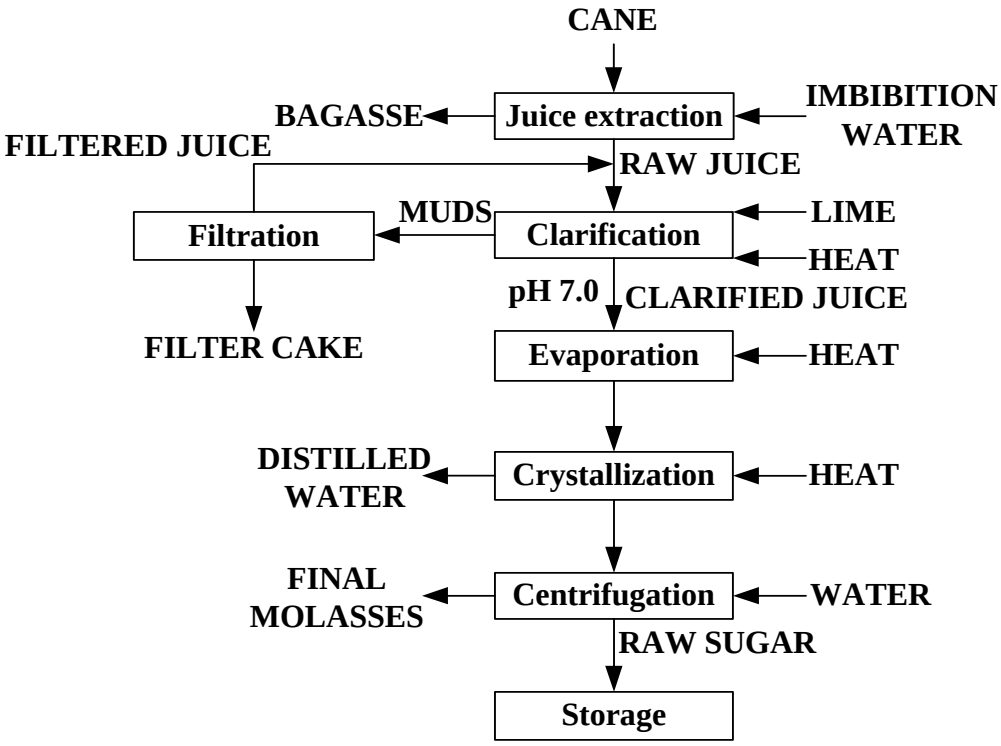


Figure 1.3 Flowchart for the production of raw sugar (adapted from Valdes Delgado and de Armas Casanova, 2001).

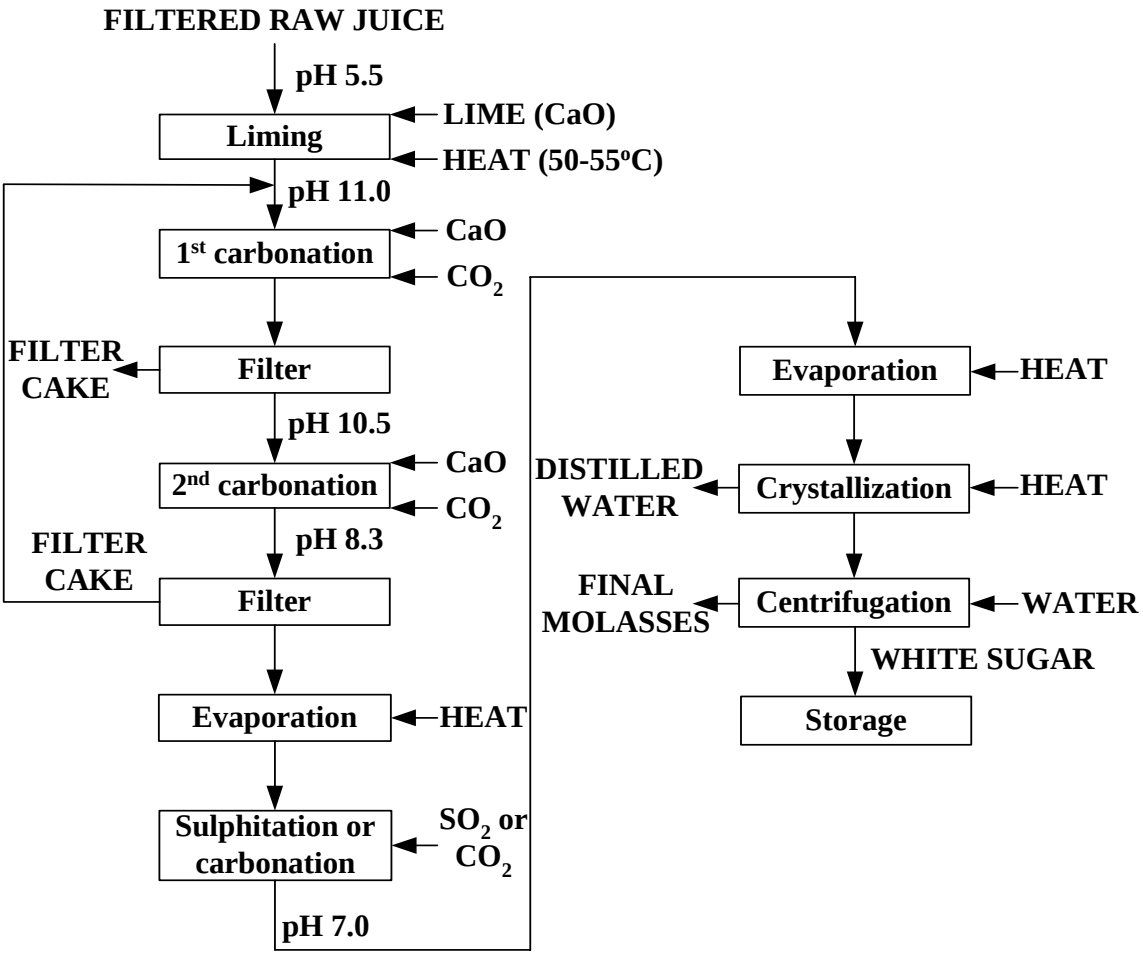


Figure 1.4 Flowchart for the production of plantation white sugar (adapted from Valdes Delgado and de Armas Casanova, 2001).

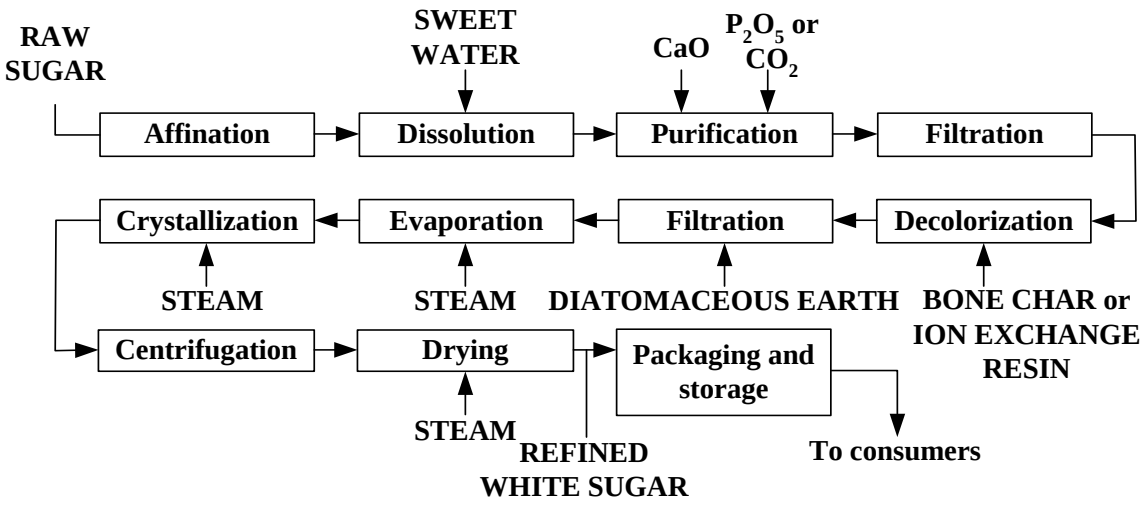


Figure 1.5 Flowchart for the production of white refined sugar (adapted from Valdes Delgado and de Armas Casanova, 2001).

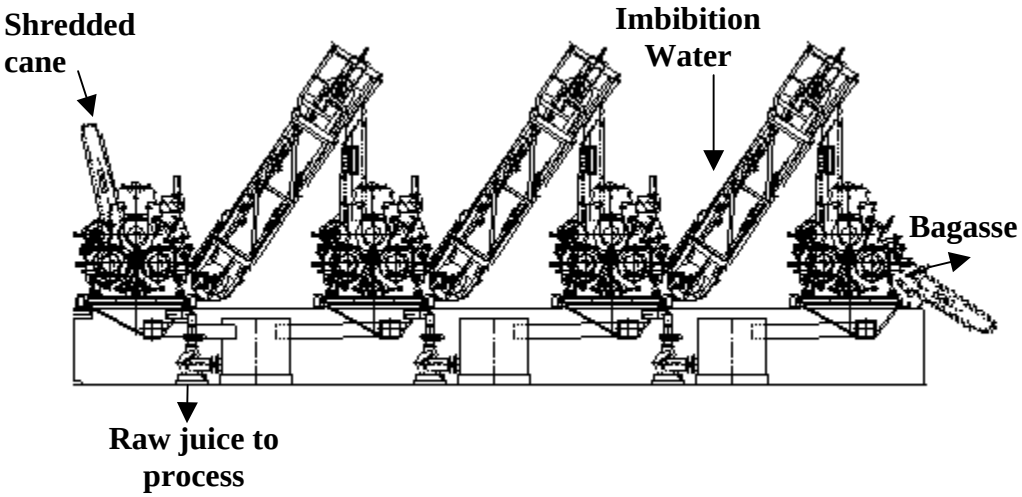


Figure 1.6 Sugarcane milling tandem.

Sugar extraction by diffusion, as it is wrongly termed, is actually a lixiviation process. The shredded and pre-crushed cane (high percentage of cell rupture) is placed on a horizontal conveyor forming a uniform bed 1 to 1.5 m in thickness. As the cane bed advances to the discharge end, liquid is repeatedly pumped on top, which flows

through the bed by gravity to extract the sugars. The liquid flows along the diffuser in stages countercurrent to the cane bed (Figure 1.7). In practice, up to 18 stages are required to perform the extraction (Walsh, 2001). This process is performed at higher temperatures than milling (~70^{o}C) to facilitate extraction and to control microbial activity; thus, the extra investment of juice heaters is required. (Hugot, 1986; Payne, 1991).

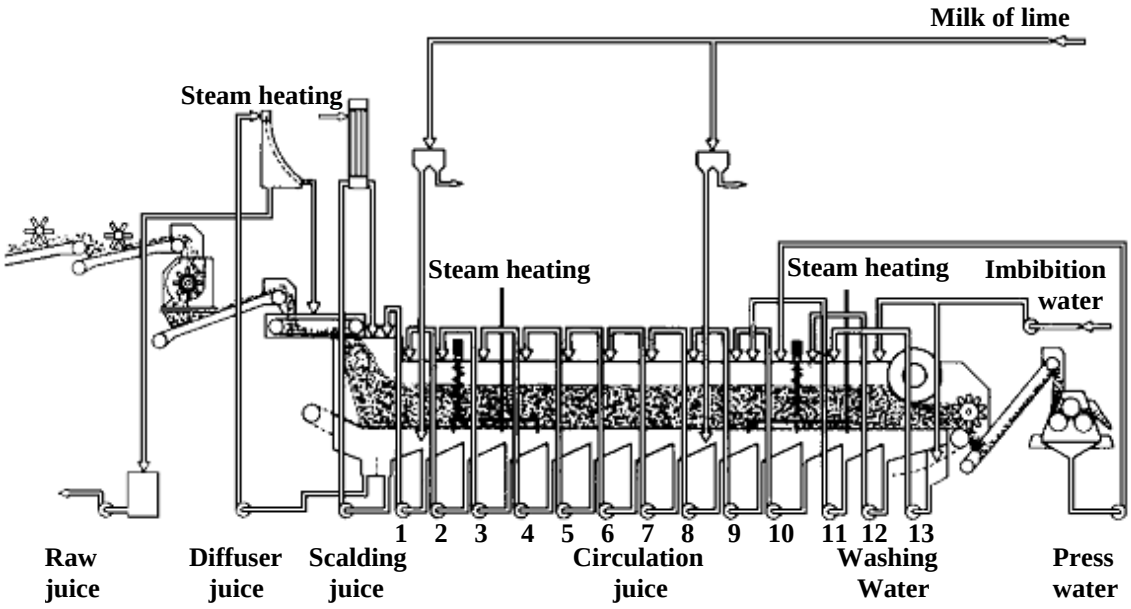


Figure 1.7 Diagram of a B.M.A. cane diffuser (Hugot, 1986).

Although sugar recovery is higher in diffusers (~98%) than in roller mills (92 – 96%), roller mills are more popular because they are easier to operate and the cane retention time is a lot shorter (i.e., 3 – 6 minutes, compared to 50 – 60 minutes in diffusers (Hugot, 1986)). This is very important to avoid losses during unexpected shut downs for maintenance and repairs.

The highest energy demand in sugarcane processing is in the evaporators. To meet such energy requirements, sugarcane-processing plants burn the bagasse produced from the sugar extraction operation. Some large processing plants also use cogeneration to produce power for other power-requiring applications, and sometimes to provide

electric energy to the regional electrical grid. The bagasse is generally sufficient to supply all the steam necessary to meet all the energy demands (Hugot, 1986).

I.3 Impact of the Three New Technologies on the Sugarcane Industry

The three technologies can improve the efficiency of the sugarcane industry as follows:

1) Vapor-compression evaporation – In conventional sugar mills, the amount of water used in sugar extraction is limited. Although more imbibing water would allow a more extensive extraction, excessive amounts dilute the product and increase the duty and size of the evaporators. Low amounts of imbibing water requires the use of massive roller mills that savagely crush the cane to squeeze the juice or the use of a very high number of stages in a diffusion system (Hugot, 1986; Payne, 1991). The high efficiency of the vapor-compression system should allow the use of more imbibing water, thus allowing a better and faster sugar extraction.
2) Efficient lime regeneration – Because conventional lime is expensive, the amount employed must be limited. However, the efficient stationary lime kiln from Altex Technologies Corp. should allow more lime use.
3) MixAlco process – Combustion of bagasse to obtain energy does not add as much value as the production of chemicals and fuels via the MixAlco process (Holtzapple et al., 1999).

To take advantage of these opportunities we proceeded to revise and improve the conventional sugarcane process in three different ways: sugarcane juice extraction, sugarcane juice preservation, and long-term lime pretreatment of bagasse to increase biological digestibility.

I.4 First Approach

The first approach to harnessing the impacts from these new technologies would be to perform the sugarcane juice extraction, sugarcane juice preservation, and lime pretreatment of bagasse all at the same time (Figure 1.8). Shredded fresh sugarcane and the appropriate amount of lime would be mixed and formed into a pile. The pile would be equipped with piping on the top. Using this pipe, the pile would be flooded intermittently in stages. Because of the high pH, the sugars should be preserved. At the same time, because of the periodic flooding, the sugars could be extracted and processed during the year for crystallized sugar production. The fiber (bagasse) would also be pretreated and rendered more digestible for biological digestion to the produce fuels and chemicals.

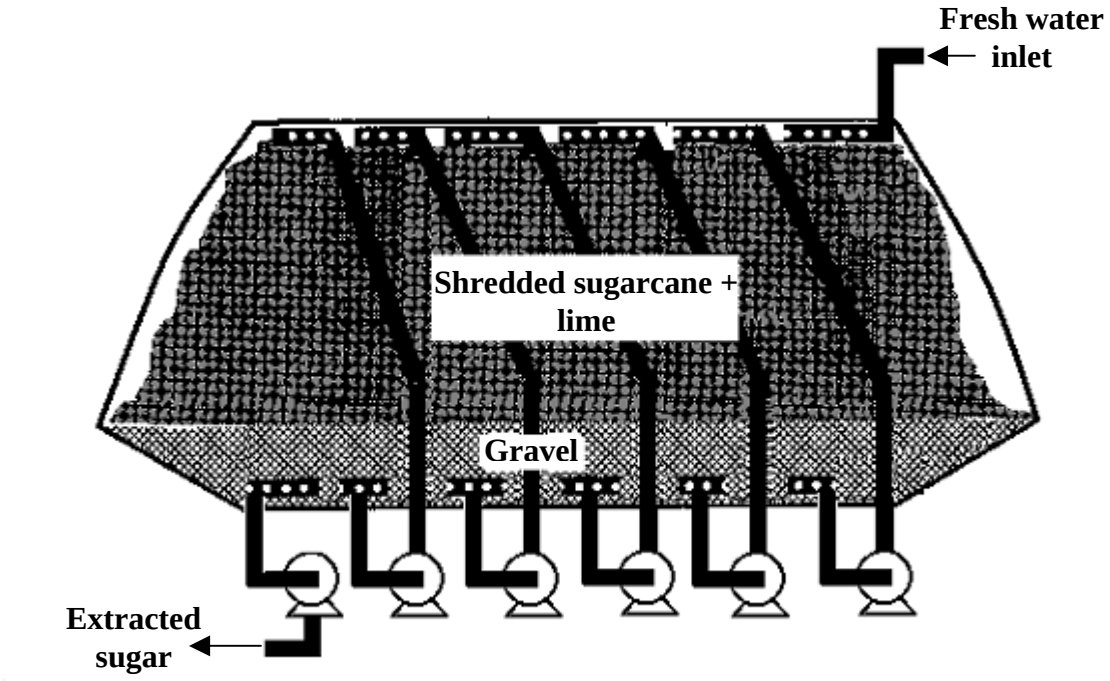


Figure 1.8 First approach.

Laboratory- and pilot-scale studies were performed to test this system. Laboratory studies were done with shredded sugarcane in PVC columns to simulate pile

conditions. Various lime loadings were implemented (i.e., 0.15, 0.2, 0.25, 0.3, 0.4 and 0.50 g $Ca(OH)_2$/g dry cane). At the beginning of the experiment, the columns were flooded with water and it was allowed to percolate. The liquid was collected in appropriate containers and this same liquid was poured on top to re-flood the column. This flooding and percolation procedure was done at different frequencies among the columns (i.e., once a day, once every other day, every four days, and every seven days). The preservation was intended to take place for a year. As time passed, and the flooding procedure continued, microbial activity took over certain columns, at which point the pH decreased drastically. Figure 1.9 illustrates the time at which the specified columns turned and microbial activity took over. The only column that survived one year was the column with the lime loading of 0.5 g $Ca(OH)_2$/g dry cane with flooding performed everyday. Such high flooding frequency and high lime loading makes the process unsuitable and economically prohibitive.

Preservation/pretreatment/extraction testing at pilot scale was done using piles of sweet sorghum and then of sugarcane. In both cases, unsuccessful results were obtained. The studies showed the system was very unstable. Even with high lime loadings, the sugar could not be preserved for long and microbial activity took over within days.

The literature also warns of the difficulties of sugar extraction in alkaline conditions, especially for such a long time, because it increases the amount of juice impurities such as gums and pectin, which under normal conditions would stay with the fiber (Brüniche-Olsen, 1966).

At this point, we made the decision to split the process and do the juice extraction, preservation, and pretreatment of bagasse separately.

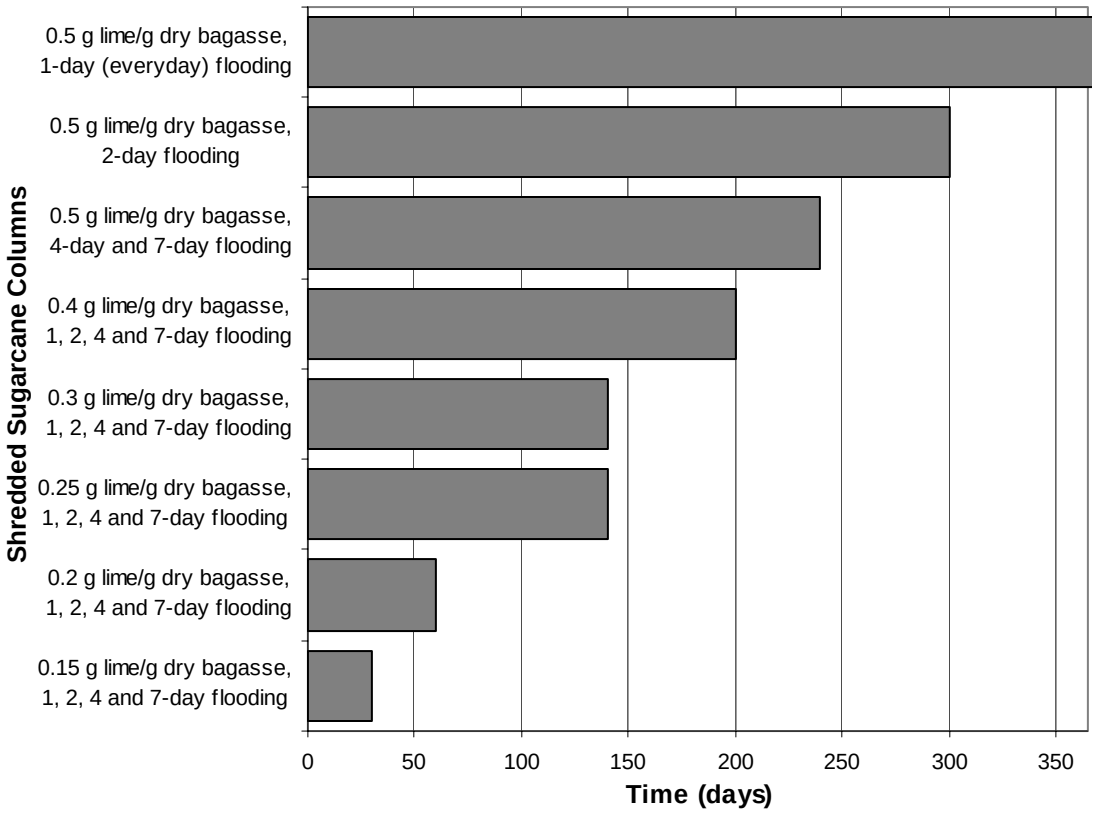


Figure 1.9 Approximate time at which microbial activity took over for the specified columns.

CHAPTER II

SUGARCANE JUICE EXTRACTION

II.1 Introduction

The high-efficiency evaporation system allows more imbibing water to be employed, making extraction easier in the following respects:

1) The extraction driving force is increased. Sugarcane extraction is a mass transfer process; therefore, a higher concentration difference between the cell interior and the extracting solvent increases speed.
2) The presence of more water facilitates homogeneous mixing, which allows equilibrium between the cell interior and the extractive phase to be achieved more easily and faster, as illustrated in Ponchon-Savarit diagrams (Figures 2.1 and 2.2).

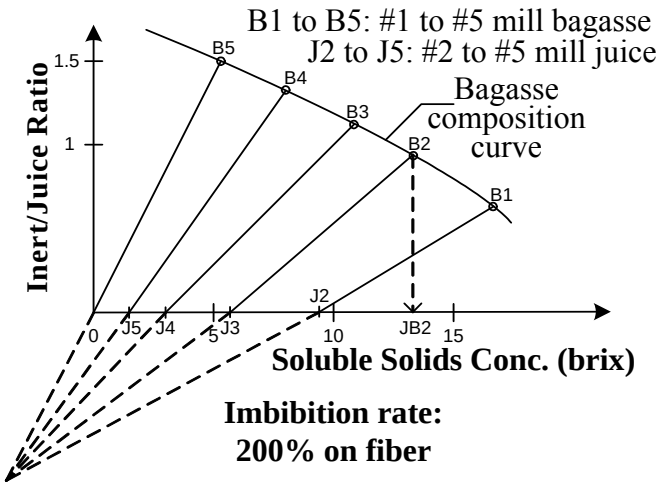


Figure 2.1 Ponchon-Savarit diagram for a tandem of five roller mills (adapted from Walsh, 2001).

Figure 2.1 shows the Ponchon-Savarit diagram for sugar extraction in a five-roller-mill tandem, as it occurs in an actual process. Within a stage, mixing inefficiencies cause the brix (soluble solid concentration in % w/w) of the juice within the exiting bagasse to be much higher than the exiting extractant. Figure 2.2 shows the Ponchon-Savarit diagram of the ideal case for sugar extraction with perfect mixing. If 100% mixing efficiency could be attained, the liquid in the bagasse from roller mill #2 (B'2) would have the same brix composition as the juice leaving the same roller mill (J2). It can be seen that the desired bagasse final brix composition is overshot with only three roller mills (two stages).

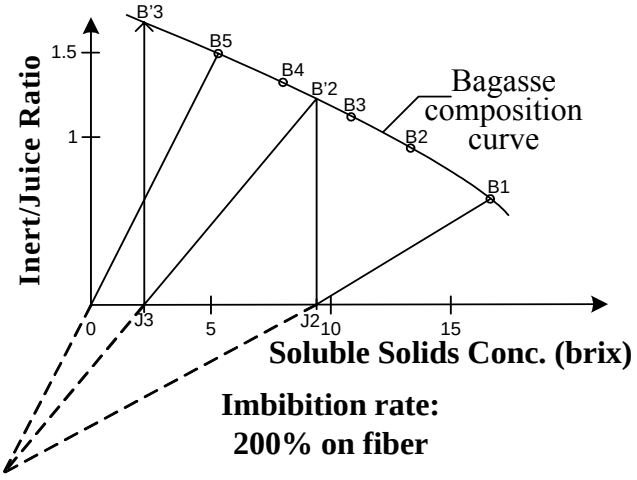


Figure 2.2 Ponchon-Savarit diagram for 100% mixing efficiency (adapted from Walsh, 2001).

Roller mill *trains* use a lot of energy to crush, shear, and squeeze juice from cane; therefore, the power consumption of these massive units is considerable and their maintenance costs are also high (Hugot, 1986; Chen and Chou, 1993). Also, they are inefficient because, although the bagasse is deprived of its juice when the pressure is first applied, the juice re-absorbs the moment the bagasse is released (Smart, 1969; Hugot, 1986). Diffusion systems, although cheaper than milling, tend to be very long

due to the high number of stages required for extraction (up to 18 stages) and they require energy for pumping, conveying, and juice heating.

What has been proposed to improve the extraction process is a "happy medium" between milling and diffusion (lixiviation), so that the energy consumption is less than in milling and the stages are fewer than in diffusion. Figure 2.3 shows a diagram of the proposed process. A series of tanks or vats are arranged in a cascade. Each tank has a screw-press conveyor, which moves solids opposite to the liquid flow. Cane, finely shredded and probably pre-crushed to rupture cells (high preparation index), is delivered to the system. In each stage, extractive solvent and liquid-saturated bagasse, known as *megasse*, are thoroughly mixed to attain brix composition equilibrium. The solids are moved by the screw-press conveyor to the next stage. As the solids are conveyed to the next stage, the screw-press conveyor also applies a light pressure to express some of the liquid embedded in the fiber into the present stage. This system is more energy efficient than a roller mill tandem because it only applies a light squeeze to the material and the maintenance costs are reduced because the excessive pressure and shear forces of the roller mills are avoided. In comparison with the diffusion system, it does not use as many stages, which decreases its length and the residence time of the materials in the process, which may avoid the need for juice heating used to control microbes. Based on these considerations, Figure 2.4 shows a sketch of the expected cost/response curve. At a constant extraction performance and capacity, there exists a minimum cost, caused by the decreasing expenses due to the decreasing number of stages (towards the left) and the decreasing applied pressure (towards the right).

Final dewatering of the megasse (to a moisture content of ~50%) will be necessary if the material is to be used directly as fuel; however, if the material is to be used in the MixAlco process (Chapter I), final dewatering may not be required. Nonetheless, it is important to consider that bagasse with a high moisture content is difficult to handle.

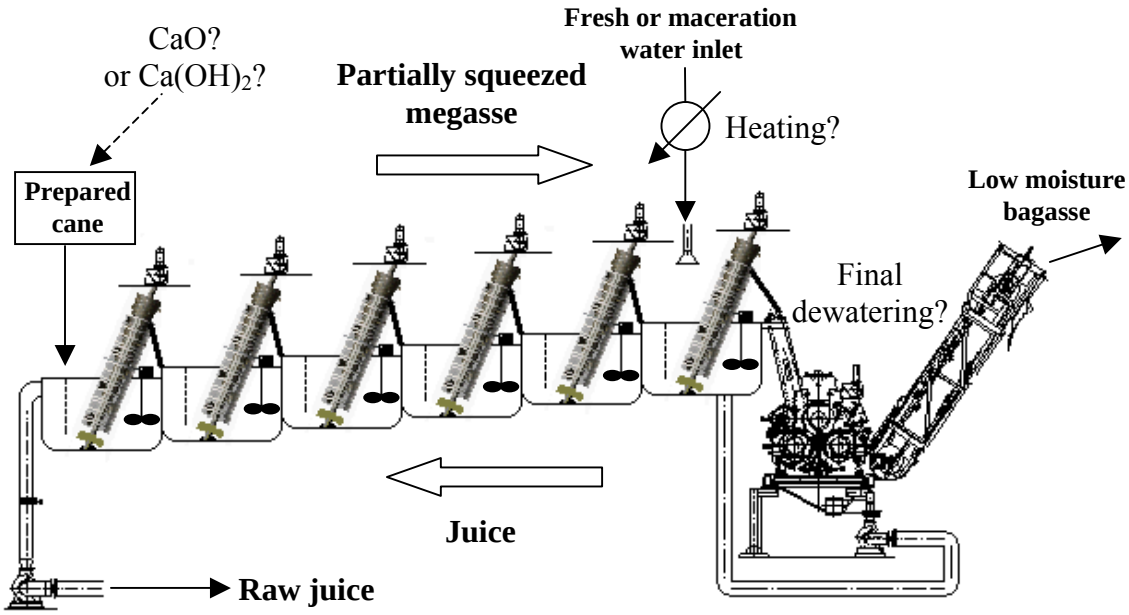


Figure 2.3 Countercurrent diffusion system with light squeeze of solids.

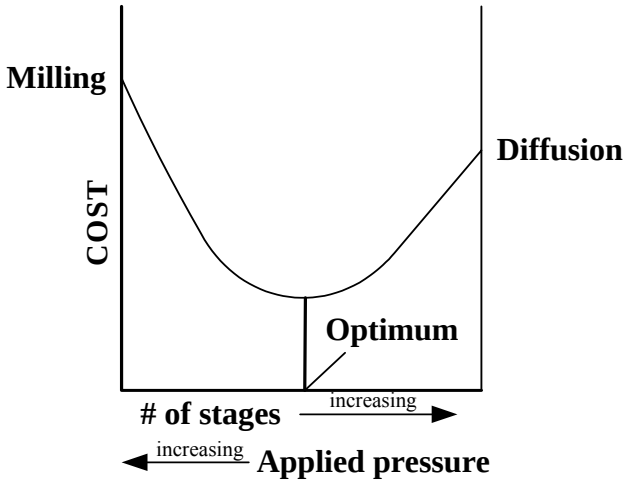


Figure 2.4 Sketch of the expected cost at constant sugar recovery and capacity.

The addition of lime to the extraction process might be advantageous because it controls both microbial activity and the inversion of sucrose to fructose and glucose, which occurs at pH lower than 6.0 (Chen and Chou, 1993). Also, it precipitates impurities from the juice, which remain in the fibers (Ponant et al., 1988). In

conventional diffusion systems, liming is only done to avoid inversion, and the pH is never allowed to go above 7.0 (Hugot, 1986). Sugar extraction in alkaline medium (pH higher than 7.0) attained by adding lime, has been reported in the literature, particularly for extracting sugar from sugarbeets, but the results are contradictive (Accorsi and Zama, 1993; Broughton et al., 1992; Brüniche-Olsen, 1962; Ponant et al., 1988; Stanek and Pavlas, 1938). Heat is necessary in the diffusion process to control microbial activity (Walsh, 2001; Brüniche-Olsen, 1966) and to make unbroken cells permeable to sucrose molecules by denaturing their protoplasm lining, action known as "killing the cells." A temperature of at least 70^{o}C is necessary to make unbroken cells permeable (Brüniche-Olsen, 1962). However, Walsh (2001) suggests that sugar extraction from well-prepared sugarcane (finely shredded and perhaps pre-crushed to achieve a high degree of cell rupture) is almost negligibly enhanced by temperature and that it could be performed at ambient temperature if the residence time of the material in the diffuser could be reduced to avoid microbial growth. More studies on alkaline extraction and the necessity to heat should be performed in the future when a fully operational process is implemented.

II.2 Literature Review

The characteristics of the proposed sugar extraction system lie between milling and diffusion, but they are closer to milling because the extraction is attained by mixing/separation, whereas diffusion should ideally occur by the mass transfer phenomenon known as displacement (Walsh, 2001). Vázquez (1928) patented a sugar extraction system, which employs mixing/separation with better mixing efficiency than roller mills by using an agitator. It is also a countercurrent extraction; however, a simple screen is used to separate the solids without any dewatering aid.

Screw presses have been used for almost a century (Egenes and Helle, 1995) and are standard dewatering equipment for many applications such as paper pulp (Egenes et

al., 1995), polymers (Kougiya, 1999), rubbers (Kougiya et al., 1996) and vegetable oil extraction (Starrett, 1967). In the sugarcane industry, screw presses have been used as dewatering aids since the beginning of the 1960's (Starrett, 1967) and became popular by the early 1970's (Cordovez, 1970). From the start, their advantages over traditional roller mills were obvious. They steadily dewatered bagasse to a fixed moisture content regardless of the bagasse moisture content at the inlet. Unlike roller mills, the extracted juice did not re-absorbed, maintenance costs were a lot lower, and the capital investment of a press was 2/3 that of a roller mill of similar capacity (Smart, 1969; Hugot, 1986). Because they were used to replace roller mills to obtain maximum dewatering capacity, the screw presses saw high abrasive stresses. They required frequent maintenance, which increased plant down-time; thus, their use was discontinued. The applied pressure should be kept below 15 kg_f/cm^2 (213 psi or 1470 kPa); above this, the resistance of the megasse increases rapidly (Leibig, 1995), increasing the power requirement exponentially and the wear and tear of the equipment. For comparison, a conventional roller mill operates in the 70 – 300 kg_f/cm^2 (995 – 4270 psi or 6865 – 29420 kPa) range (Hugot, 1986). This exposes an inefficiency of roller mills because they must spend a lot of their energy "fighting" bagasse resistance rather than dewatering it. Starrett (1967) performed power consumption studies of the dewatering of sugarcane bagasse with screw presses, but, as mentioned, his conditions were different than ours because he was trying to attain maximum dewatering capacity. In contrast, in our proposed process, only light pressure is applied.

To extract sugar from sugarcane, the De danske Sukkerfabrikker (D.d.S.) slope diffuser (Figure 2.5) (Brüniche-Olsen, 1962) has been designed to aid the usual surface extraction by "frequent, repeated light compressions of the cane, which permits re-absorption of juice somewhat less concentrated than that squeezed out." This is accomplished by using a long twin-screw conveyor (S.C.). The S.C. carries the cane upwards through the diffuser, which is designed as a sloping vessel and fits around the two screws, while the juice flows downwards by gravity. The screws rotate in opposite directions and the cane gently slides around the screw shafts as it is conveyed. Each

time the cane rotates, it is squeezed in the narrow space between the shafts of the intermeshing screws. The advantage of this system is that it does not depend on cane preparation; shredded/crushed and shredded-only cane yield approximately the same extraction (Brüniche-Olsen, 1966). These studies confirm the effectiveness of the applied gentle squeeze in sugar extraction. A disadvantage of this diffuser is the long residence time of the material in the system (Schiweck and Clarke, 1994), which makes heating imperative to avoid microbial activity.

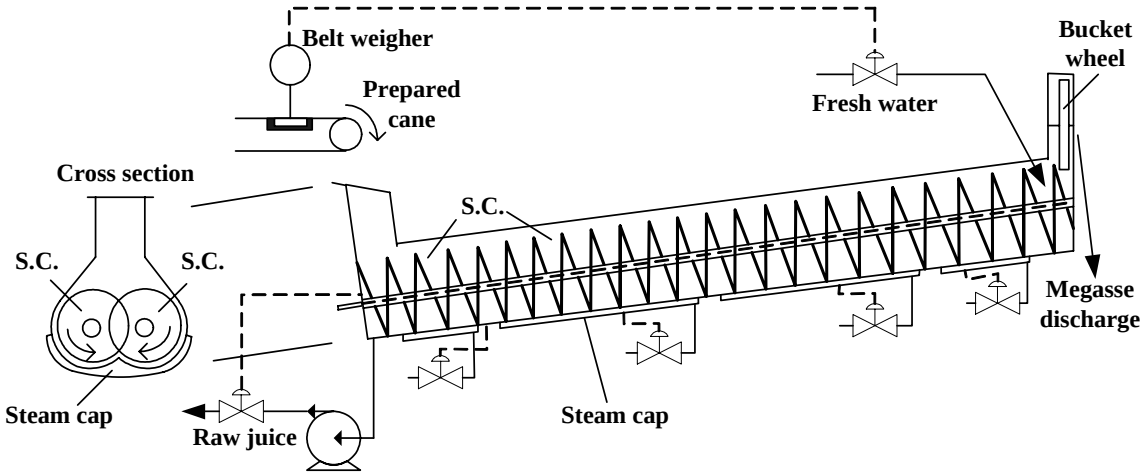


Figure 2.5 Schematic of the D.d.S. slope diffuser
(adapted from Brüniche-Olsen, 1962).

Leibig (1995; 2001) invented the Low Pressure Extraction System (LPE-System), which operates on the same principles as our proposed process by finding a "happy medium" between milling and diffusion to minimize cost. The dewatering units in the LPE-system consist of roller pairs lying one on top of the other, which interact in a manner similar to conventional mills to apply light pressure to the megasse as it passes between them. To overcome the limitation of juice re-absorption in conventional roller mills, the lower roll in the extraction units of the LPE-System is perforated with drainage canals. The system uses four or five of these units in series to allow conventional countercurrent operation of the cane and imbibing fluid. Figure 2.6 shows the details of one of the units in one of the stages of the system. One of the observations they make

about this system is the necessity for attaining a high preparation index for the cane before it enters the process, which is required to expose the cell contents to the imbibing fluid. Plants in Brazil, Mexico, and India employ this system and have yielded promising results. However, some limitations of this system are the fact that mixing inefficiencies cannot be overcome. They must supplement maceration with lixiviation, as in a conventional diffuser, at the front of the process to improve extraction or they have to increase the number of stages. Also the roller pairs cannot handle throughputs as large as those handled by screw presses of similar size; thus, their initial investment will be higher.

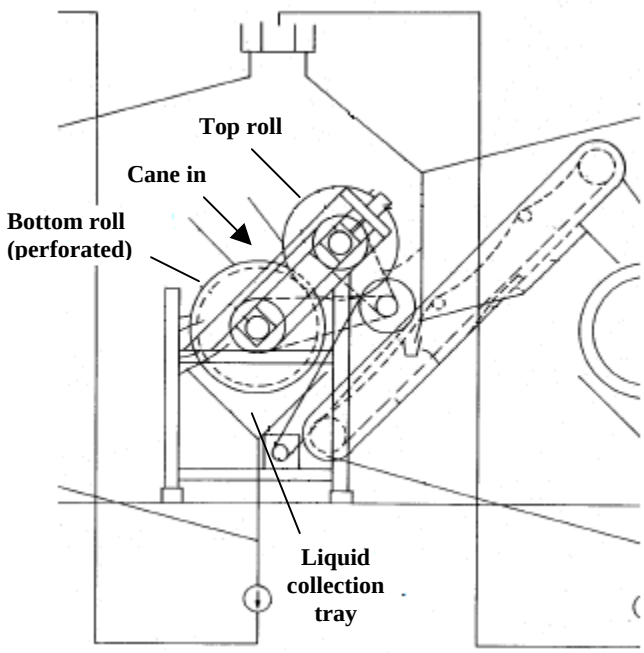


Figure 2.6 Details of one unit of the LPE-system (adapted from Leibig, 1987).

II.3 Experimental Methods

II.3.1 Objective

The goal of the present study was to test the performance of a pilot-scale screw-press conveyor on bagasse dewatering and to develop a relationship between dewatering capability (% moisture of megasse), dry fiber (lb/h of fiber processed), and power consumption (hp). These parameters should allow a preliminary evaluation of the process.

II.3.2 Equipment Description

A 6-ft-long carbon-steel screw-press conveyor (Screw conveyor Corporation, Winona MS) was covered with a high-resistance epoxy paint to decrease friction and corrosion. It was equipped with a perforated outer casing. The screw-press conveyor, as do many conventional screw presses, accomplished the squeezing of the material by the action of its increasing shaft diameter along its length from the inlet to the outlet side, against the perforated outer casing. As the squeezing occurs, the liquid is allowed to escape through the perforations of the outer casing. The flight diameter, on the other hand, remained constant and it was only slightly smaller than the inner diameter of the perforated outer casing so that the screw-press conveyor fits snugly inside of it all along its length. This feature is important to efficiently convey the material through the channels of the screw towards the outlet. The pitch length was also constant.

Because the screw-press conveyor was set up vertically, the inlet (i.e., the part with the smallest diameter) was at the bottom. Figure 2.7 shows the details and dimensions of the screw-press conveyor and the perforated outer casing.

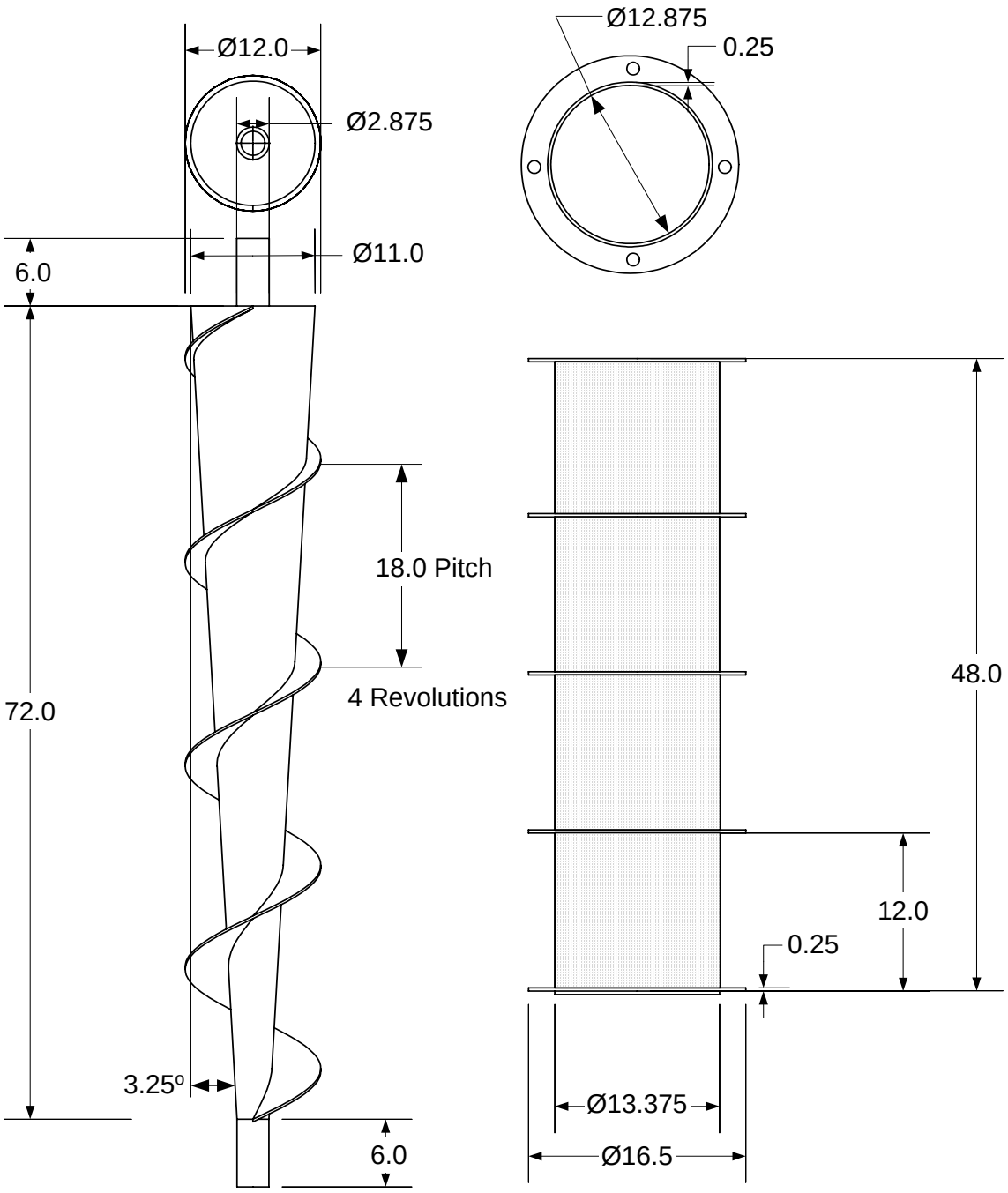


Figure 2.7 Details and dimensions (in inches) of the screw-press conveyor and the perforated outer casing.

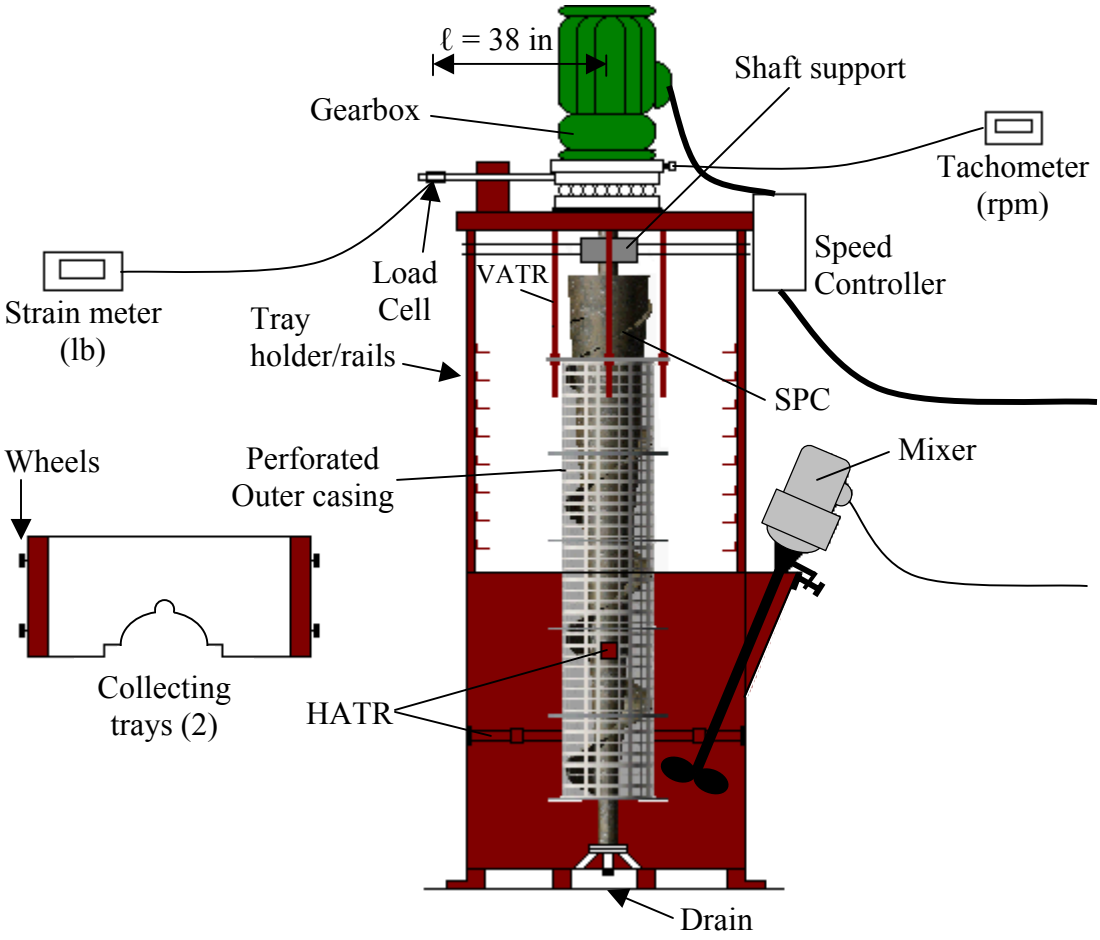


Figure 2.8 Diagram of the screw-press conveyor apparatus.

Figure 2.8 shows a diagram of the screw-press conveyor system after its installation. The screw-press conveyor (SPC) and the perforated outer casing were fitted inside a tank, which was placed on a metal pedestal. On top of this apparatus sat a three-phase 5-hp electrical motor (type SK100 LA/4, Nord Gear Corp, Waunakee WI) equipped with a gearbox (1/20 gear reduction ratio, type 572F-100 L/40, Nord Gear Corp, Waunakee WI) and a speed controller (J7 Drive,Yaskawa Electric America Inc., New Berlin WI), which provided the mechanical work for the screw-press conveyor. The motor rested on a thrust bearing, which allowed it to rotate freely to measure torque. Torque was measured using a load cell (LC100, Omega Eng., Stamford CT) that was attached to the tips of two rods. One of the rods was attached to the thrust bearing and

the other rod was attached to the metal pedestal. The rods yielded a 38.0-in-long lever arm (ℓ). The load-cell was connected to a strain meter (DP25B-S, Omega Eng., Stamford CT) from which the resulting force (lb_f) could be read. A magnetic sensor sent signals to a tachometer (AP1000, Electro-sensors Inc, Minnetonka MN) to measure rotational speed (rpm). The power was calculated using the following equation:

$$P = 2\pi\tau\varpi \qquad = 2\pi F\ell\varpi \qquad \text{(SI units)}$$

$$= \frac{2}{3.3\times10^4}\pi\tau\varpi = \frac{2}{3.3\times10^4}\pi F\ell\varpi \quad \text{(English units)} \qquad (2.1)$$

where the English units follow:

P	=	Power, hp
τ	=	Torque, $lb_f \cdot$ ft
ϖ	=	Rotational speed, rpm
F	=	Force recorded from strain meter, lb_f
ℓ	=	Length of the arm that anchors the motor, ft

To prevent misalignments, a support was implemented for the shaft that connected the motor to the screw-press conveyor. This support consisted of two blocks that embraced the shaft, and were held in the proper place by threaded rods, which could be adjusted accordingly. The shaft support was equipped with a grease fitting to provide lubrication.

To ensure alignment with the screw-press conveyor, the perforated outer casing was supported vertically by four threaded rods, which also allowed for vertical adjustment (VATR) and horizontally by six threaded rods (HATR) (Figure 2.8), which permitted horizontal adjustment as well.

Two collecting trays that fitted around the perforated casing were used to capture samples of the processed material. These trays were equipped with wheels so that they

could be easily and quickly pushed in to start collecting the sample and pulled out to stop. The collecting trays rested on the tray holders/rails (Figure 2.8) and could be removed to obtain the weight of its contents on an appropriate weighing scale.

To keep perfectly mixed conditions in the tank at all times, a 1/3-hp portable mixer (PG-13, Chemineer Inc, Dayton, OH) was used, which was mounted on one side of the tank where an extension had been rigged. The mixer came equipped with a gearbox, which allowed it to operate at a constant speed of 430 rpm. Figures 2.9 to 2.14 show various photographs of the equipment.

II.3.3 Methodology

For these preliminary studies, only water and exhausted bagasse (no sugars) were used. The throughput was controlled by increasing or decreasing the screw-press conveyor rotational speed. The steady-state throughput of the screw-press conveyor was measured by timing the amount of megasse that was collected in the trays. The collecting trays could be positioned at different heights according to the tray holder/rails used to support them. The moisture content depends on the position of the perforated outer casing, which could be moved upwards to restrict the flow or downwards to loosen it. The megasse (wet bagasse) collected in the trays was squeezed to remove loosely held water, and the resulting bagasse was collected in a 28 × 30 in well-sealed Ziplock bag (14545T23, McMaster-Carr, Atlanta GA). The samples were kept in a walk-in cooler at 4^{o}C until analyzed for moisture. The moisture content was determined in the laboratory by drying in a 105^{o}C oven until constant mass was achieved (2 to 3 days). The moisture content of the megasse is the difference between weight of the megasse collected in the trays and the weight of the dry bagasse obtained after drying in the oven at 105^{o}C divided by the weight of the megasse collected in the trays. Each data set relates moisture content and throughput (amount of cane processed) to power consumption.

Figure 2.9 Photograph of screw-press conveyor system.

Figure 2.10 Photograph of the motor and torque-measuring system.

Figure 2.11 Photograph showing details of the screw-press conveyor flight, the tray holder/rails for the collecting trays, and the shaft support.

Figure 2.12 Photograph of inside the tank while being filled with water.

Figure 2.13 Photograph of the screw-press conveyor during operation.

Figure 2.14 Photograph of inside the tank during operation.

Because of the high degree of fluctuation in the system, a steady torque reading could not be attained. A digital camera was used to film the reading of the strain meter during the time the megasse was collected. These filmed values were later averaged to obtain the torque parameter for each data point.

II.3.4 Computational Approach

Figure 2.15 shows a diagram of one stage of the extraction process. Assuming 100% mixing efficiency and knowing the relationship between liquid fraction in the megasse and power consumption (operating cost), the following equations may be developed to simulate the system and optimize parameters (derivation in Appendix A):

$$C_{N+1} = \frac{\frac{L_N}{1-L_N} S_0 C_N + F_N C_N - \frac{L_{N-1}}{1-L_{N-1}} S_0 C_{N-1}}{\frac{L_N}{1-L_N} S_0 - \frac{L_{N-1}}{1-L_{N-1}} S_0 + F_N} \tag{2.2}$$

$$F_{N+1} = F_N + \frac{L_N}{(1-L_N)} S_0 - \frac{L_{N-1}}{(1-L_{N-1})} S_0 \tag{2.3}$$

where

L_N	=	Liquid mass fraction in megasse attained in the *N*th stage, lb H_2O + soluble solids/lb total megasse
L_{N-1}	=	Liquid mass fraction in megasse attained in the *N*-1th stage, lb H_2O + soluble solids/lb total megasse
C_N	=	Soluble solids mass fraction in the *N*th stage, lb soluble solids/lb total liquid
C_{N-1}	=	Soluble solids mass fraction in the *N*-1th stage, lb soluble solids/lb total liquid
F_N	=	Mass flow rate of juice coming out of the *N*th stage, lb/h
S_0	=	Dry fiber mass flow rate as fed to the system, lb/h
C_{N+1}	=	Soluble solids mass fraction in the *N*+1th stage, lb soluble solids/lb total liquid
F_{N+1}	=	Mass flow rate of juice coming out of the *N*+1th stage, lb/h

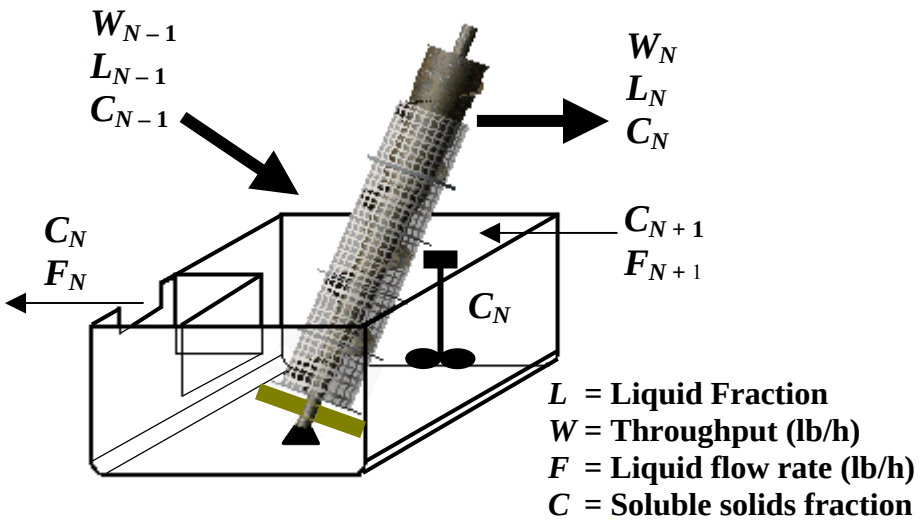


Figure 2.15 Diagram of one stage of the extraction process.

As the applied pressure increases, the liquid fraction in the bagasse decreases and the number of required stages also decreases, thereby reducing initial investment. However, as the moisture decreases the power required to operate the screw-press conveyors increases, thus increasing operating costs.

The starting (i.e., S_0, L_0, C_0, F_0, $C_{\text{imbibition}} = C_{\text{last stage+1}}$) and target values (i.e., C_1, $C_{\text{last stage}}$) must be specified. From the overall material balance, the value for F_1, and $F_{\text{imbibition}} = F_{\text{last stage+1}}$ must be obtained. In addition, the relationship between power consumption (operating cost), moisture content, and throughput, must also be given. Then, the optimal number of stages and optimal moisture content for each stage that would yield the lowest cost can be found through an optimization procedure. It must be noted that if bagasse is to be burned for fuel, then it is necessary to decrease the moisture content of the bagasse exiting the system to about 50%. This parameter ($L_{\text{last stage}}$) must also be specified.

It is important to note that the liquid fraction in the megasse includes the water plus soluble solids. In the case of exhausted bagasse, as in our studies, this value is virtually equal to the moisture content as determined by drying. If fresh cane had been

used instead of exhausted bagasse, the material would have been extensively washed to rid it of the soluble solids prior to drying.

II.4 Results and Discussion

Attempts to operate the screw-press conveyor with high flow restriction settings failed. The material accumulated inside the screw-press conveyor without ever getting to steady state. This is a common phenomenon in screw presses that is normally fixed by implementing flight interrupters (Figure 2.16). Flight interrupters are pins mounted to the housing (i.e., the perforated outer casing) that keep the material from simply rotating inside the screw-press due to slippage. The screw-press conveyor must be modified in this manner before more data can be obtained.

The perforated outer casing was lowered as much as possible to have the lowest possible flow restriction and a total of 29 data sets were taken at only this setting at three different rotational speeds (i.e., 40, 60 and 80 rpm).

Various amounts of bagasse and water were added into the tank to vary the loading to the screw-press conveyor. As the bagasse concentration in the tank increased, the load increased and the screw-press conveyor processed more material.

Three different bagasse concentrations in the tank were studied: ~ 4% (96% moisture), ~ 6% (94% moisture) and ~ 8% (92% moisture).

II.4.1 Parameter Correlations

The correlation between dry fiber throughput (lb dry/h) and power is shown in Figure 2.17.

The relationship was found to have an exponential response with the following equation derived from the regression:

$$S = k \cdot e^{9.20 \pm 0.48 \cdot P} \tag{2.4}$$

where

S = Dry fiber throughput, dry lb/h

P = Power, hp

k = Exponential term intercept, $e^{3.54 \pm 0.11} = 34.6$

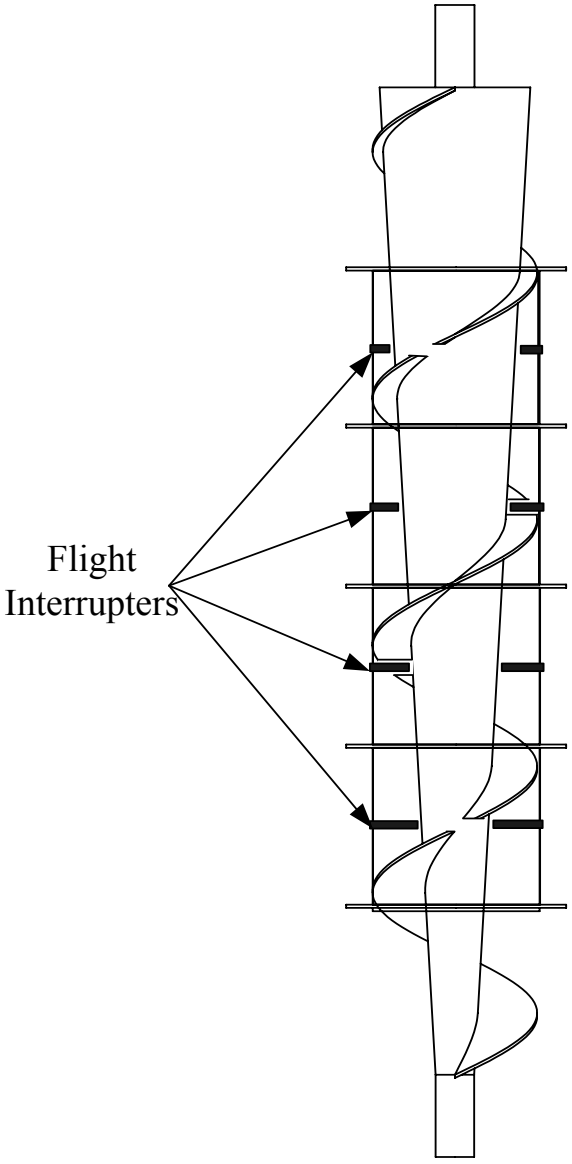


Figure 2.16 Screw-press conveyor equipped with flight interrupters.

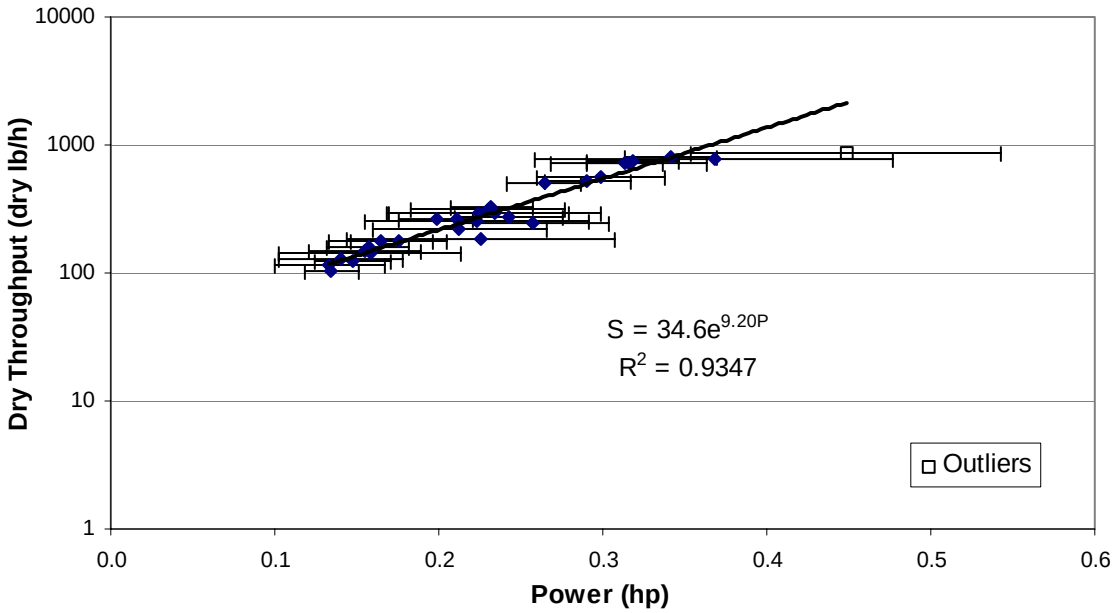


Figure 2.17 Dry fiber throughput as a function of power
(Error bars = ± 1 standard deviation).

The statistical analysis for the significance of this fit and the estimation of the standard error for the regression parameters can be found in Appendix B.

Because it was only possible to operate the screw-press conveyor at one flow-restriction setting, the moisture content attained in the system only varied slightly from 88.7% to 92.2%. This observation agrees with the literature, which suggests that screw presses steadily dewater bagasse to a fixed moisture content regardless of the moisture content at the inlet (Smart, 1969).

In spite of the small variation in moisture content, the ANOVAS of the resulting relationships between moisture content and power and between moisture content and dry throughput showed the regressions to be significant (see statistical analysis in Appendix B).

Figure 2.18 shows the relationship between moisture content and power. It is interesting to note that when flow restriction is fixed, as the final moisture content decreases, so does the required power, which might seem counterintuitive. This can be

explained by the fact that throughput is expressed on a dry basis, but the screw-press conveyor is required to convey water also; thus, less wet material means less water moved and less power consumed (direct relation). If the moisture content was reduced by increasing flow restriction, then a power increase is expected (inverse relation).

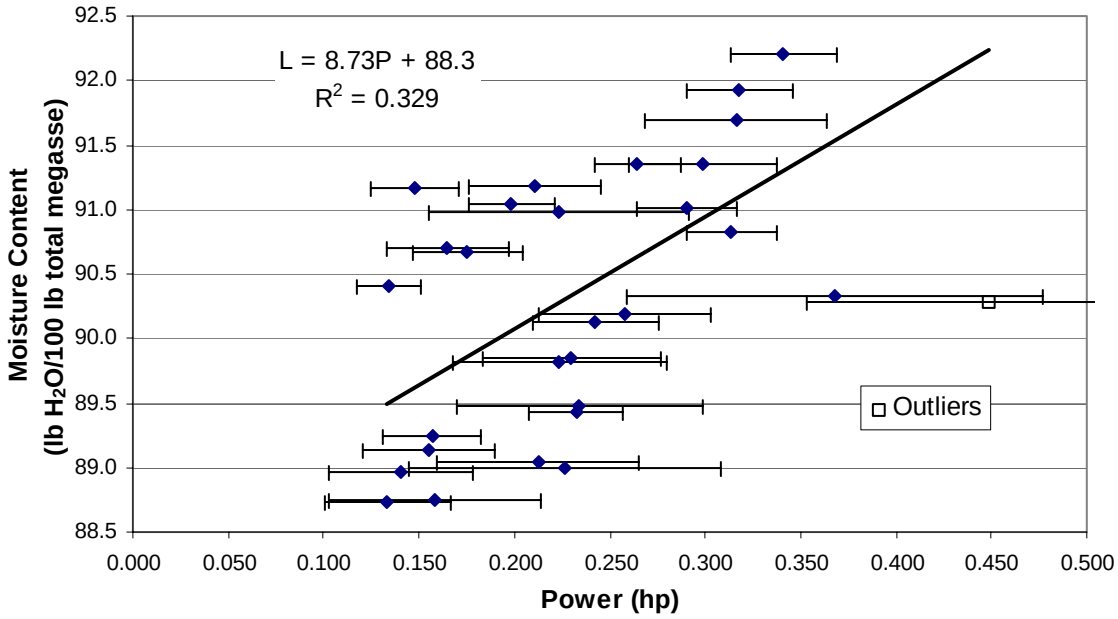


Figure 2.18 Megasse moisture content as function of power
(Error bars = ± 1 standard deviation).

The regression for the relationship between moisture content and power yields the following linear equation:

$$L = 8.73 \pm 2.45 \cdot P + 88.3 \pm 0.6 \qquad (2.5)$$

where

L = Attained liquid or moisture content of the megasse, lb H_2O/100 lb total megasse

P = Power, hp

Figure 2.19 shows the relationship between dry fiber throughput and moisture content. The observed trend at a fixed flow-restriction setting shows there is a direct relation between throughput and moisture content. Although not considerable, as mentioned above, it results because as bagasse concentration in the tank becomes larger (more throughput) the screw-press conveyor dewatering capability decreases slightly (higher attained moisture content).

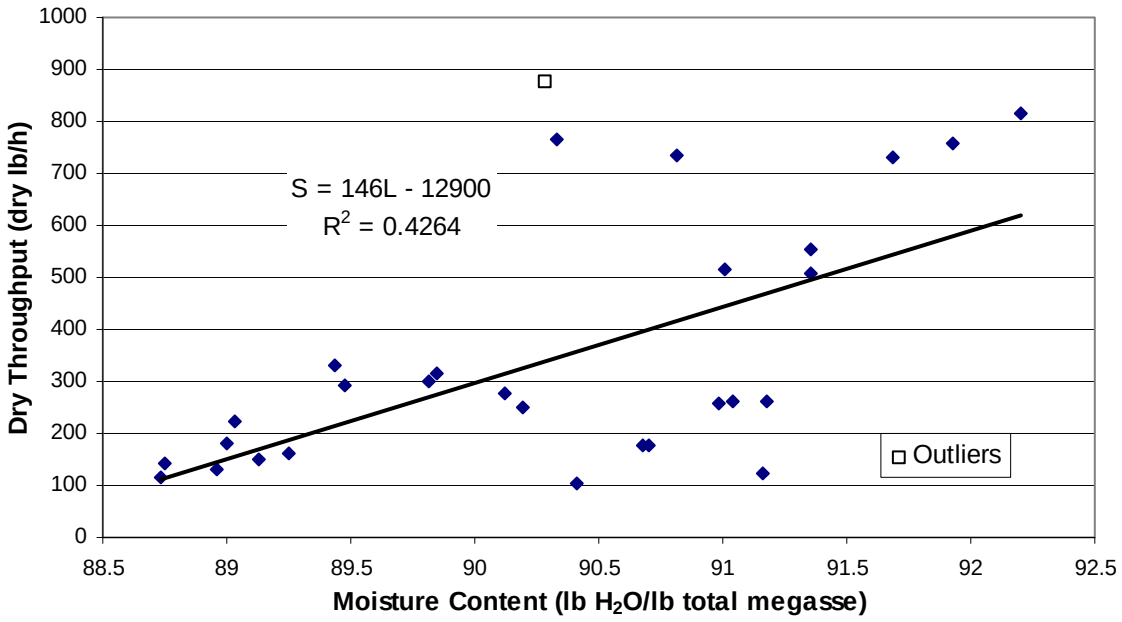


Figure 2.19 Dry fiber throughput as a function of megasse moisture content.

The resulting linear equation for the regression is as follows:

$$S = 146 \pm 33 \cdot L - 12900 \pm 3000 \qquad (2.6)$$

where

S = Dry fiber throughput, dry lb/h

L = Attained liquid or moisture content of the megasse, lb H_2O/100 lb total megasse

II.4.2 Simulation of process conditions

Optimization of a process involves minimizing the initial investment and operating costs. The attained megasse liquid fraction or moisture content affect the initial investment because as the dewatering capability increases (lower liquid or moisture content), the number of required stages needed to achieve the desired extraction will decrease. However, as the liquid fraction in the megasse decreases due to flow restriction, the operating costs increase because the power will be higher. Therefore, to optimize the process, it is necessary to find an optimum number of stages and an optimum liquid fraction attained in the screw-press conveyors that will yield the minimum total cost.

Optimization of the process in these studies was not possible because the screw-press conveyor could not be operated at higher flow-restriction settings; thus, it was not possible to obtain the necessary power and throughput profiles at lower moisture contents. The screw-press conveyor must be modified to handle higher flow restrictions before an optimization can be attempted.

Nonetheless, it was possible to obtain realistic numbers for the parameters, which although not optimized, produce conservatively realistic results of the performance of the process.

Equations 2.2 and 2.3 were implemented in an iterative procedure using a MatLab™ program (Appendix C) to simulate an extractor that would utilize our existing non-optimized pilot-scale screw-press conveyor as dewatering units in several stages as shown in Figure 2.3. As mentioned, these equations assume that equilibrium is achieved in each stage.

II.4.2.1 Process Specifications

For the simulation we assumed the screw-conveyor would process 150 dry fiber lb/h of fresh, well-prepared cane, which is homogeneously 15 lb dry fiber/100 lb cane,

17 lb soluble solids/100 lb cane and 68 lb water/100 lb cane (85 lb liquid/100 lb cane), which are typical values for these parameters.

A summary of specified parameters is shown in Table 2.1. As mentioned before, there are two target parameters in these computations: 1) the brix of the juice exiting the system, which is also the soluble solids mass fraction in Stage 1 (C_1), and 2) the soluble solids mass fraction of the liquid remaining in the bagasse, which is equal to the soluble solids mass fraction in the last stage ($C_{\text{last stage}}$). The former is important because it is inversely related to the duty and size of the boilers and evaporators, whereas the latter determines how effective the extraction is.

The soluble solids mass fraction in the last stage is related to the overall extraction or recovery and other parameters in Table 2.1 by the following equation:

$$C_{\text{last stage}} = C_0\left(1-\frac{E_{\text{overall}}}{100}\right)\left(\frac{L_0}{L_{\text{last stage}}}\right)\left(\frac{1-L_{\text{last stage}}}{1-L_0}\right) \tag{2.7}$$

Given the specified dry fiber mass flow rate (S_0), Equation 2.6 was rearranged to find the moisture content or liquid mass fraction that can be attained under the conditions of the screw-press conveyor studied. For the simulation, this represents the liquid mass fraction attained in the screw-press conveyors in each stage (L_N), which is one of the parameters that should be optimized but we are unable to do so due to the limited data. Equation 2.6 yielded a value for L_N = 88.9 lb liquid/100 lb total megasse.

Table 2.1 Specified parameters and their respective values used in the simulation.

Parameters	Nomenclature	Specified Value
Soluble solids mass fraction in fresh cane liquid fraction	C_0	0.2 lb sol. solids/lb liquid
Soluble solids mass fraction in liquid in Stage 1. This is also the brix of the mixed juice leaving the system	C_1	0.15 lb sol. solids/lb liquid
Mass flow rate of juice pre-extracted from fresh cane prior to entering the system	F_0	0.0 lb/h
Dry fiber mass flow rate as fed to the system	S_0	150 lb/h
Liquid mass fraction in fresh cane prior to entering the system	L_0	0.85 lb liquid/lb cane
Soluble solids mass fraction in the imbibing liquid entering the system at the last stage	$C_{\text{imbibition}} = C_{\text{last stage+1}}$	0 lb sol. solids/lb liquid
Liquid mass fraction in the bagasse or *megasse* leaving the system	$L_{\text{last stage}}$	0.45 lb liquid/lb total bagasse
Liquid mass fraction in the *megasse* attained in Stage N, where $N = 1$ through last stage-1	L_N	88.9 lb liquid/100 lb total megasse*
Overall extraction or recovery	E_{overall}	98 lb sol. solids recovered/100 lb sol. solid in cane

* megasse ≡ soaked bagasse

The specifications call for bagasse to be burned as fuel; therefore, a high-pressure dewatering device must be included to decrease the moisture content of the megasse exiting the last screw-press conveyor to below 50% (50 lb liquid/100 lb total bagasse). One conventional roller mill alone cannot handle such high moisture levels at its inlet to achieve a final moisture content of less than 50%. The alternatives in this case would be to either 1) use two roller mills in series, 2) set the last screw-press conveyor to dewater to a moisture content of about 70% before discharging to the roller mill, 3) employ one

high-pressure screw press, or 4) a cone press (Hugot, 1986). The last two devices can dewater bagasse to moisture contents below 50% even with high-moisture-content feed. Results demonstrate that for bagasse coming out of a diffuser, one mill is not enough, but two mills is excessive; therefore, the first option is not recommended (Chen and Chou, 1993). Regardless of the alternative chosen, the simulation assumes that the last unit (i.e., last vat, mixer and screw-press conveyor in the series) and the high-pressure dewatering device(s) are one single stage as illustrated in Figure 2.20. Thus, the moisture content achieved in the high-pressure device is taken as the moisture content achieved in the last stage ($L_{\text{last stage}}$).

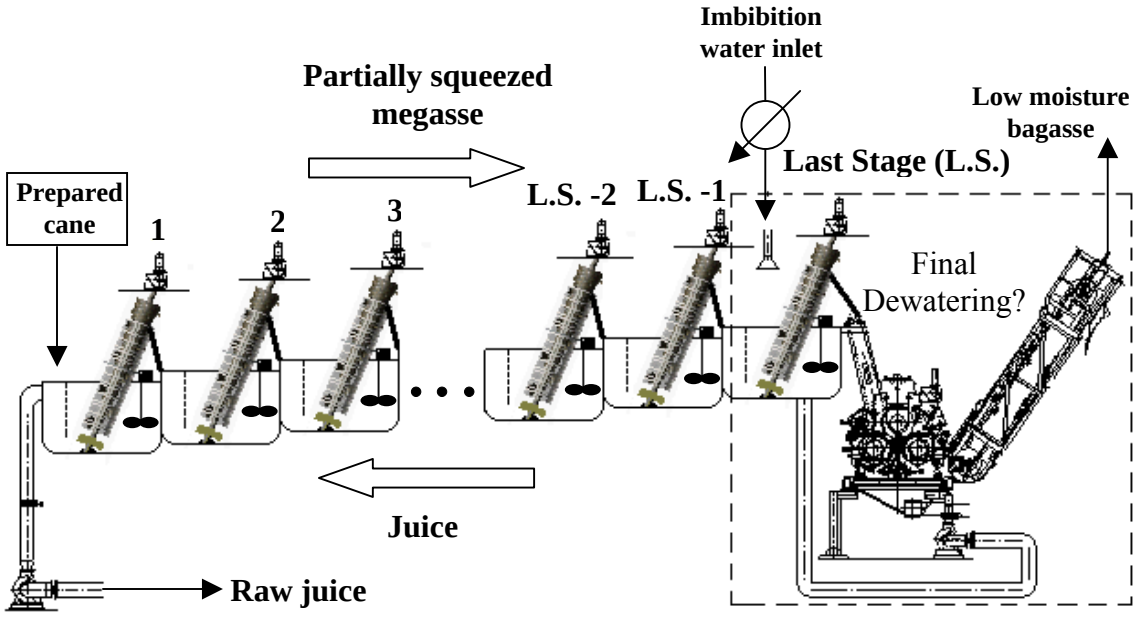


Figure 2.20 Illustration of the simulation conditions.

II.4.2.2 Simulation Results

Table 2.2 shows the simulations results. Because the number or stages is an integer value, the simulation was set to find the minimum number of stages that would give an extraction equal to or higher than the specified overall recovery (E_{overall}). This

number of stages yields an actual overall extraction (E_{actual}), which is slightly higher than $E_{overall}$.

Table 2.2 Summary of simulation results.

Parameters	Nomenclature	Simulation Result
Number of stages required		9
Actual overall recovery, % (lb of soluble solids recovered/100 lb of soluble solids in the cane)	E_{actual}	98.4
Soluble solids mass fraction in specified stage (lb soluble solids/lb liquid)	C_0	0.20*
	C_1	0.15*
	C_2	0.12
	C_3	0.10
	C_4	0.08
	C_5	0.06
	C_6	0.05
	C_7	0.04
	C_8	0.03
	$C_{9,\text{last stage}}$	0.02
Mass flow rate of juice pre-extracted from fresh cane, lb/h	F_0	0.0*
Mass flow rate of juice exiting Stage 1, lb/h	F_1	1110
Mass flow rate of juice coming out of Stage N, where N = 2 through 9, lb/h	F_N	1470
Mass flow rate of imbibing liquid, lb/h	$F_{\text{imbibition}}=F_{\text{last stage+1}}$	388
Imbibition level, % on fiber (lb imbibing liquid/100 lb dry fiber processed)		259

* These values are specifications of the process.

Table 2.3 shows the recovery attained after each stage. The highest recovery occurs in the first stage, and subsequent stages improve recovery only slightly. This

profile is important because it appeals to engineering common sense about the actual number of stages necessary. Thus, the target recovery ($E_{overall}$) in the process specifications was 98% (98 lb soluble solids recovered/100 lb soluble solids fed to the system in fresh cane) but this profile shows that after Stage 8 the extraction attained is already 97.8%, which is very close to our target $E_{overall}$. When 97.7% is specified for $E_{overall}$, the simulation returns an E_{actual} = 98.0% after eight stages, thus meeting our original $E_{overall}$, and confirming that only eight stages are necessary.

Table 2.3 Soluble solids overall recovery after each stage.

Actual overall recovery	Nomenclature	Simulation Result
Stage 1	$E_{actual,1}$	89.2%*
Stage 2	$E_{actual,2}$	91.3%
Stage 3	$E_{actual,3}$	93.0%
Stage 4	$E_{actual,4}$	94.4%
Stage 5	$E_{actual,5}$	95.5%
Stage 6	$E_{actual,6}$	96.5%
Stage 7	$E_{actual,7}$	97.3%
Stage 8	$E_{actual,8}$	97.8%
Stage 9	$E_{actual,9}$	98.4%

* % ≡ lb soluble solids recovered/100 lb soluble solids in cane fed to system

Another important observation is that the typical overall recovery in conventional roller mills is about 94 – 96%. The results in Table 2.3 show that we are already in that range after the 4th stage.

The level of imbibition (260 lb imbibing water/l00 lb dry fiber or 260% on fiber) is in the range used for diffusion (Chen and Chou, 1993), although, in places like South

Africa, the imbibition levels for their diffusers is in the order of 320 – 400% on fiber. The imbibition levels in milling are in the order of 160% on fiber (Chen and Chou, 1993).

The power consumption (*P*) was calculated by rearranging Equation 2.4. At the specified dry fiber mass flow rate (150 lb dry/h), $P = 0.160 \pm 0.02$ hp or 2.13 ± 0.27 hp·h/dry ton of fiber processed (hp/tfh) in each screw-press conveyor.

The accumulative total amount of power required by all eight screw-presses is 1.28 ± 0.16 hp (0.955 ± 0.12 kW) or 17.0 ± 2.1 hp/tfh (14.0 ± 1.7 kW·h/dry metric tonne of fiber).

Starrett (1967), who studied the implementation of screw presses for aggressive dewatering of sugarcane bagasse, suggests that screw presses, as many other types of equipment, require less power per unit of material processed as their capacity increases. He reports that a screw press with a capacity of 20 wet tons of cane/h (tch) uses about 8 hp/tch (53 hp/tfh) to dewater bagasse to a moisture of about 45%. On the other hand, a screw press with a capacity of 125 wet tch could dewater bagasse to the same moisture content using only 5 hp/tch (34 hp/tfh). This value is fairly comparable to the power consumption of a conventional mill, which ranges between about 30 hp/tfh in the first roller mill of the tandem to about 20 hp/tfh in the last one (Hugot, 1986)

The effect of capacity is important because the power consumed by a screw-press conveyor (P=2.13±0.27 hp/tfh) is a conservative number for scale up; as we increase the capacity of the screw-press conveyor, the power consumption per ton of fiber processed will actually decrease to our advantage.

It is encouraging to notice that the cumulative power consumption for all eight screw-press conveyors in our system is less than the power consumed by only one conventional roller mill of a tandem of four or five mills. We achieved this, in spite of reporting numbers from an unoptimized pilot-scale (i.e., low-capacity) screw-press conveyor. Also, the power consumed by the material-conveying equipment in the milling process is not included, an action that is also performed by the screw-press conveyors as they dewater the megasse.

When compared to our unoptimized low-capacity screw-press conveyor, power consumption per extraction unit in the Low Pressure Extraction system (LPE-System) (Leibig, 1987; 1995; 2001) is lower (~ 1.3 hp/tfh or 1.1 kW·h/dry metric tonne of fiber, effective power demand for a tandem of eight units) (Leibig, 1995). Nonetheless, their capacity was almost 50 times larger than ours. In addition, the conveying equipment must be added to these values because the screw-press conveyors also perform this task.

The LPE-system works on the same principles as our process (i.e., lixiviation aided by gentle squeeze) and attains in each of their low-pressure dewatering units, a moisture content (L_N) of about 70% (Leibig, 1995). If this value for L_N is used in the simulation, the number of required stages decreases to four stages with an overall extraction (E_{actual}) of 98.6% (98.6 lb of soluble solids recovered/100 lb of soluble solids in cane fed). The LPE-system yields no more than 97% extraction with five stages and a lixiviator/macerator in the front end or with eight extraction units. Table 2.4 shows the simulation results for the number of required stages and E_{actual} at different values of L_N.

Table 2.4 Simulation results as L_N is varied.

L_N	Number of Required Stages	E_{actual}	E_{actual} before last stage
70.0%	4	98.6%	97.0%
75.0%	5	98.8%	97.8%
80.0%	5	98.1%	96.9%
82.0%	6	98.5%	97.6%
85.0%	7	98.5%	97.8%
87.0%	8	98.5%	97.9%
88.9%	9	98.4%	97.8%

Units: L_N ≡ lb liquid/100 lb total megasse
E_{actual} ≡ lb soluble solids recovered/100 lb soluble solids in cane fed

II.5 Conclusions

The most important outcome from this study is that even though the results were very conservative, they showed that the power consumption in this system is much lower than in conventional roller mills. Further, the number of stages, and thus the residence time of the cane, will also be considerably lower than in diffusion.

The light pressure applied is more energy efficient than an aggressive squeeze as it occurs in roller mills. As mentioned previously, after a certain applied pressure, bagasse resistance increases drastically; thus, in milling a considerable amount of energy is wasted in friction caused by the bagasse. On the other hand, the light squeeze makes countercurrent extraction more efficient because it ensures that the liquid is going in the right direction (i.e., opposite to the solids, as opposed to with the solids).

The intimate contact between the liquid and the cane allows equilibrium to be achieved rapidly, which gives an advantage over roller milling where the mixing efficiency is very low. Also, it is better than diffusion because in these systems, although high mixing efficiencies are attained, stagnant pockets of liquid exist even at high flow rates (Rein, 1971), which is one of the main reasons for requiring long cane residence times in diffusers.

Besides the expected savings in power in comparison to milling, there is also the savings, both in capital and operating costs, in conveying equipment necessary to move the cane, megasse or bagasse, which the screw-press conveyor performs as it dewaters the material.

II.6 Future Work

There is still much to be done to improve this system. Improvements must start with modifying the screw-press conveyor to increase its efficiency.

Firstly, interrupters (Figure 2.16) must be installed so that it can operate at higher restriction settings and develop a power and throughput correlation at lower moisture contents that will allow optimization of the system. Without the interrupters, the material accumulates inside the screw-press conveyor, unable to achieve steady state, until eventually it overloads and shuts itself down.

Another necessary modification is to reduce the pitch length of the screw-press conveyor. Figure 2.21 shows the screw-press conveyor right after operation, being pulled out from the perforated casing for clean-up. Although there is bagasse compaction, only the lower part of the pitch is used. Commonly, efficient screw presses not only have an increasing shaft diameter from inlet to outlet, but also, have a decreasing pitch length. In this way, if cylindrical coordinates are considered, the squeezing not only occurs in the *r* direction, as in these studies, but also in the *z* direction.

The clearance between the outer perforated casing and the flight must be decreased. This change will decrease the power consumption as a function of throughput, because the bagasse will not slip though this crevice as it is being conveyed upwards. It should be noted that this modification will require a more strict alignment of the apparatus.

The way the screw-press conveyor is fed is different from conventional screw presses. The screw-press conveyor works as an auger picking up the bagasse as it randomly finds it in the constantly stirred tank. This causes some irregularities that represent an inefficiency; thus, it was not possible to have a steady torque reading. In the conventional way, on the other hand, material is directly conveyed to the inlet of the press, having a constant feed rate. Studies should be performed to ascertain if these irregularities may be corrected or at least minimized. Parameters to check could be solids loading in the tank, modification of the lower part of the flight so that it may "catch" the shredded cane more efficiently, depth of the tank, placement depth of the screw-press conveyor, mixing profiles, which depend on mixer impeller size, shape, baffles presence and placement, positioning of the mixer, and among others.

Figure 2.21 Photograph of the screw-press after operation being pulled out of the perforated outer casing.

Another necessary parameter is retention time both of the liquid and of the fiber. This parameter allows the sizing of the vats and mixer or agitators to be used. Studies with screw-press conveyors on mixing and equilibrium of sugar extraction with fresh cane must be performed for its determination.

Other factors that must be studied are extraction temperature, the use of lime during extraction, and power consumption and performance of the agitator.

CHAPTER III

SUGARCANE JUICE PRESERVATION

III.1 Introduction

After extracting sugar from cane, sugar crystals (either raw or white) must be produced immediately to avoid juice spoilage. The sugarcane season in the United States lasts 3 to 7 months. The rest of the year, sugarcane-processing plants do not operate except to sell the raw sugar produced during the season. The equipment must be oversized to handle all the juice produced during the harvest season.

To reduce the size of downstream processing equipment, preserving the extracted juice with lime might allow it to be processed during the whole year instead of the few harvest months. The high pH (> 11.0) keeps sucrose from inverting to fructose and glucose, which occurs at low pH, and also inhibits microbial growth, thus preserving the juice. Then, the juice undergoes carbonatation (as it is known in the sugar industry jargon), which consists of carbonating the juice by bubbling carbon dioxide to decrease pH, followed by filtration. This process clarifies the juice and recovers calcium carbonate. A stationary lime kiln developed by Altex Technologies Corp. (Sunnyvale CA), as described in Chapter I, economically produces lime from calcium carbonate. To more efficiently dissolve carbon dioxide in the liquid, a device, such as the modified Isbell agitator (Aldrett Lee, 1999), may be used, especially near neutral pH, where the reaction is mass transfer limited.

Sucrose is a non-reducing sugar; thus, it is very stable in alkaline medium. In contrast, reducing sugars – such as glucose, fructose, or xylose – readily degrade in alkali (Yang and Montgomery, 1996). Sucrose degrades rapidly under alkaline conditions at temperatures higher than 100^{o}C (Goodacre et al., 1978; Montgomery and

Ronca, 1953; Kopriva, 1973; Montgomery, 1953; O'Donnell and Richards, 1973; Manley-Harris and Richards, 1981; Manley-Harris et al., 1980; Yang and Montgomery, 1996), but studies have demonstrated that at ambient or lower temperatures, no degradation is detected (Lloyd et al., 1995) even after a long time (Williams and Morrison, 1982). Goodacre et al. (1978) used ^{14}C-U-sucrose to detect small amounts of sucrose degradation at conditions close to those in a sugar refinery. He showed that as temperature increased, the rate of sucrose degradation also increased. In the case of pH, the degradation curve presented a minimum around 10.2. Extrapolating from his data at pH 11.1, suggests that at 45^{o}C (113^{o}F), sucrose degradation is about 3%/month (g degraded/100 g initial sucrose per month). However at 40^{o}C (104^{o}F), which is approximately the record high temperature for a Texan summer, the degradation rate is nil.

Calcium carbonate solubility varies with pH and sucrose concentration (Dartois, 1941), reaching a peak at about 10^{o} Brix (Chen and Chou, 1993). These parameters are important because they limit the amount of lime that can be recovered. At the sucrose concentration of raw juice obtained from mills, calcium carbonate solubility is close to that in water. Carbonatation (i.e., reaction with CO_2 followed by filtration) should be performed between 55^{o}C and 45^{o}C. Higher temperatures cause sugar losses, and below 45^{o}C the reaction is slow (Hugot, 1986).

To use the stationary lime kiln system, the organic content of the carbonatation sludge must be below 10% (w/w) to yield robust pellets, otherwise, they disintegrate as the organics are burned, clogging the reactor. In the actual process, the carbonatation sludge would be thoroughly rinsed during filtration to avoid sugar losses. However, sugarcane contains waxes, gums, and among other compounds (Chen and Chou, 1993) that precipitate with the carbonatation sludge (Azzam, 1984) and cannot be extracted by water; thus, the sludge will have a high organic content. It is suggested then, that the sludge be pre-burned to lower its organic content to the appropriate level and then be re-pelletized for calcination or, if integrated with the MixAlco process, the raw sludge can be used to control the pH in the fermentation.

III.2 Literature Review

Storage of clarified concentrated syrups is a common practice in the sugarbeet industry, which allows their preservation for up to 2 years (Sargent et al., 1997; Cosmeur and Mathlouthi, 1999). However, their conditions are different; they store concentrated syrups (~67% dry substance), whereas our juice concentrations are much lower (~15%). Nonetheless, they have recognized that low temperatures (< 30^{o}C) and high pH (9.0 ± 0.2) must be maintained. Preserving concentrated syrups has limitations because the sugars are crystallized directly after storage, so any complexes or impurities formed cannot be eliminated and end up in the crystals (Cosmeur and Mathlouthi, 1999). Further, the juice extraction, clarification and evaporation equipment must be oversized. In our case, we store the raw juice under more alkaline conditions. Finally, we carbonate it and filter it, which is a common practice for juice purification or clarification. For our process, only the extraction equipment needs to be oversized.

Thin (i.e., low-concentration) sugarcane juice storage with ammonia has been performed (Bobadilla and Preston, 1981; Duarte et al., 1981) and they concluded that high pH (> 9.5) is necessary to preserve the juice. Sodium benzoate (Bobadilla and Preston, 1981) and formalin (Bobadilla and Gill, 1981) have also been used to preserve thin sugarcane juice, but the preservation cannot be maintained for a long time because of the prohibitive costs of the preservatives and because high concentration of these substances are noxious and unsafe for human consumption. Lime is much cheaper and safer.

To the knowledge of the author, no one has used lime as a preservative for thin sugarcane juice.

Recovery and conversion of carbonatation sludge to lime is also a common practice (Bento et al., 1999).

III.3 Experimental Methods

III.3.1 Preliminary Studies

To determine the amount of lime needed to maintain adequate pH to preserve sucrose, a preliminary study was performed. It was assumed that lime addition should be proportional to the sucrose concentration or to the soluble solids concentration (brix) in the juice. During sucrose extraction from cane, other substances are co-extracted that may react with the lime. Because their concentrations are co-dependant and because the nature and exact concentration of the other substances are generally unknown, sucrose concentration is a reasonable parameter for determining lime addition.

III.3.1.1 Experimental Approach

III.3.1.1.1 Experiment and Equipment Description

Shredded Louisiana sugarcane was extracted with distilled water to yield a solution with a sucrose concentration of about 40 g/L. Half of this juice was diluted 2 fold to produce a juice with a sucrose concentration of about 20 g/L.

Each batch of juice was then distributed among 10 polyethylene 200-mL bottles equipped with a sealing lid. The volume in each bottle was 150 mL.

Hydrated lime (certified 99.3% calcium hydroxide, Fisher Scientific Co., Pittsburgh PA) was added to each of the 10 bottles in each batch in the following percentages: 0.5, 1.5, 3, 4, 5, 7, 10, 15, 20 and 30% (g lime/100 g of sucrose in solution).

These 20 bottles (10 for each of the two batches) were kept in a shaker at ambient temperature (~23^{o}C). To monitor both the lime consumption and sucrose degradation, pH and samples for sucrose analysis were taken periodically. pH was measured with an electrical-potential-difference pH meter (ORION™, Orion, Inc.,

Boston MA) and sucrose concentration was measured using High Pressure Liquid Chromatography system (HPLC) equipped with a Bio-Rad HPX-87C ion exchange column (Bio-Rad Laboratories, Hercules CA) and a refractive index detector (Perkin Elmer Series 200, Perkin Elmer Life and Analytical Sciencies, Boston MA).

Bottles were taken off line when the pH became acidic and showed considerable microbial activity (which was easily detected due to gases that inflated the polyethylene bottles) and the sucrose concentration became nil.

The experiment was designed to find the minimum amount of lime addition required that preserves sugarcane juice for 1 year.

III.3.1.1.2 Observations, Results and Discussion

Table 3.1 shows the pH attained at Day 0 for all the bottles after adding lime. It is obvious that 0.5% lime was not enough because the pH is only slightly alkaline. Interestingly, for every percentage of lime added, the pH of every 40-g/L bottle was very close to the pH of its corresponding 20-g/L bottle, even though only half the amount of lime was added. Electrical-potential-difference pH meters are known to be affected by differing sugar concentrations; however, the solutions are too dilute for this effect to be significant. The response described above is rather explained as follows: 1) In the 40-g/L batch, there was about twice as much substances that consume lime compared to the 20-g/L batch, and 2) lime solubility increases in the presence of sucrose because it forms calcium saccharate (Chen and Chou, 1993). Thus, as the sucrose concentration increases, lime solubility increases as well as acidic substances that neutralize lime. Therefore, adding lime in proportion to sucrose maintains a constant equilibrium concentration of hydroxide ions, and thus pH. The consumption of hydroxide ions due to higher concentration of acidic substances is cancelled out by the increase in hydroxide ions due to the higher amount of lime that solubilizes. This observation gives us another indication that adding lime based on sucrose concentration is appropriate.

Table 3.1 Initial pH of sugarcane juice at different lime loadings.

40-g/L Sucrose Batch

0.5%	1.5%	3%	4%	5%	7%	10%	15%	20%	30%
8.46	10.48	11.23	11.56	11.75	11.97	12.17	12.37	12.43	12.49

20-g/L Sucrose Batch

0.5%	1.5%	3%	4%	5%	7%	10%	15%	20%	30%
8.31	10.14	11.22	11.50	11.68	11.91	12.13	12.31	12.41	12.46

After 1 year of treatment, only the 20% and 30% lime loadings for both batches showed no sign of microbial activity or sucrose degradation (Figures 3.1 through 3.4). In Louisiana and other places, sugarcane season lasts about 3 months per year. Because we want to preserve the juice during the off-season when there is no fresh juice to process, 9 months is the maximum time that should be required.

Figures 3.5 and 3.6 show the pH and sucrose concentration for 15% lime loading for both batches. The observed response and similar ones from lower lime loadings (Figures 3.7 through 3.20) suggest that a pH above 10 must always be maintained to avoid microbial activity. If pH control is implemented, the set point should be kept at pH 11 because pH 10 is the threshold; operation on or about this value could be risky.

To reduce lime consumption, lime may be added as it becomes necessary to maintain pH above 11 or the juice could be segmented into batches that have different lime loadings depending on the desired preservation time. Figure 3.21 illustrates this response. It can be observed that there is a sharp lime consumption in the first two weeks which requires about 7 g $Ca(OH)_2$/100 g initial sucrose to maintain preservation. A significant decrease in the lime consumption rate follows, requiring for preservation a daily amount of lime (not the same as the lime consumed) of about 0.0301 g $Ca(OH)_2$/(100 g initial sucrose · day).

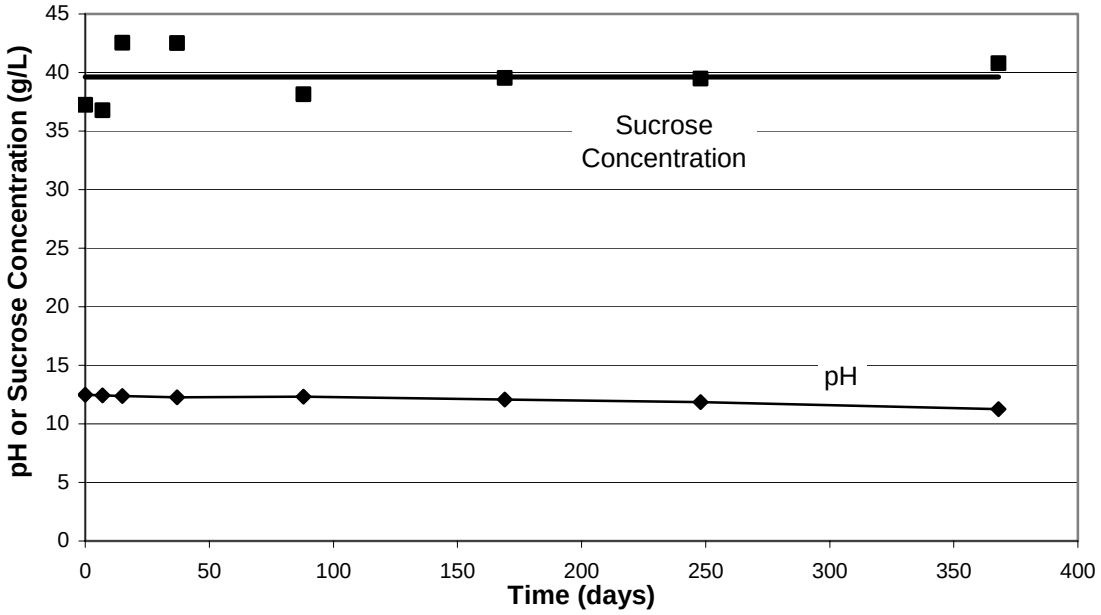


Figure 3.1 pH/sucrose concentration against time for the 40-g/L batch at 23°C (30% lime).

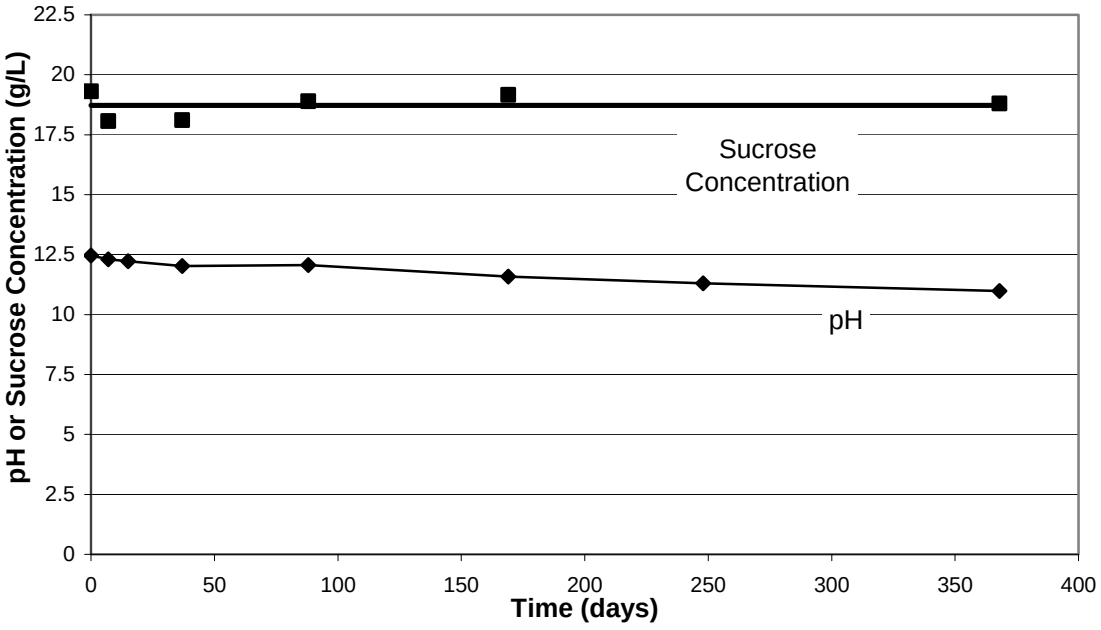


Figure 3.2 pH/sucrose concentration against time for the 20-g/L batch at 23°C (30% lime).

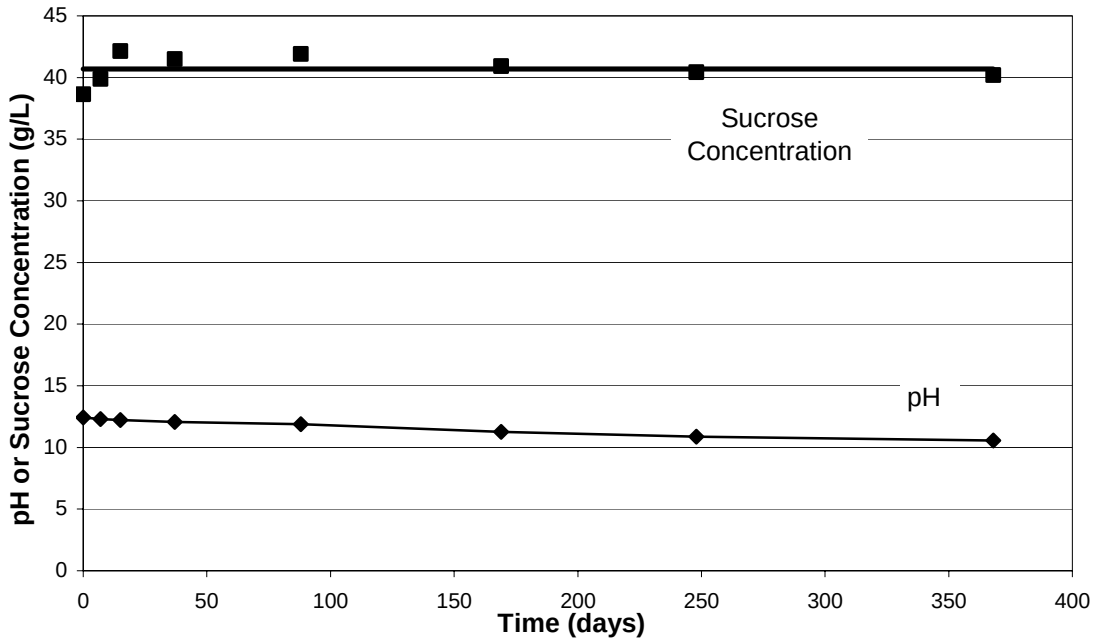


Figure 3.3 pH/sucrose concentration against time for the 40-g/L batch at 23°C (20% lime).

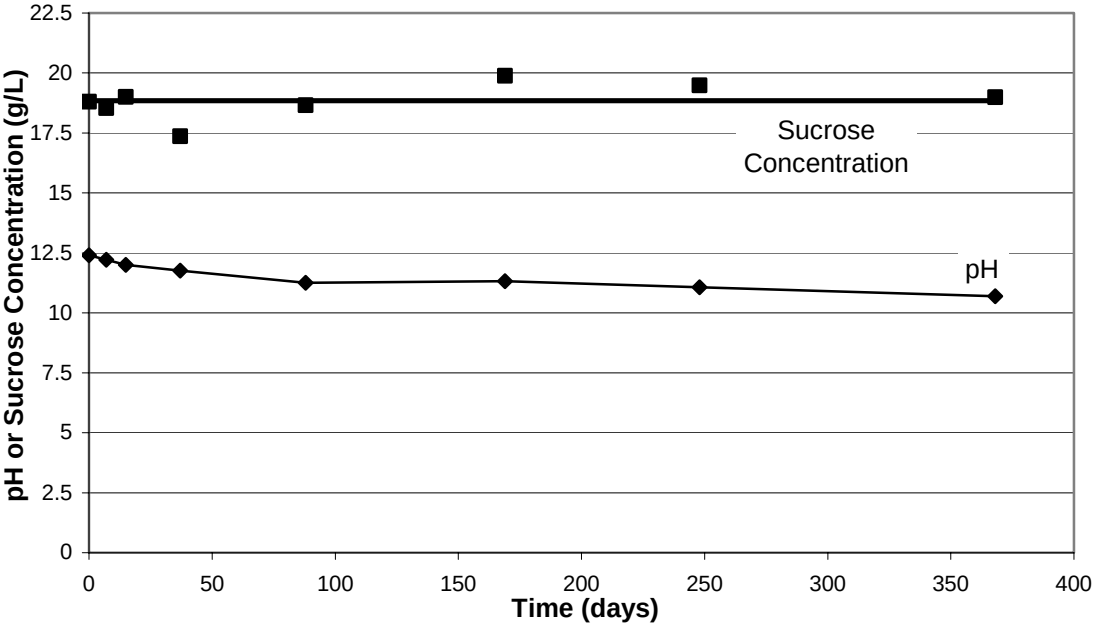


Figure 3.4 pH/sucrose concentration against time for the 20-g/L batch at 23°C (20% lime).

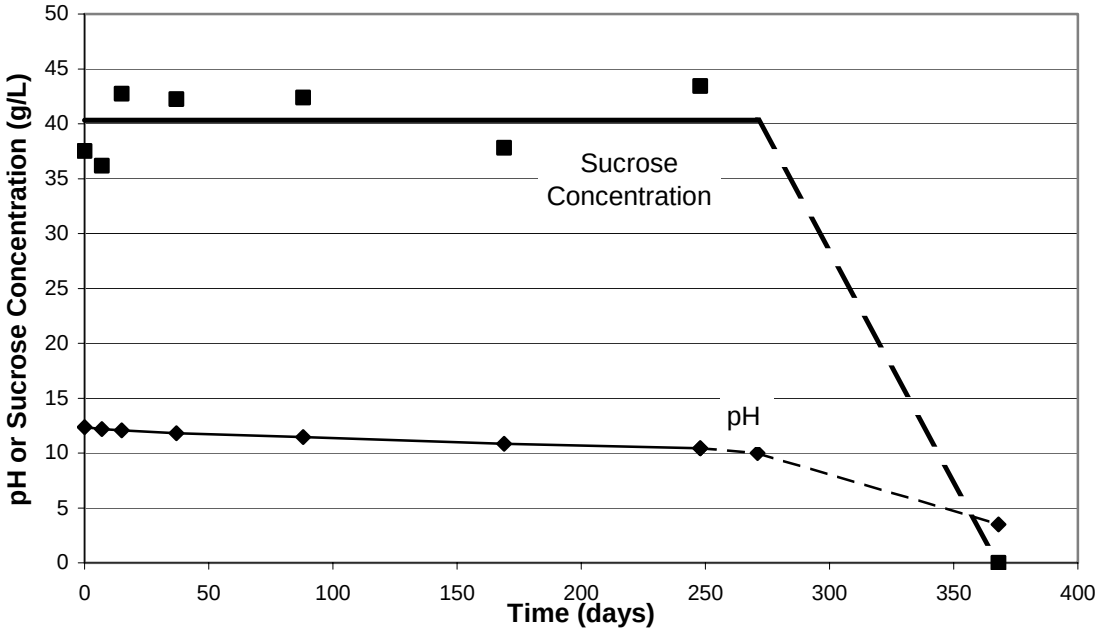


Figure 3.5 pH/sucrose concentration against time for the 40-g/L batch at 23°C (15% lime).

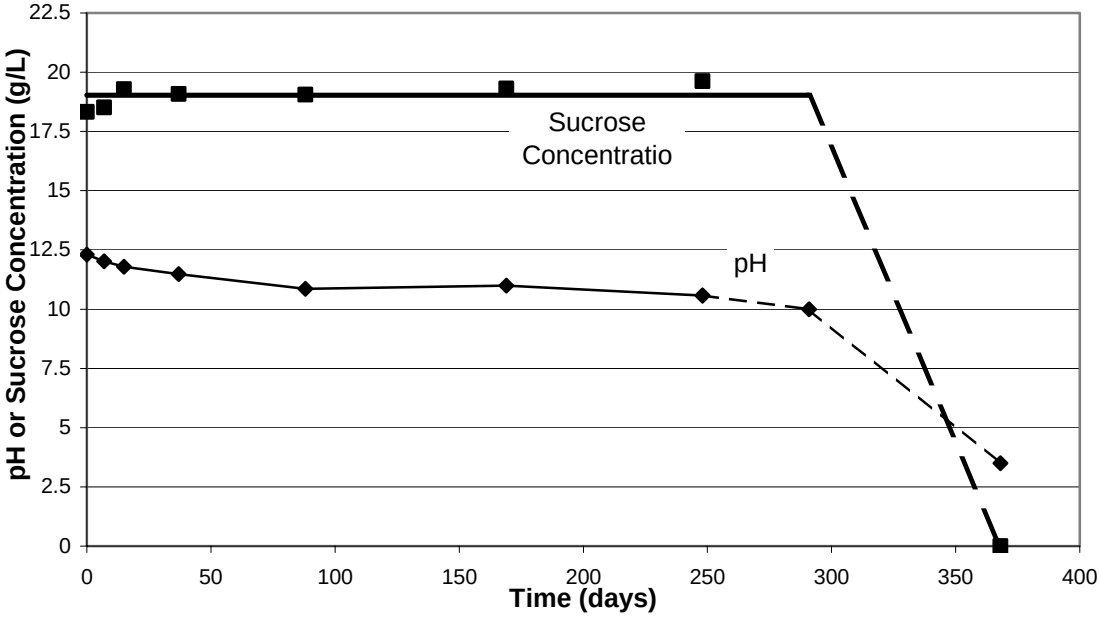


Figure 3.6 pH/sucrose concentration against time for the 20-g/L batch at 23°C (15% lime).

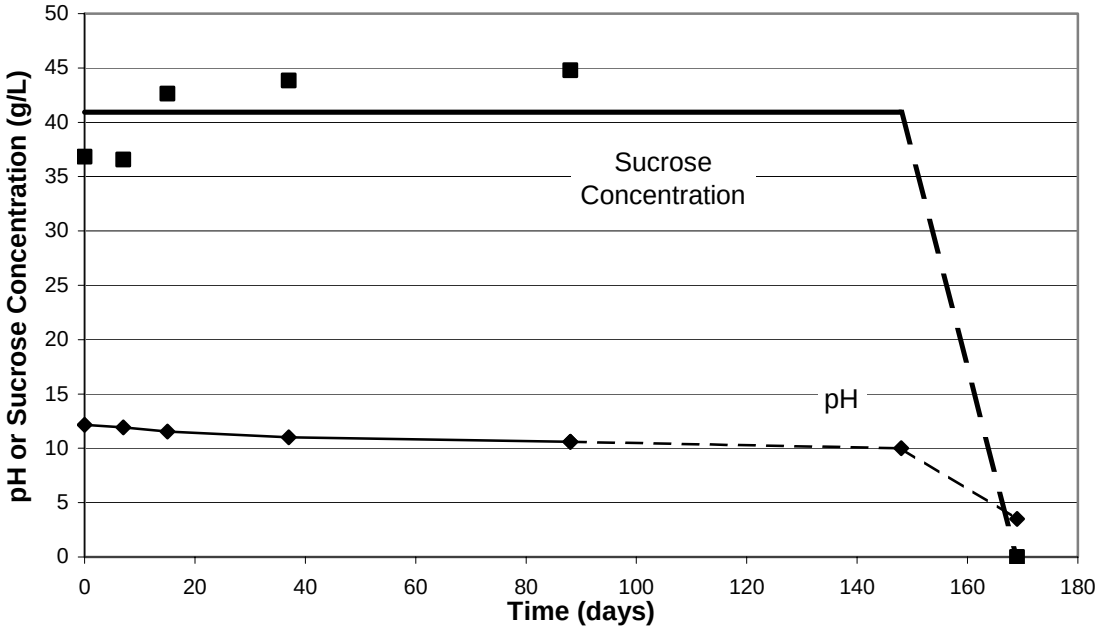


Figure 3.7 pH/sucrose concentration against time for the 40-g/L batch at 23°C (10% lime).

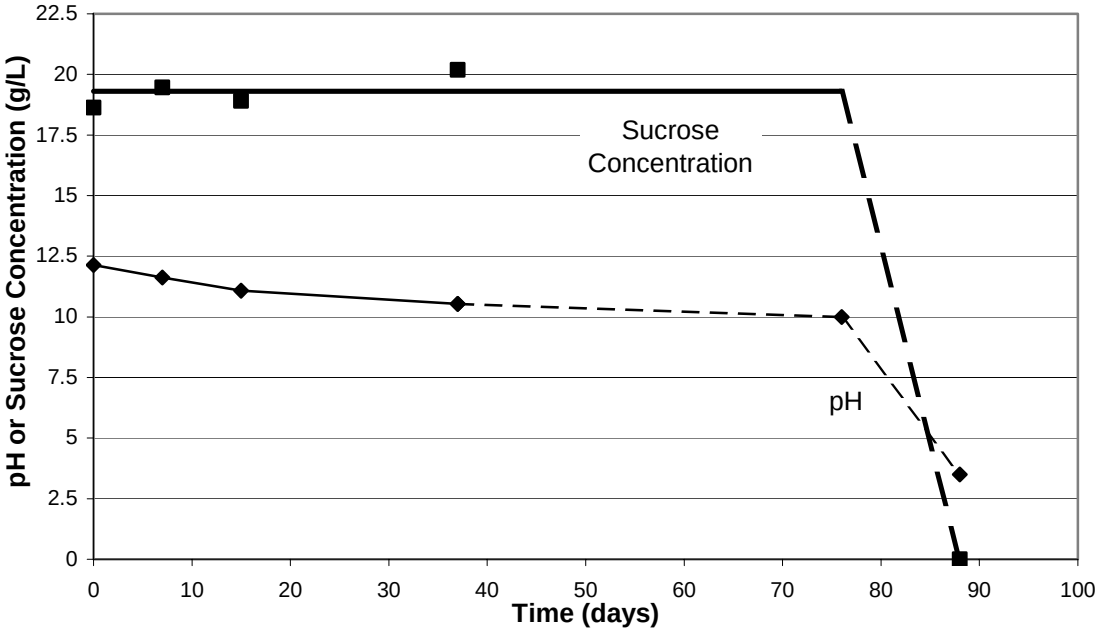


Figure 3.8 pH/sucrose concentration against time for the 20-g/L batch at 23°C (10% lime).

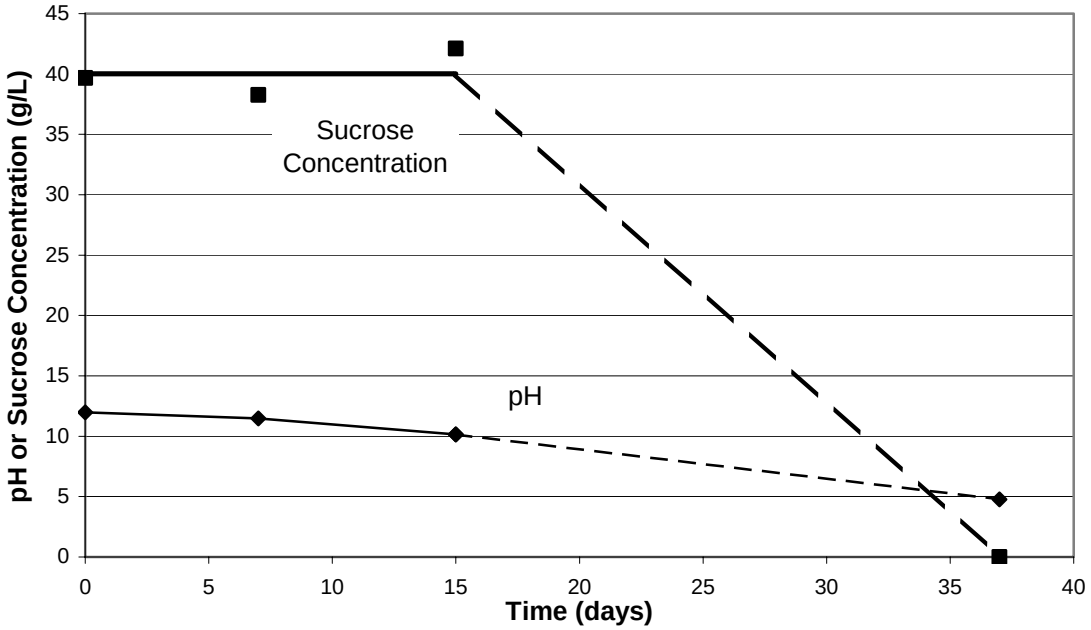


Figure 3.9 pH/sucrose concentration against time for the 40-g/L batch at 23°C (7% lime).

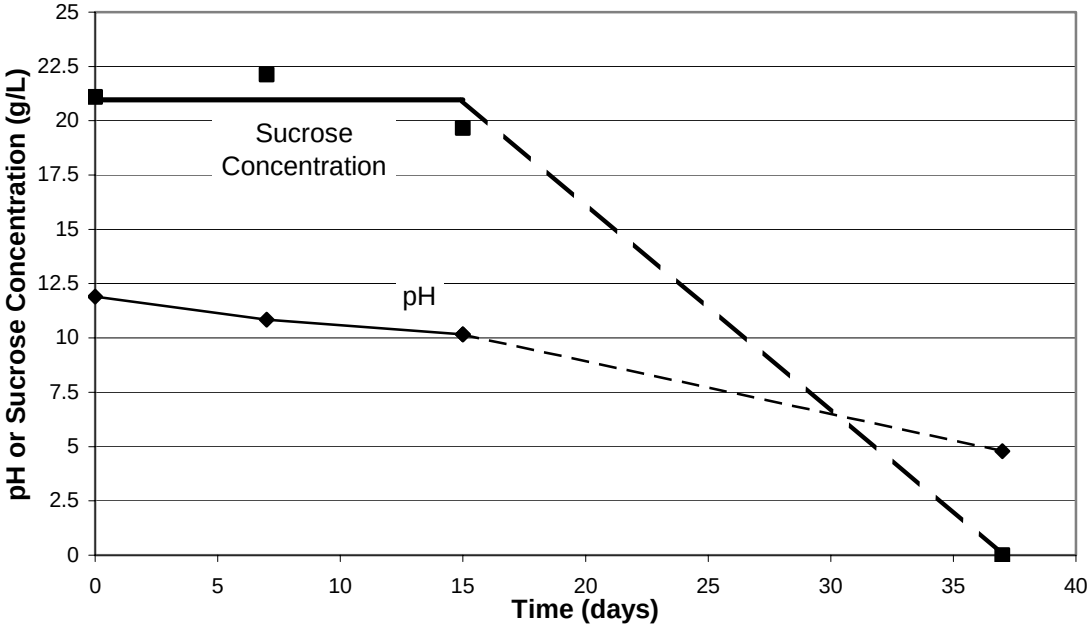


Figure 3.10 pH/sucrose concentration against time for the 20-g/L batch at 23°C (7% lime).

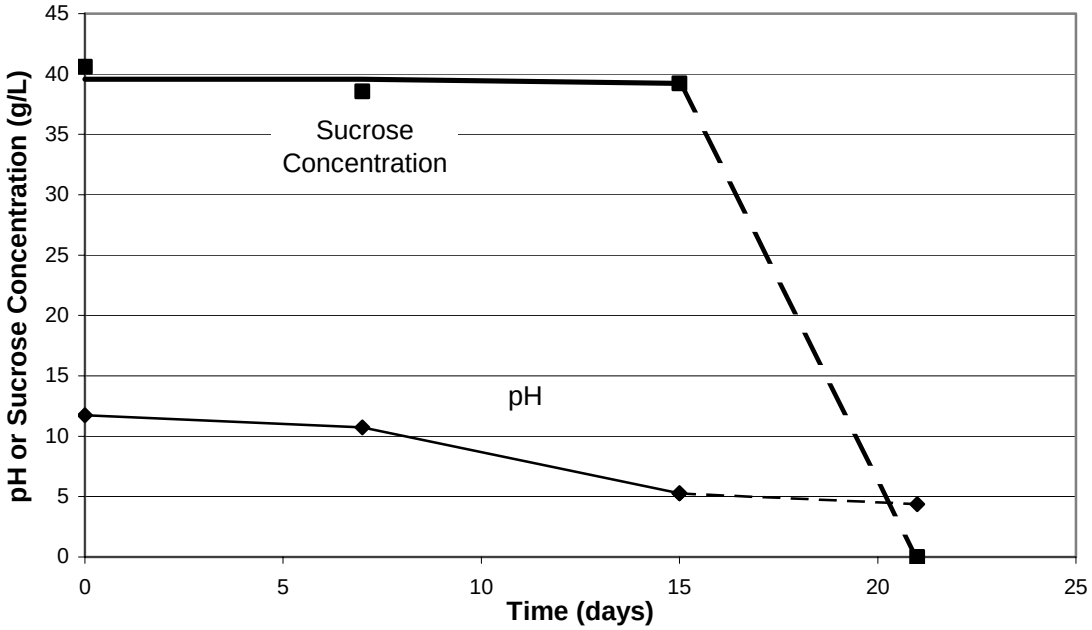


Figure 3.11 pH/sucrose concentration against time for the 40-g/L batch at 23°C (5% lime).

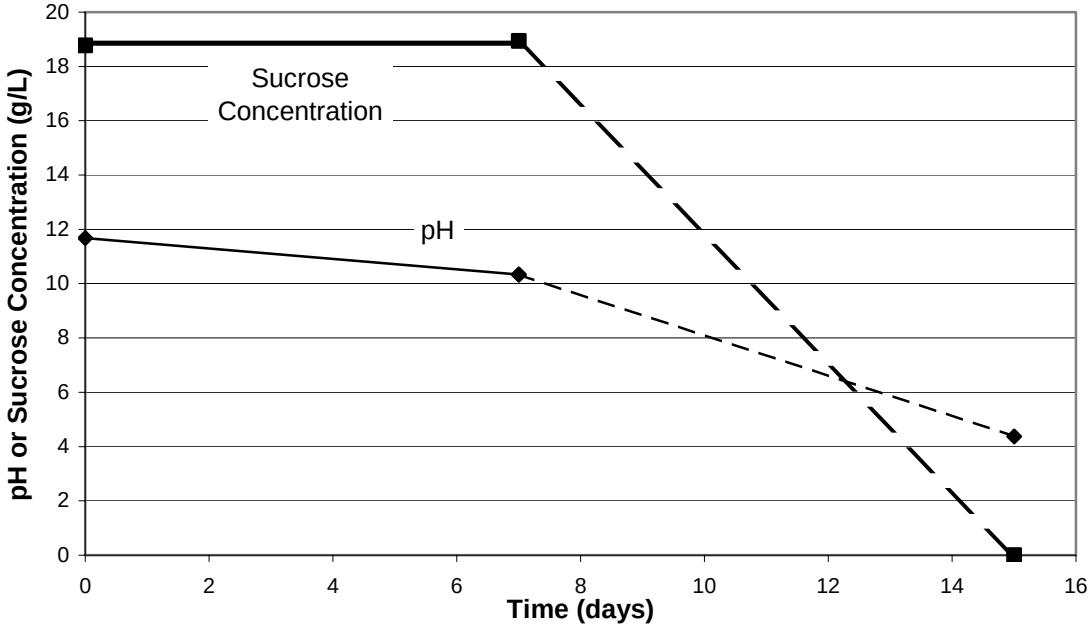


Figure 3.12 pH/sucrose concentration against time for the 20-g/L batch at 23°C (5% lime).

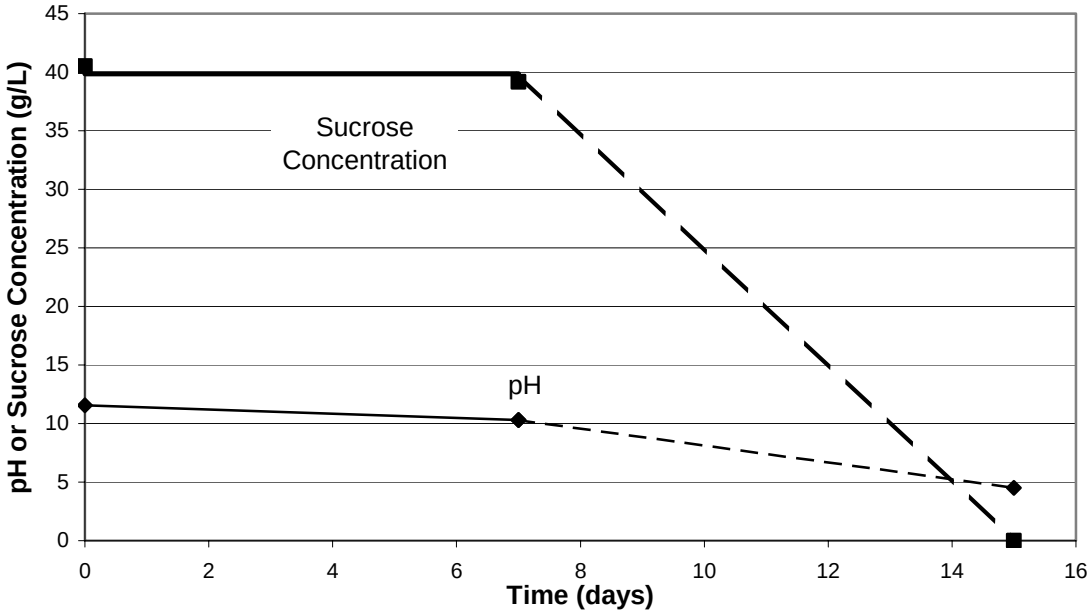


Figure 3.13 pH/sucrose concentration against time for the 40-g/L batch at 23°C (4% lime).

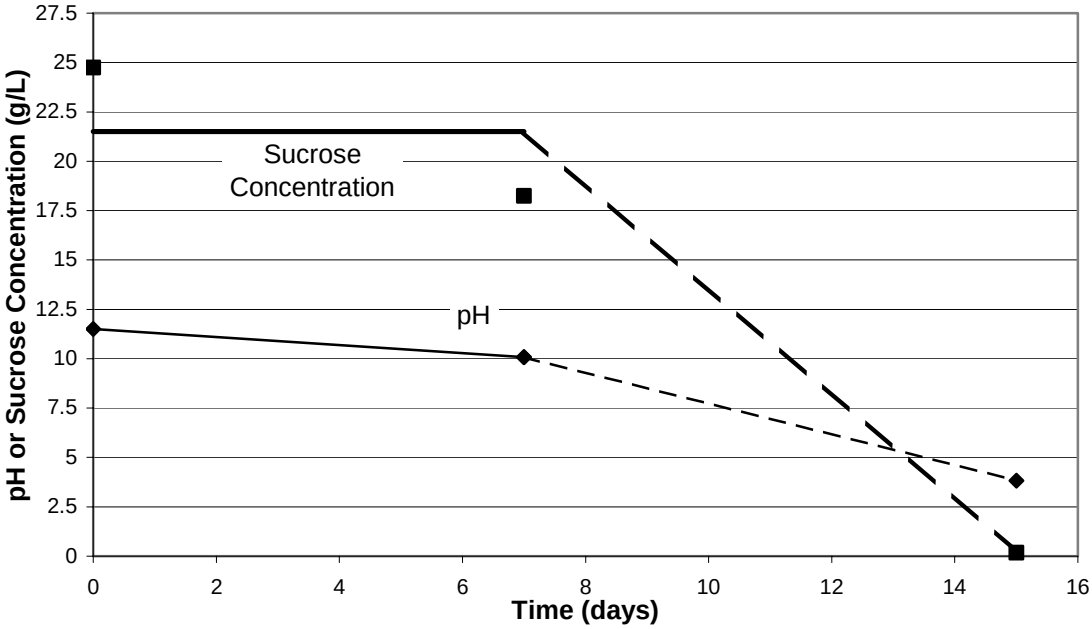


Figure 3.14 pH/sucrose concentration against time for the 20-g/L batch at 23°C (4% lime).

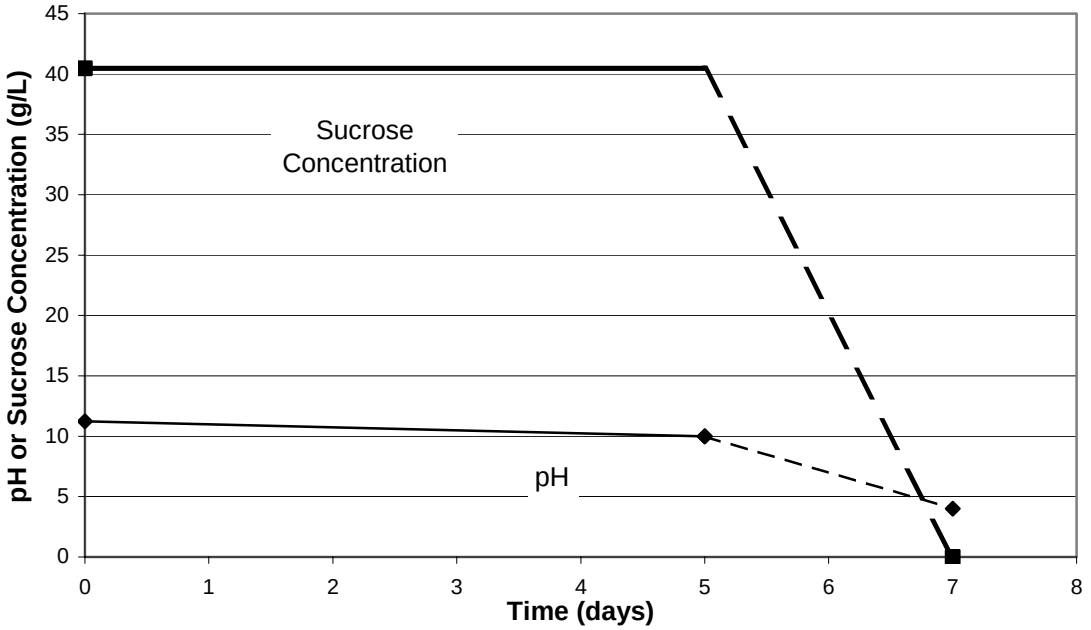


Figure 3.15 pH/sucrose concentration against time for the 40-g/L batch at 23°C (3% lime).

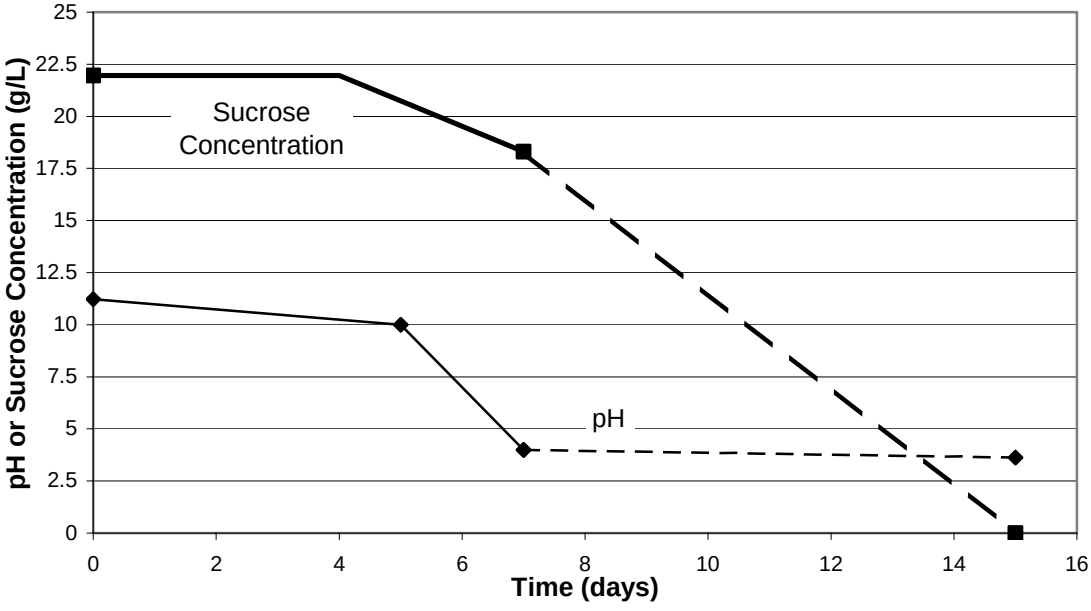


Figure 3.16 pH/sucrose concentration against time for the 20-g/L batch at 23°C (3% lime).

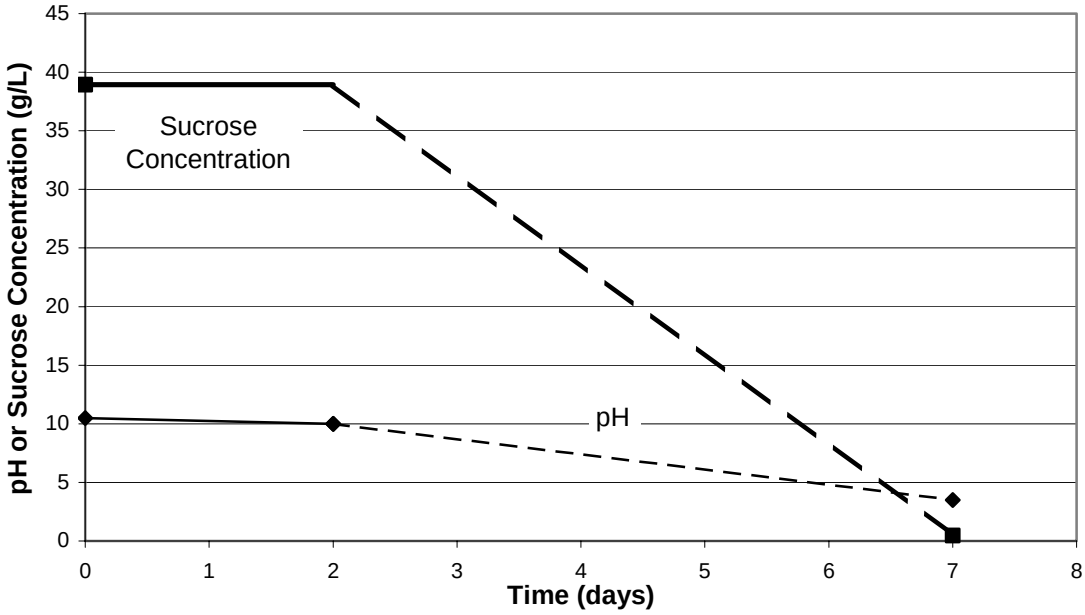


Figure 3.17 pH/sucrose concentration against time for the 40-g/L batch at 23°C (1.5% lime).

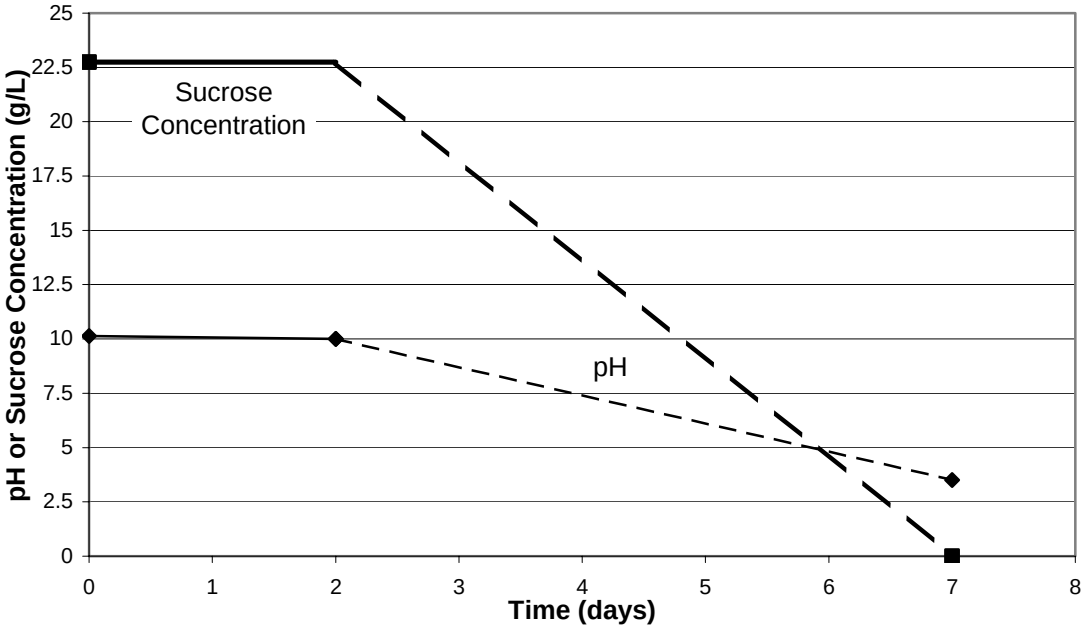


Figure 3.18 pH/sucrose concentration against time for the 20-g/L batch at 23°C (1.5% lime).

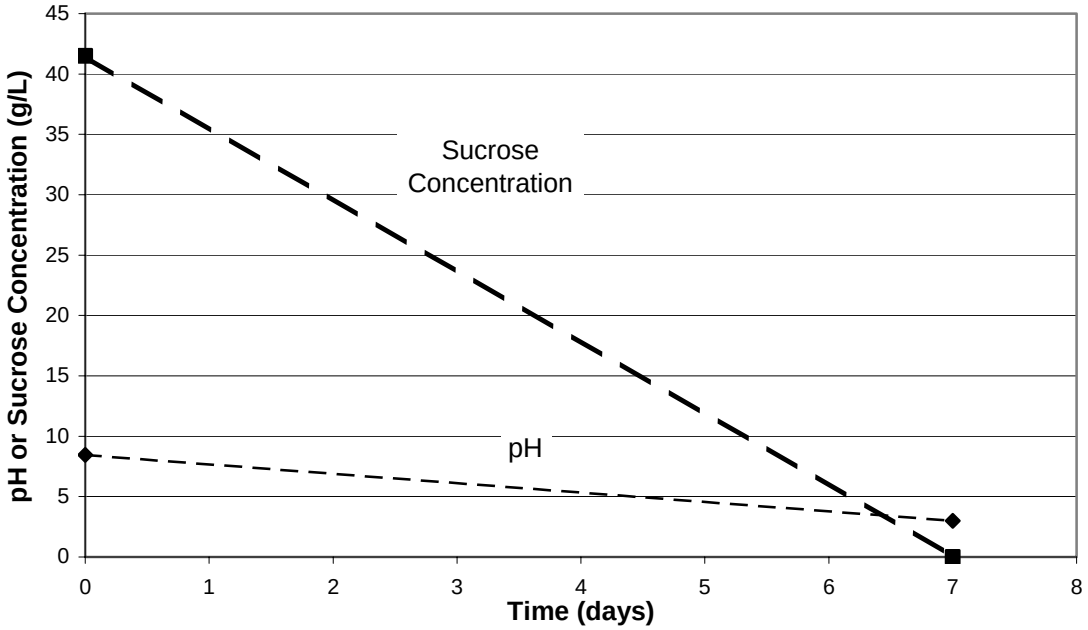


Figure 3.19 pH/sucrose concentration against time for the 40-g/L batch at 23°C (0.5% lime).

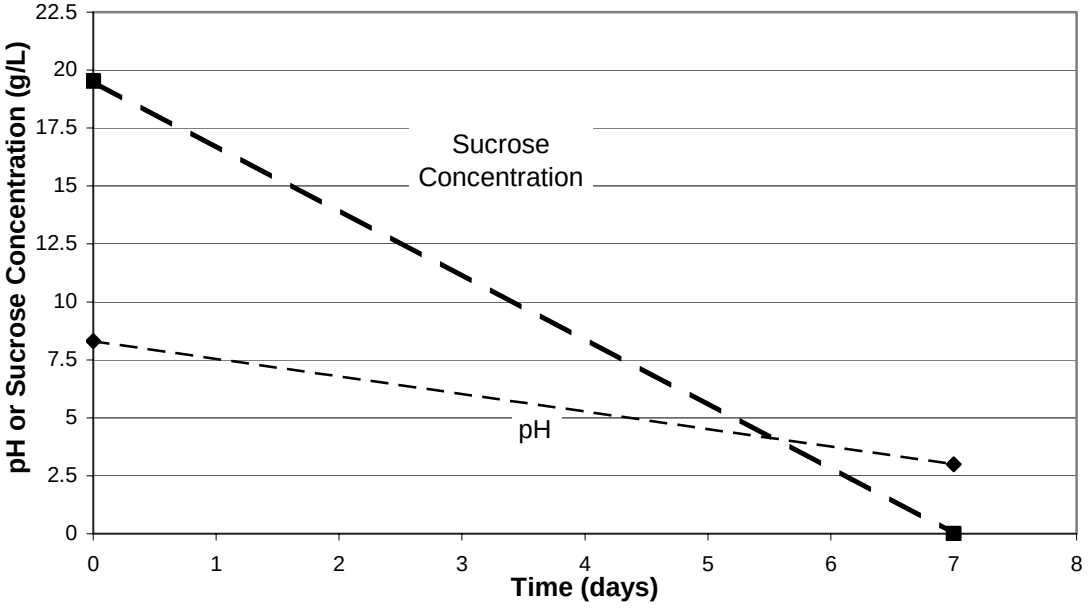


Figure 3.20 pH/sucrose concentration against time for the 20-g/L batch at 23°C (0.5% lime).

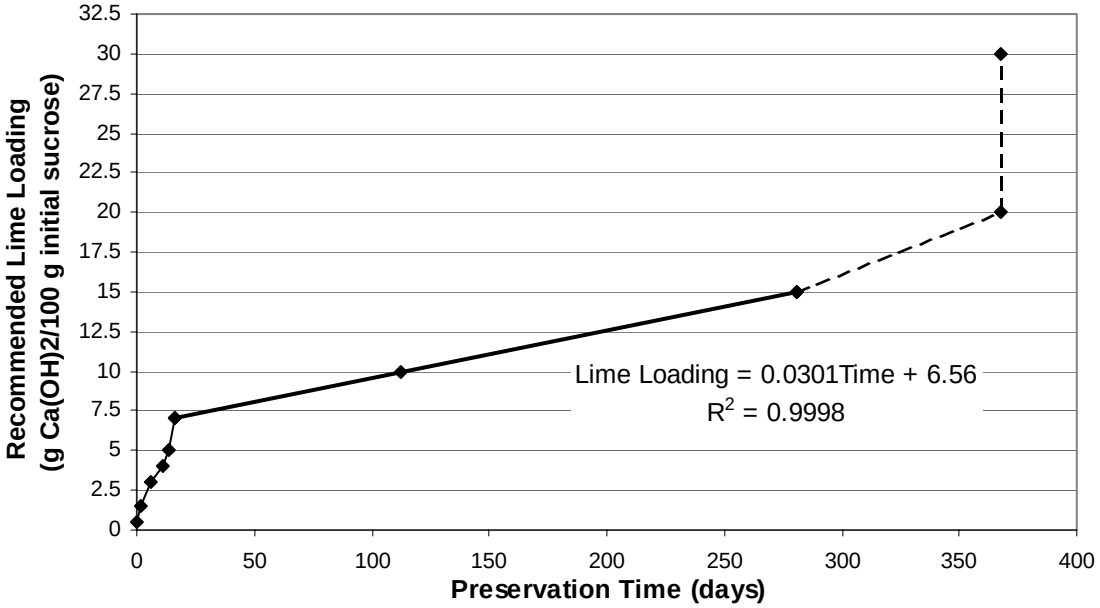


Figure 3.21 Recommended lime loading as a function of preservation time at 23°C.

The dotted lines in Figures 3.5 through 3.20 reflect not an actual response, but rather they simply connect consecutive measurements after the pH had decreased below 10 and microbial activity had been detected. The dotted line in Figure 3.21 between the 15 and 30% lime loadings means that there are no actual data there to correlate for the required lime rate because the experiment was stopped at Day 368. At this time, no microbial activity, pronounced pH decrease below 10 and/or sucrose degradation had yet been detected for the 20 and 30% lime loadings.

One important conclusion from these studies is that the required lime addition should be based on the sucrose or soluble solids concentration (i.e., brix). This observation has been confirmed by Duarte et al. (1981), who used ammonia to preserve thin sugarcane juice. They also observed a relation between the amount of sugar present and the amount of ammonia necessary for preservation.

III.3.2 Objectives

To assess the degradation of sucrose and juice quality, studies on sugarcane juice preservation with lime were performed both at bench scale and at pilot scale at ambient temperature for several months. At the end of the study, the juice was carbonatated (i.e., carbonated and filtered) to recover calcium carbonate as carbonatation sludge. The recovered sludge was then sent to Altex Technologies Corp. (Sunnyvale CA) to be tested for suitability for regeneration in their stationary lime kiln system described in Chapter I.

III.3.3 Experiment and Equipment Description

The bench- and pilot-scale equipment were similar, except for their size and the fact that the recovery of carbonatation sludge was done by vacuum filtration at the bench scale and by pressure filtration at the pilot scale. Hydrated or slacked lime (92% $Ca(OH)_2$, 8% inerts, industrial lime, Chemical Lime Co., New Braunfels TX) was used in all experiments.

III.3.3.1 Preservation Set-up

For the pilot-scale experiments (Figure 3.22), the solutions were kept outdoors in two conical 2500-gallon tanks each with a 1½-hp open-impeller pump (A-72030-40, Cole-Parmer Instrument Co., Vernon Hills IL) for constant recirculation to keep solids in suspension. For the bench-scale experiments, a 4-gallon container and a 1/40-hp open-impeller pump (AC-2CP-MD, March Mfg., Inc., Glenview IL) were used indoors. One of the bench-scale batches, which was used to assess if intermittent mixing, as opposed to constant recirculation, was adequate for preservation, was kept in a 5-gal polyethylene sealed bucket, and mixing occurred once a day by vigorously shaking for 10 – 30 seconds.

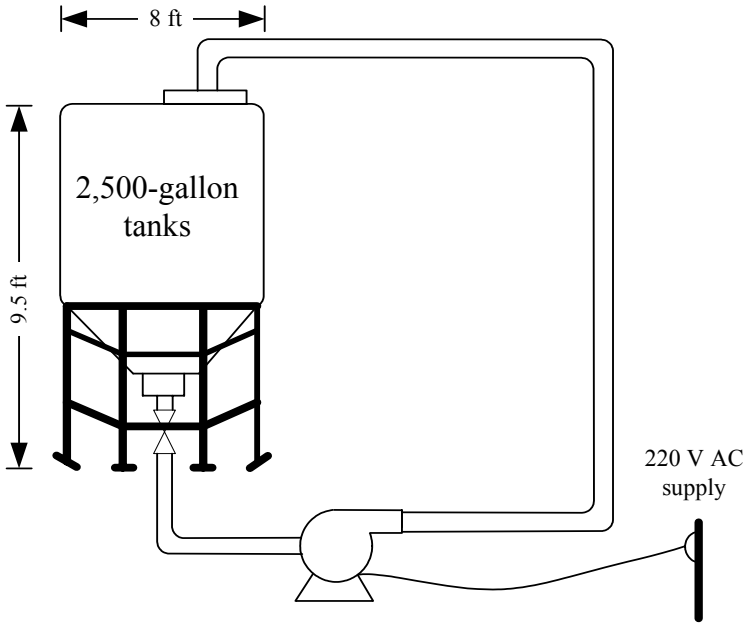


Figure 3.22 Pilot scale sugarcane juice preservation experiment setup.

The juice was obtained from the W. R. Cowley Sugar House, a sugar mill in Santa Rosa TX. The preliminary laboratory experiments (Section III.3.1) tested different lime amounts added to different concentrations of cane juice. The data showed that the slacked or hydrated lime addition should be proportional to the sugar concentration in the juice. The experiments determined that to preserve sugarcane juice for 1 year, the lime concentration should be slightly less than 20% on sucrose (20 lb of slacked lime/100 lb of sucrose present), or 16% on brix (16 lb of slacked lime/100 lb of soluble solids) assuming 80% purity (80 lb sucrose/100 lb of soluble solids). Based on these findings, typical raw sugarcane juice from a mill requires slacked lime concentrations of 2.2 to 2.4% on juice (2.2 to 2.4 lb/100 lb of total juice) because it has a soluble-solids concentration of approximately 14 to 15% (14 to 15^{o} Brix). This is about the same amount of lime used in the single carbonatation and the continuous double carbonatation processes (40 lb or 18 kg quicklime/ton of cane) (Hugot, 1986). However, the stationary lime kiln produces lime that is 56% cheaper than conventional lime kilns

(Namazian, 2004); thus, the lime expense for these conventional carbonatation processes is actually higher.

Although an industrial process might add lime based upon pH control (pH > 11), bench- and pilot-scale experiments were performed at a fixed $Ca(OH)_2$ loading of about 2.8 to 2.9% (lb/100 lb of juice), which corresponds to about 0.29 lb of industrial lime (92% $Ca(OH)_2$) added/gal of juice or 35 kg of industrial lime/m^3 of juice. This value is slightly higher than the amount required to preserve the juice 1 year (i.e., 2.4% w/w).

A small amount of lime was added to the juice at the mill to preserve it during transportation. Table 3.2 shows the description of the different batches that were preserved and shows how they were prepared prior to preservation. After the juice had been prepared accordingly as described in Table 3.2, the remaining lime needed for preservation, as described above, was then added.

III.3.3.2 Carbonatation Procedure

After the set time for preservation ended, the juice underwent carbonatation (i.e., carbonation by bubbling carbon dioxide followed by filtration) to decrease its pH and to clarify it, which also occurred at both pilot and bench scale. Carbon dioxide (Praxair Inc., College Station TX) was bubbled through a diffuser stone of appropriate size (1.5-ft-long diffuser stone, A-70025-28, Cole Parmer Instrument Co, Vernon Hills IL for pilot scale; a 1.5-in-diameter diffuser stone, 11-139A, Fisher Scientific Co., Pittsburgh PA for bench scale), at ambient temperature until a pH of 9.0 ± 0.2 was attained. This is the pH recorded when pure calcium carbonate is added to a sucrose solution of about 14 to 15^o Brix at 20-25^{o}C. Ideally, at this pH, calcium carbonate recovery is maximized.

Table 3.2 Description of the different batches of preserved juice.

Batch I.D.	Dates	Scale	Preparation Prior to Preservation	Mixing Frequency
$B_{filtered}$	12/5/2001-11/9/2002	Bench	Vacuum filtration using trigger-type cloth, 65% cotton - 35% polyester, pore size 250 × 125 μm. Filterable solids left after filtration: 2.6 g/L (from 0.45-μm membrane)	Constant recirculation
$B_{clarified}$	12/9/2002- 2/10/2003	Bench	Clarification by carbonatation, where the limed juice was carbonated and then vacuum filtered, using Whatman filter paper No.1	Constant recirculation
$B_{screened}$	3/7/2003-8/9/2003	Bench	Screening, where the juice was passed through a ~ 20-mesh strainer; thus, removing most of the *bagacillo* or *cush cush* (i.e., fine bagasse particles)	Constant recirculation
$B_{periodic}$	5/11/2003-8/9/2003	Bench	Screening, same preparation as $B_{screened}$	Periodic mixing once a day by vigorous shaking. Juice was kept in a sealed bucket
$P_{no\text{-}prep}$ #1	12/8/2000-4/25/2001	Pilot	None, preserved as obtained from mill (i.e., no filtration, screening or carbonatation)	Constant recirculation
$P_{no\text{-}prep}$ #2	5/11/2001-3/22/2002	Pilot	None, preserved as obtained from mill (i.e., no filtration, screening or carbonatation)	Constant recirculation
$P_{clarified}$	3/8/2003-9/14/2003	Pilot	Clarification by conventional defecation (Chapter I) as obtained from the process at the mill	Constant recirculation

The carbonatation sludge was collected to assess recovery and to test its suitability for the stationary lime kiln. Carbonatation sludge from conventional raw juice had a high organic content which is excessive for the stationary lime kiln; thus, the juice was prepared as shown in Table 3.2 to determine if the modifications would decrease the organic content of the resulting sludge.

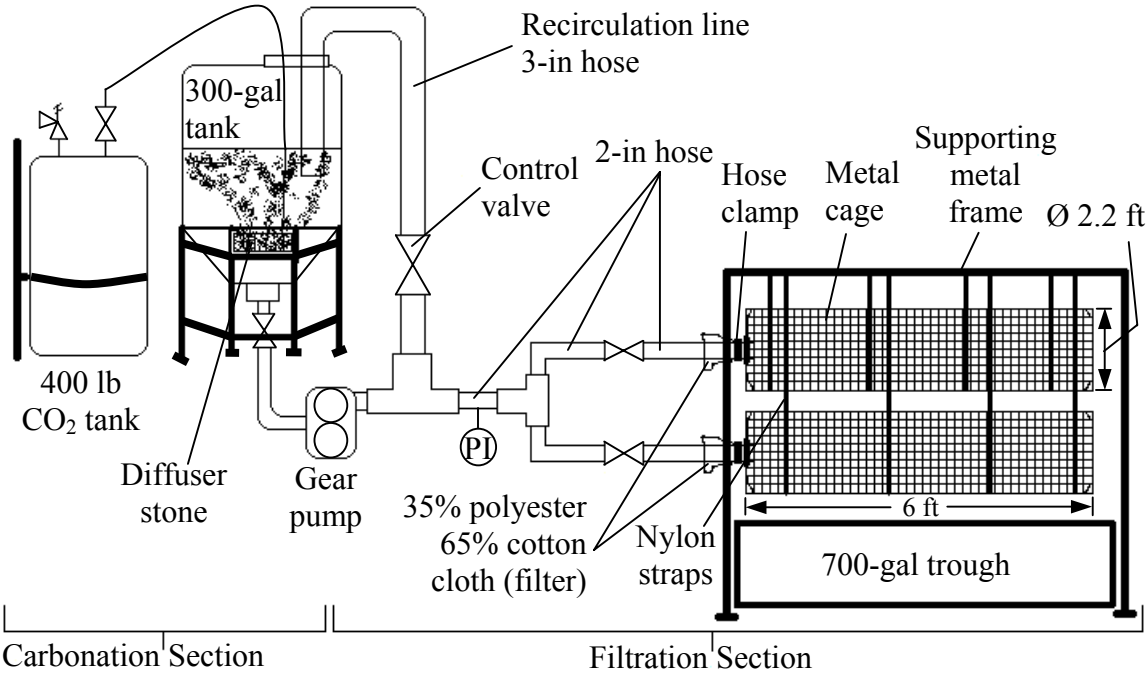


Figure 3.23 Pilot scale carbonation and filtration (carbonatation) setup.

Bench-scale filtration of the carbonatation sludge was done by conventional vacuum filtration using a Buchner funnel, Whatman filter paper No.1 (Fisher Scientific Co, Pittsburgh PA), and the appropriate Erlenmeyer flask. A minimal amount of water was used to rinse the resulting cake and wash off any sugars present. No filter aid was used allowing mass balances to be performed for recovery calculations. At the pilot scale, the carbonatation sludge was recovered by pressure filtration using the equipment shown in Figure 3.23. After carbonating in a 300-gal tank, the tank outlet was connected to a 1½-hp positive-displacement gear pump (Ray Ford Pumps, Houston TX) using 2-in

flexible PVC hoses. The slurry (i.e., carbonatation sludge + pH-9 clarified juice) was then pumped through a resistant cloth (trigger type, 35% polyester/65% cotton, Hancock Fabrics, College Station, TX). This was the same type of cloth used to prepare batch $B_{filtered}$ (Table 3.2), which had been sown into two 9×2½ -ft, pillowcase-like bags, and were supported inside two 6-ft-long cylindrical metal cages to resist the pressure. The cages had a lid at one end, held in place by nuts that could be removed to install the cloth inside and, after filtration, to pull out the sludge-filled cloth. Each lid had a 2.5-in-diameter orifice through which the mouth of the cloth bag protruded out of the cage. The cages and the cloth were hung from a supporting metal frame by eight (i.e., four each) adjustable nylon straps. To connect the pump to this filtration equipment, 2-in PVC hoses were used, which were held in place by securing them to the mouth of the bag with hose clamps. The system was also equipped with a 3-in recirculation line, which was purposely larger to reduce flow resistance and be able to adequately control flow and pressure; thus, the flow and pressure in the filtration equipment (i.e., cloth and cages) were controlled by regulating the valve in the 3-in. recirculation line. To avoid foaming, it was important to keep the recirculation line inside the liquid in the tank. The filtrate, which was a yellow clear juice, poured down abundantly from the filters and was collected in a 700-gal galvanized trough to be disposed of after sampling.

At the beginning of the project, only one filter (i.e., one cloth and one cage) was used, and to drive the filtration, the centrifugal pumps used for juice recirculation were employed. However, the filtration took too long, and the seals on the centrifugal pumps tended to fail. It was decided to increase the surface area, by adding an extra filter and use a gear pump. This system was sufficiently efficient, completing the filtration of about 200 gallons of slurry in about 10 minutes.

To rinse sugar off the carbonatation sludge cake, the cake was then washed with about 100 gallons of water, which were added to the tank and pumped through the system while the sludge was still in the filters.

Although it is known that carbonatation occurs faster, is more efficient, and saves carbon dioxide at higher temperatures (45^{o}C to 55^{o}C) (Hugot, 1986), our concern was

only to recover the sludge; thus heating equipment was not implemented. This cold juice carbonatation is the original single carbonatation process (Honig, 1953). Also, a mass balance of lime recovery could only be done at the bench scale. The recovery at the pilot scale was not quantitative because of losses in handling

After the carbonatation sludge was recovered, it needed to be dried before it could be sent to Altex Technologies Corp. for testing in their stationary lime kiln system. At the bench scale, the drying was done in a 105^{o}C oven for 24 hours. At the pilot scale, the mud was spread on tarps and sun-dried or, if the weather did not permit it, a dryer equipped with a natural gas heater (Figure 3.24) was used.

The carbonatation and drying took several days to complete (10 to 30 days) due to the large amount of juice to be processed; hence, it was important to do the carbonatation in 300-gal batches to keep the remaining juice at high pH and avoid spoilage. Figures 3.25 and 3.26 show photographs of one of the filters (i.e., cage and filtering cloth) after assembly and during filtration. As mentioned, the surface area of a single filter, as in the figures, was not enough; thus, an extra filter had to be added.

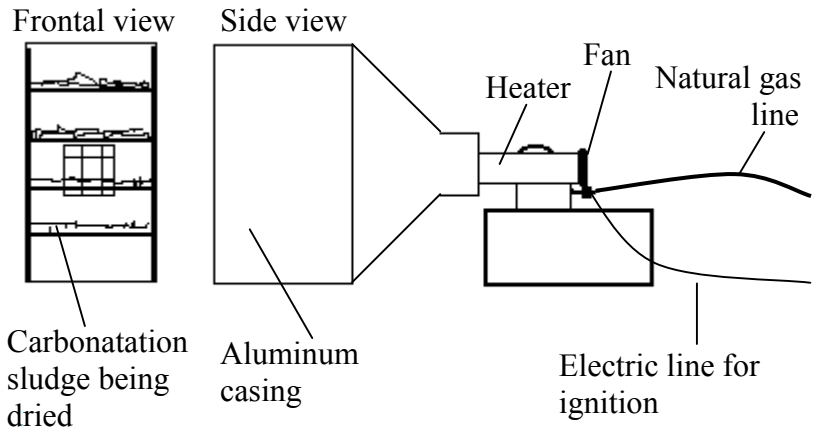


Figure 3.24 Carbonatation-sludge dryer setup.

Figure 3.25 Photograph of one of the filters (i.e., cloth and cage) after assembly.

Figure 3.26 Photograph of the pilot scale filtration taking place (only one filter being used).

III.3.3.3 Bench-scale Crystallization

The ultimate objective in the sugar industry is to produce sugar crystals, which are the product of both sugar mills and sugar refineries. The former produces raw sugar crystals, whereas the latter produces white refined sugar crystals.

Our process can be used to produce white sugar directly if carbonatation conditions are improved and adjusted for a direct white process (Valdes Delgado and de Armas Casanova, 2001; Chen and Chou, 1993); however, the expected product in these studies was raw sugar.

The production of sugar crystals allowed assessment of the effect of juice preservation methods on their quality (i.e., color, shape and purity) and the assessment of

the quality of the intermediate products, such as the syrup, and the *massecuite* (i.e., mixture of crystals and molasses), and the final by-product (i.e., molasses).

After the juice was preserved, it was carbonated to a pH of 9, allowing the carbonatation sludge to be recovered. In this way, the juice was clarified. However, because the pH was still 9, carbonation of the clear juice was continued to a pH of 6.5 to 7.0. This is important because crystallization requires that the juice be boiled to remove water, and, as previously mentioned, at high temperatures, pH > 7.0 causes sucrose losses.

The bench-scale crystallization was done at the Audubon Sugar Institute (Baton Rouge, LA). After preservation and carbonatation, the clarified and neutralized juices from batches $B_{screened}$ and $B_{periodic}$ were poured into eight separate 1-gal jugs (four jugs for each batch), placed in Styrofoam coolers, and covered completely with dry ice for transportation from Texas to Louisiana.

Once in Louisiana, at the Audubon Sugar Institute, the juices were thawed and separately concentrated in a bench-scale forced-recirculation evaporator (Figure 3.27), which used a motor to drive an impeller, which provided the recirculation necessary for good heat transfer. The heat was provided to the system by steam. The evaporation temperature was 55^{o}C at a constant applied vacuum of 28 in Hg.

During the evaporation, foaming seemed to be higher than normal (Figure 3.27), but it was attributed to entrapped air from freezing, which was now being released. As evaporation continued, the foaming stopped.

Batches $B_{screened}$ and $B_{periodic}$ were concentrated from 13.3 and 16.1^{o} Brix to 60.5 and 67.8^{o} Brix, respectively.

At this point, the concentrated syrup from $B_{periodic}$ and a small sample of the syrup from $B_{screened}$ were stored in the refrigerator at 4^{o}C for further analysis of purity and cations. The crystallization process continued only with $B_{screened}$.

The amount of syrup was only about 1 gal, and it was further concentrated to supersaturation conditions in a small Rotavapor® at 70^{o}C.

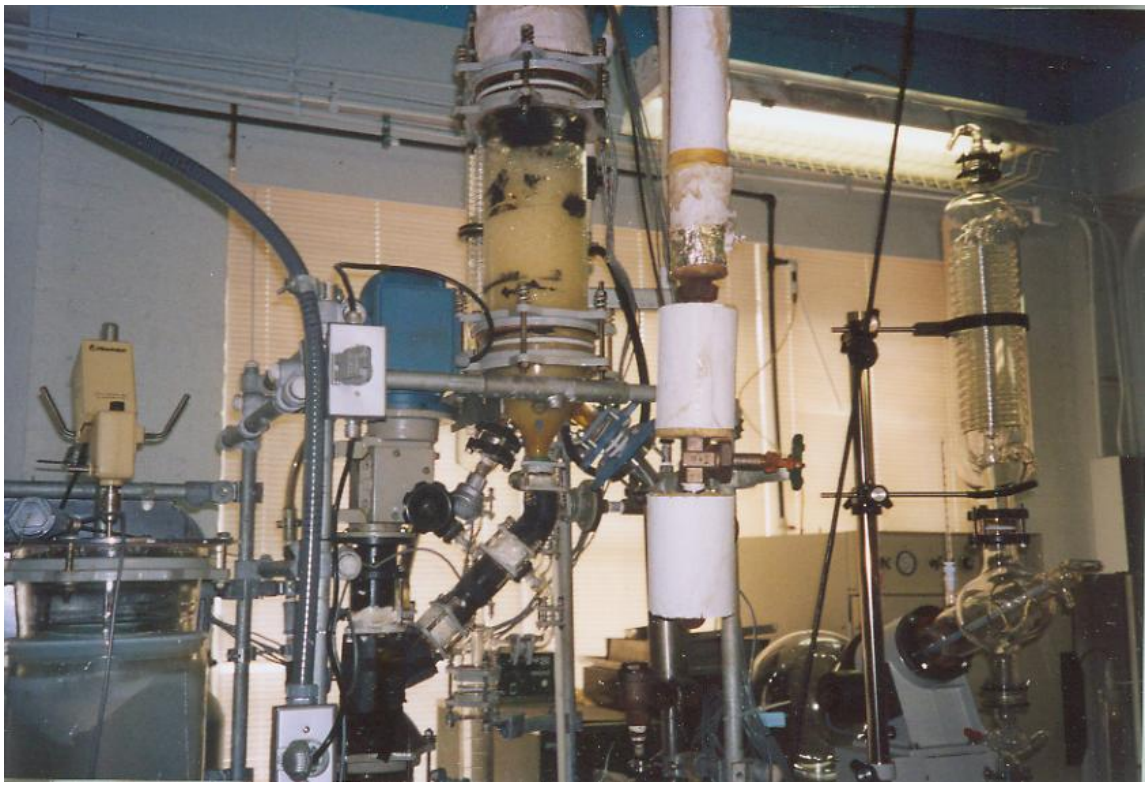


Figure 3.27 Bench-scale forced-recirculation evaporator (Audubon Sugar Institute).

At the point of supersaturation, seed crystals, which had been soaked in alcohol were supposed to be added. However, because of the little control that could be implemented at bench scale, spontaneous crystallization occurred; thus, seed crystals were not added.

The already-crystallizing *massecuite* (cooked mass) was transferred to a bench-scale crystallizer (Figure 3.28), equipped with an electric motor for driving the internal mixing mechanism (Figure 3.29), which ensured good mass transfer during crystallization. This mixer was set at a speed of about 10 to 15 rpm. The *massecuite* was placed in a jacketed vessel, which was mounted to the rest of the equipment using a cam-lock type fitting. To control temperature, water from a water bath, whose temperature was gradually decreased from 70^{o}C to 40^{o}C during the crystallization, was circulated through the jacket of the vessel. The crystallization was allowed to occur overnight.

Figure 3.28 Photograph of the bench-scale crystallizer (Audubon Sugar Institute).

Figure 3.29 Internal details of the bench-scale crystallizer (Audubon Sugar Institute).

The next day, the *massecuite* in the jacketed vessel was transferred to a centrifuge basket, which had been equipped with a typical separation screen used in the sugar industry. The crystals and molasses in the *massecuite* were thus separated by centrifugation (Figure 3.30).

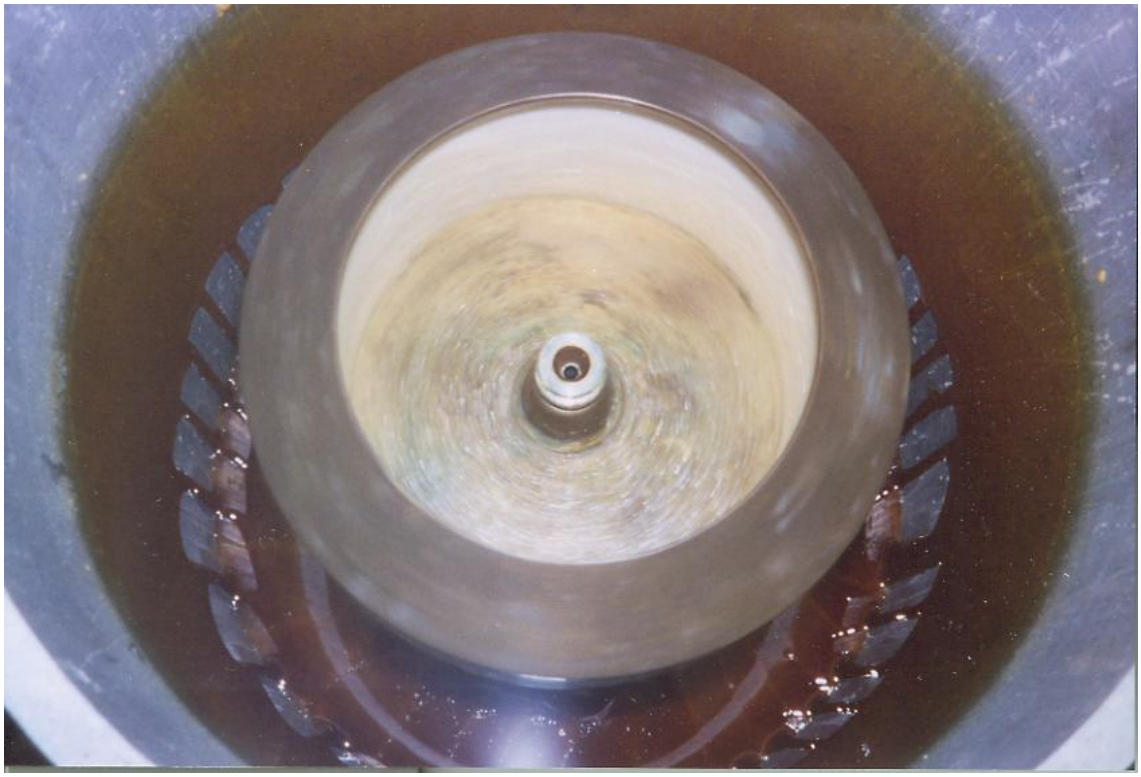


Figure 3.30 Photograph of the separation by centrifugation of sugar crystals from molasses in *massecuite* from preserved juice (Audubon Sugar Institute).

The resulting crystals left in the basket (Figure 3.31) were then transferred to a container and vacuum dried and then further analyzed for purity. The resulting molasses was also analyzed for purity.

In an industrial setting, the resulting molasses from the first crystallization or strike, known as A-molasses, still contains a high proportion of sugars that can be crystallized; therefore, it is used to build up other *massecuites* and repeat the crystallization procedure. This process is repeated once or twice more to exhaust the

molasses and recover as much sugar as possible. The crystallization was done only once in this bench-scale experiment; thus, the *massecuite* and molasses are of the A type only.

Figure 3.31 Photograph of centrifuge basket showing the crystals from preserved juice crystallization attached to its interior (Audubon Sugar Institute).

Samples of both syrups (i.e., from batch $B_{screened}$ and $B_{periodic}$) and molasses were stored in a refrigerator at 4°C until color measurements (ICUMSA, 1994) were performed. Sugar crystals were stored at ambient conditions and color measurements were performed on them as well. To assess any abnormality in their shape that might indicate the presence of substances interfering or affecting crystallization, the sugar crystals were observed under a microscope (Reichert 310, Reichert Scientific Instruments, Buffalo NY).

III.3.3.4 Quantitative Analysis

The sucrose and reducing sugars concentrations in thin juice was measured in duplicate by HPLC, using an ion-exchange calcium-based resin column (Bio-Rad HPX-87C, Bio-Rad Laboratories, Hercules CA), and a refractive index detector (Perkin Elmer Series 200, Perkin Elmer Life and Analytical Sciencies, Boston MA). To quickly assess juice concentration, a hand-held refractometer (0-32^{o} Brix, ASANUMA, Tokyo Japan) was used. However, it gave correct results only for low-pH (< 9.0) clarified juice. In juice at higher pH, dissolved lime contributed to the refractive index and the value was overestimated by about 3^{o} Brix. When the method required it, an Abbé refractometer (MARK II, Reichert Scientific Instruments, Buffalo NY), temperature-controlled at 20^{o}C, was used.

Quality assessment of some of the preserved juice was done by technicians at the mill in Santa Rosa TX. The parameters measured at the mill were, reducing sugars concentration (Lane and Eynon method), pol (polarimeter) and brix (Abbé refractometer).

The Audubon Sugar Institute (Baton Rouge LA) analyzed $B_{screened}$ and $B_{periodic}$, after being concentrated into a syrup, for brix (automatic digital refractrometer), and HPLC sucrose and reducing sugars concentrations (Bio-Rad HPX-87K column and a refractive index detector). In addition, the Audubon Sugar Institute measured the dextran concentrations in the thin juices of these two batches (monoclonal antibodies immunoassay).

The Audubon Sugar Institute also analyzed the resulting *massecuite*, molasses, and sugar crystals from the crystallization of $B_{screened}$ for brix, and HPLC sucrose and reducing sugars concentrations.

From these values, the purity of the juice, syrup, massecuite, and molasses can be found as follows:

$$\text{Pol purity} = \frac{\text{pol}}{\text{brix}} \tag{3.1}$$

$$\text{HPLC purity} = \frac{\text{HPLC sucrose}}{\text{brix}} \tag{3.2}$$

Pol purity (or refractometer purity) and HPLC purity are both a measure of the sucrose present in percentage of soluble solids (g sucrose/100 g soluble solids). Pol is a value close to the percentage of sucrose present (g sucrose/100 g total weight). HPLC sucrose is the true sucrose concentration (g sucrose/100 g of total weight). The brix is given in g optically active soluble solids/100 g total weight, which is very close to the true percentage of soluble solids present (as determined by drying) (Chen and Chou, 1993).

Reducing sugars degradation forms colorants known as HADP (hexoses alkaline degradation products) (Bento et al., 1999) and other melanoidin-type pigments, which are formed by reactions with amino acids present (Goodacre et al., 1978). These compounds have medium to high molecular weights and are moderately pH sensitive. Unfortunately, they are not easily removed by clarification methods, such as carbonatation or phosphatation, and decolorization techniques, such as bone char or ion exchange (Yu, 1998). However, both the degradation of reducing sugars and the formation of the colorants decreases with temperature, and colorant formation is very low at pH > 11.0 (Yu, 1998), which are the conditions of our preservation method. To further test the quality of the preserved juice for unusual substances that might interfere with crystallization and might cause colorant formation, the bench-scale crystallization described above was performed. Spectrophotometric measurements at 420 nm using a Spectronic 1001 spectrophotometer (Milton Roy Co., Riviera Beach FL) ascertained the colorant levels (ICUMSA, 1994) in the thin juice, syrup, molasses, and sugar crystals.

The presence of minerals is also an important parameter because high concentrations of some elements might interfere with crystallization. For instance, potassium chloride changes the morphology of sucrose crystals (Mathlouthi and Reiser, 1995). The analysis of minerals in preserved/clarified juice was done using an inductively coupled plasma emission spectrophotometer (ICP) at the Soil Testing Laboratory (Texas A&M University, College Station TX). HPLC cation concentrations

were measured on the syrups of $B_{screened}$ and $B_{periodic}$ at the Audubon Sugar Institute, using a Dionex IonPac CS12 (Sunnyvale CA) and a pulse electrochemical detector (PED).

To assess lime recovery from the bench-scale batches, it was necessary to find dry weight, organic contents, and calcination solids of the carbonatation sludge. An oven at 105°C and a muffle furnace at 575°C and at 915°C were employed in these tasks. A sample of sludge was analyzed for mineral constituency using ICP at the Texas A&M Soil Testing Laboratory (College Station TX). The sludge was also sent to Altex Technologies Corp., where they tested its suitability for the stationary lime kiln,

III.3.4 Results and Discussion

III.3.4.1 Sucrose Preservation in Thin Juice Batches

The main objective is to preserve sucrose in thin (i.e., low-concentration) juices; thus, the most important goal is to demonstrate that sucrose concentrations are maintained in the juice in the alkaline medium under normal ambient conditions. This objective has been demonstrated both in the preliminary studies (Section III.3.1) and in the literature (Lloyd et al., 1995; Williams and Morrison, 1982; Goodacre et al., 1978).

Seven batches were tested, four at the bench scale and three at the pilot scale, as described in Table 3.2. Figures 3.32 and 3.33 show the sucrose concentrations for the batches at bench scale and pilot scale, respectively as measured in duplicate by HPLC. The figures show that the preservation was successful, even for periods of almost a year, as was the case with $B_{filtered}$ and with $P_{no\text{-}prep}$ #2.

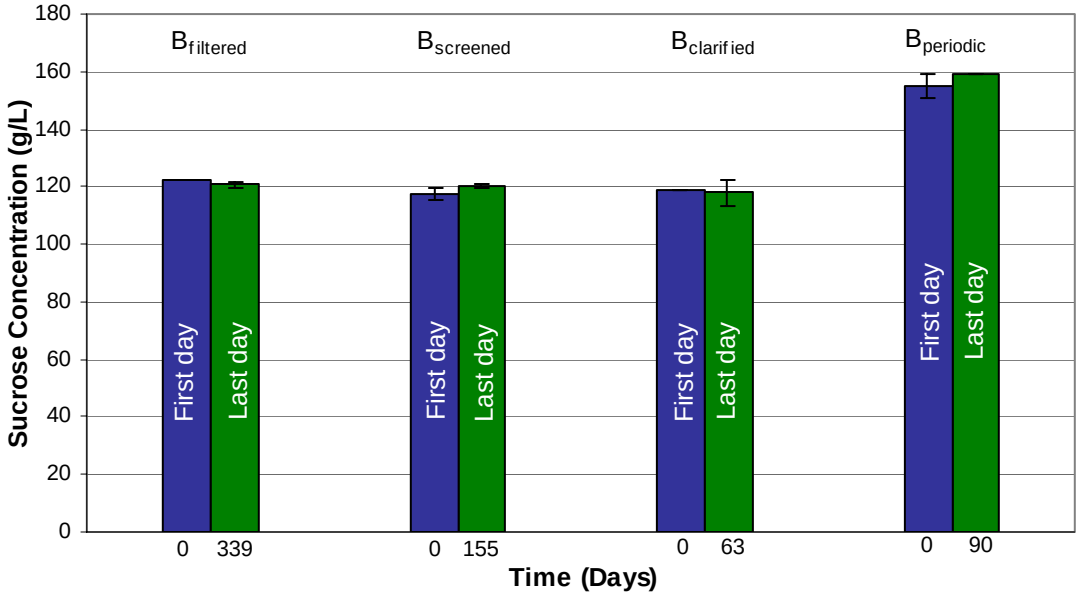


Figure 3.32 Sucrose concentrations in batches of juice preserved at bench scale (error bars = ± 1 standard deviation).

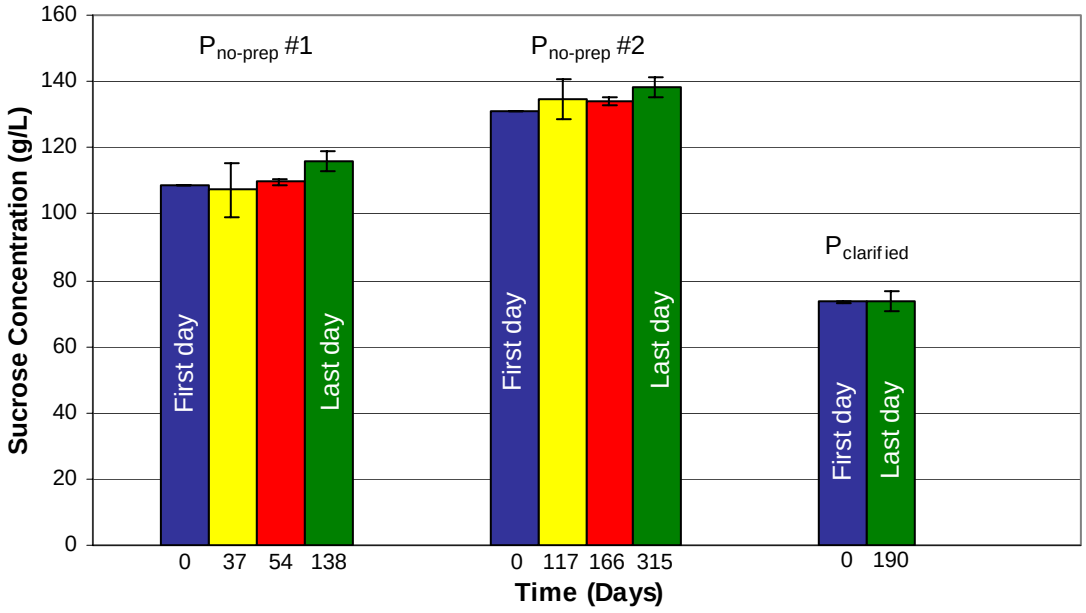


Figure 3.33 Sucrose concentrations in batches of juice preserved at pilot scale (error bars = ±1 standard deviation).

Experience has shown that for the preservation to be successful, mixing or recirculation must be implemented. Several small batches of juice were lost due poor mixing. This probably resulted from substances in the juice (e.g., minute bagasse particles) that degraded and produced acids, especially at the beginning of the preservation. When these acids were produced, they created microhabitats where the pH was low enough for bacteria to subsist. These bacteria produced acid, which further decreased the pH in their surroundings, which gave better conditions for more bacterial growth. This resulted in more acid production and thus more bacterial growth, causing an exacerbating effect that grew exponentially until they consumed the whole batch of sugar. When mixing or recirculation was implemented, acids produced from the degradation of these substances were immediately neutralized and the pH was kept high, giving no chance for bacterial growth.

Although keeping mixing or recirculation was imperative, it was hypothesized that intermittent mixing, as opposed to constant mixing, was enough to keep the pH high enough to avoid bacterial growth. To our good fortune, it was found that the sucrose concentration was also maintained for $B_{periodic}$, which was intermittently mixed. This is good news because it means that constant recirculation, which costs money because of energy consumption, is not necessary.

$P_{clarified}$ had a low sugar concentration because the day the juice was obtained from the mill they had to shut down for repairs and the juice in the settling tank was diluted.

III.3.4.1.1 Temperature effect on the preservation

The high pH at which the juice is preserved inhibits microbial growth. Although alkalophilic bacteria exist, which can live at pH as high as 13, these microorganisms are rare and are unlikely to proliferate in our process. The remaining concern is chemical degradation.

As mentioned previously, at high pH, high temperatures might chemically degrade sucrose.

In the case of $P_{no\text{-}prep}$ #2 and $P_{clarified}$, their preservation occurred during the summer. This is remarkable because it means that preservation was not affected by the high ambient temperatures encountered during a summer in Texas, where summer temperatures can range between 90°F (32°C) to even as high as 100°F (38°C) (www.weather.com).

The successful preservation of the two batches confirms our postulate formulated from the previously described correlation developed by Goodacre et al. (1978) using ^{14}C-U-sucrose, that suggests that even at pH > 11, at temperatures < 40°C (104°C), the chemical degradation of sucrose is nil. The correlation suggests that even at about 45°C, the degradation is slow (~3%/month).

To further assess the applicability of Goodacre's correlation to long-term exposure of sucrose to high pH and temperature, a simple experiment was devised. A portion of raw juice with the same industrial-lime (92% $Ca(OH)_2$) loading as used in all the batches (~0.29 lb/gal or 35 kg/m^3) was put in an incubator at 45°C (113°F) for 4 months. The juice was constantly mixed, and samples were withdrawn weekly. As a control, some of this same juice, with the same lime loading, was put in an incubator at 30°C (86°F), and samples were withdrawn monthly.

Figure 3.34 shows that, as expected, sucrose was preserved at 30°C, and that it degraded at 45°C at an average apparent zeroth-order reaction rate of 0.31 g/(L·day) or about 8%/month (8 g sucrose degraded/100g initial sucrose per month). This number is similar to the value of 3%/month from Goodacre et al. (1978), bearing in mind that this figure was an extrapolation of data collected from short-term experiments (hours), at higher temperatures (70 to 80°C), and at lower pH (11.1). The pH in our studies was ~ 12.

Alkaline sucrose degradation is a second-order reaction. Manley-Harris et al. (1980) suggest that when there is a constant concentration of hydroxyl ions or hydroxyl ions excess, which is the case for these studies, sucrose degradation presents pseudo-

first-order conditions; thus, this reaction at 45°C shows a pseudo-first-order rate constant of 0.00323±0.00021 $days^{-1}$ (error = ± 1 standard error).

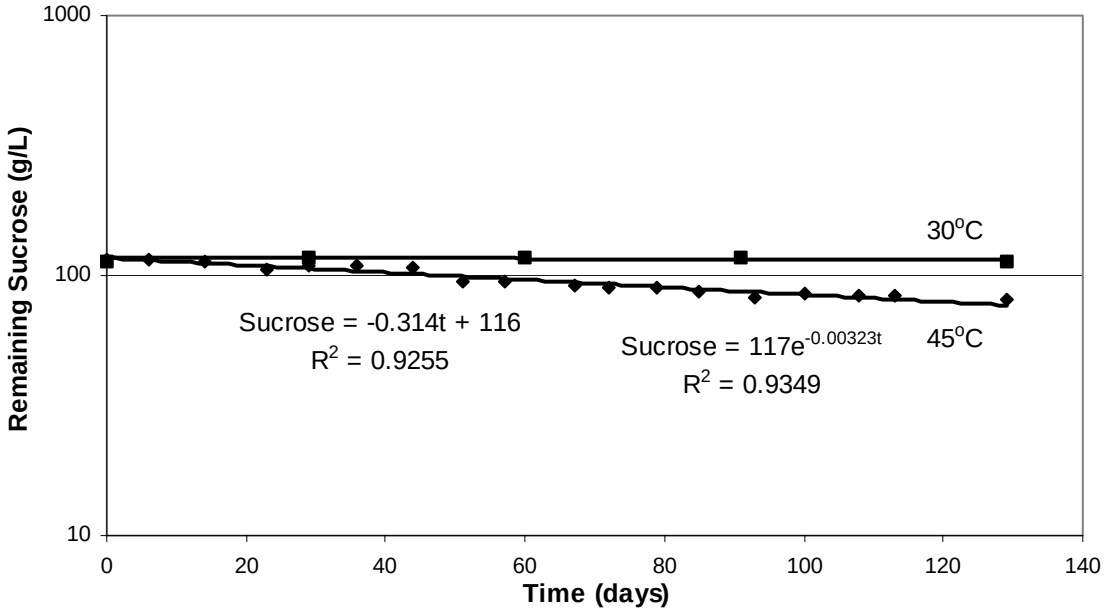


Figure 3.34 Sucrose concentrations as a function of time for sugarcane juice kept with lime at 45°C and 30°C.

III.3.4.2 Juice Quality Assessment

The sucrose concentrations were maintained at pH > 11 and temperatures < 40°C; thus, the preservation was proved successful. However, this would be useless if the quality of the juice deteriorates; therefore, it was imperative to determine other quality parameters of the resulting juice.

III.3.4.2.1 Purity and Reducing Sugar Levels in Thin Juices

Table 3.3 shows the purity (i.e., ~ g sucrose/100 g soluble solids) and the reducing sugar content (g reducing sugars/100 g total juice) for all the batches of

preserved/clarified juice. The brix (~ g soluble substances/100 g total juice) was determined using an Abbé refractometer or a digital refractometer. The Pol was determined by the technicians at the mill in Santa Rosa TX and it is expressed as ~ g sucrose/100 g total juice. HPLC-sucrose is the average of the values for the samples taken at different times during the preservation for each batch as reported previously in Figures 3.32 and 3.33. Because these values were reported as g sucrose/L of juice, they were converted to g sucrose/g total juice using Table 16 in page 998 of the Cane Sugar Handbook (Chen and Chou, 1993).

Table 3.3 Assessment of the purities and reducing sugar (R. S.) concentrations for all batches of preserved/clarified juice.*

Batch	Brix	Pol	Pol Purity	HPLC† Sucrose	HPLC Purity	L&E** R. S.	HPLC R. S.
$B_{filtered}$	14.3	11.86	82.9	11.6	81.1	0.27	N/D††
$B_{screened}$	13.3	N/M††	N/M	11.4	85.7	N/M	N/D
$B_{clarified}$	12.6	N/M	N/M	11.3	89.7	N/M	N/D
$B_{periodic}$	16.1	N/M	N/M	14.9	92.5	N/M	N/D
$P_{no\text{-}prep}$ #1	12.8	10.65	83.2	10.6	82.8	N/D	N/D
$P_{no\text{-}prep}$ #2	15.0	12.59	83.9	12.8	85.3	N/D	N/D
$P_{clarified}$	8.5	6.61	77.8	7.2	84.7	N/D	N/D

*All values are expressed as % on a weight basis
** Lane and Eynon detection method for reducing sugars
† Values in g sucrose/L were converted to % (g sucrose/100 g total juice) using Table 16 in Chen and Chou (1993)
†† N/M ≡ not measured; N/D ≡ below detection limits

The observed purities reported in Table 3.3 are typical of normal conventional clarified juice, which ranges between 80 to 90% (Wu, 2002). However, because of the alkaline conditions, there is destruction of reducing sugars.

In conventional juice, reducing sugars contribute to the refractive index when measuring brix by refractometer; therefore, the fact that the purity is normal in spite of the absence of reducing sugars, means that there are optically active soluble substances in the juice that have replaced the reducing sugars and can be detected by the refractometer. It is interesting to observe that the juice that was intermittently mixed had a higher purity than all the other batches.

III.3.4.2.2 Bench-scale Crystallization Products and By-products Analysis

The bench-scale crystallization of $B_{screened}$, described previously, yielded several products and by-products. Because only one crystallization was performed, they are of the A type. Their analysis is important to assess juice quality. These products follow:

1) Syrup, obtained from evaporative concentration of the clarified juice. Also, the juice from $B_{periodic}$ was concentrated, but no further treatment was done to this juice.
2) A-*massecuite* (i.e., cooked mass), the mixture of molasses and sugar crystals after crystallization.
3) A-molasses, which was separated from the sugar crystals by centrifugation.
4) Sugar crystals.

It is important to mention that the crystallization did not go completely as planned due to the little control that could be implemented at bench scale. As mentioned previously, uncontrolled supersaturation unexpectedly caused spontaneous crystallization. To produce good nucleation and avoid spontaneous crystallization, and thus obtain better yields and better quality crystals, crystallization must be seeded. Spontaneous crystallization forms twin crystals and crystal conglomerates that entrap impurities that should be eliminated by the crystallization (Mathlouthi and Reiser, 1995).

Nonetheless, even by visually inspecting the crystals it was obvious that their color was lower than conventionally obtained raw sugar from a defecation/clarification process (Chapter I).

III.3.4.2.2.1 Purity and Reducing Sugar Concentrations

Table 3.4 shows the HPLC purity and HPLC reducing sugars for the products and by-products of the bench-scale crystallization. The brix values were found using a digital refractometer and the HPLC sucrose levels and reducing sugar level were found using a HPX-87K Bio-Rad, ion exchange column (Bio-Rad Laboratories, Hercules CA). The units for each measurement follow:

- Brix ≡ g soluble solids/100 g total juice
- HPLC sucrose ≡ g sucrose/100 g total juice
- Purity ≡ g sucrose/100 g soluble solids
- HPLC reducing sugars ≡ g reducing sugars/100 g total juice

Table 3.4 Purity and reducing sugar (R. S.) levels for products and by-products of the bench-scale crystallization*.

Batch	Brix	HPLC Sucrose	HPLC Purity	HPLC R.S.
$B_{screened}$-syrup	60.5	50.1	82.9	N/D**
$B_{periodic}$-syrup	67.8	61.4	90.6	N/D
$B_{screened}$-A-*massecuite*	86.8	74.2	85.4	N/D
$B_{screened}$-A-molasses	76.6	57.4	74.9	N/D
$B_{screened}$-crystals	100.0	99.4	99.4	N/D

* All values are expressed in % on a weight basis
** N/D ≡ below detection limits

Due to mass conservation, one might be tempted to think that the purity of the thin juice, syrup and *massecuite* should always be the same, but this is not necessarily the case (Hugot, 1986). In fact, sometimes the purity decreases in the evaporator (e.g., if there is inversion that increases reducing sugars and decreases sucrose). Alternatively, there might be an increase in purity (e.g., from the elimination of certain gases) or an apparent rise in purity (e.g., due to transformation of reducing sugars).

The purity of the thin juice for $B_{screened}$ *and* $B_{periodic}$ (Table 3.3) and the purity of their respective syrups (Table 3.4) differ slightly (i.e., ~2% lower in the syrup). This could be due possibly to inversion of sucrose to glucose and fructose, followed by their destruction as no glucose or fructose were detected. Inversion and destruction of reducing sugars occurs if pH > 7.5 (Chen and Chou, 1993). This could have resulted from inefficiencies when the clarified juice was carbonated to neutrality. Mass transfer of carbon dioxide to an aqueous solution is very poor near neutrality; therefore, unless the carbonation occurs for long enough, at adequate conditions with an effective agitator, the juice pH might rise again, especially under boiling conditions where undissolved carbon dioxide can be easily released.

To confirm if pH increased during evaporation, the pH of the syrup and the A-*massecuite* from $B_{screened}$ were measured and were found to be 8.12 and 7.99, respectively, demonstrating that pH in fact did rise. The conditions in the bench-scale evaporator were mild (55^{o}C), but in an industrial setting, where temperatures might be higher, the situation might worsen; therefore, improving carbonation efficiency is imperative. Adding sulfur dioxide (SO_2) is another common alternative that could be used for the last stage of neutralization (Chapter I). Because of its acidity, SO_2 is a better neutralizing agent than CO_2 near pH 7, and its use improves clarification; however, the United States limits the residual SO_2 in food products (10 ppm according to the USFDA), so its use is rather restricted.

The purity of the A-*massecuite* for $B_{screened}$ was higher than that of the syrup, and compares better with the purity of its correspondent thin juice purity. This could have resulted because the temperature to attain supersaturation in the Rotavapor® was 15^{o}C

higher than the temperature in the evaporator; therefore, the different conditions might have caused different events, such as destruction of optically active degradation products of reducing sugars. In fact, because the syrup pH was high, the degradation products of reducing sugars under these conditions may continue to degrade further either to color or to carbon dioxide that leaves the solution (Klinke et al., 2002).

Nonetheless, the purities of the syrup and A-*massecuite* are comparable to typical values for these parameters (~80 to 85% purity). In an industrial setting, the A-massecuite results from footing (combination) of syrup and magma. The magma is formed by mixing sugar crystals from the last crystallization with syrup and it has a higher or similar purity to the syrup entering the first crystallizer (Hugot, 1986). Also, the purity of the sugar crystals is slightly higher than typical raw sugar, which is about 98.5 % for sugars from the first strike (A-*massecuite*).

The purity of the obtained A-molasses is high. Expecting a normal purity drop of about 18-20 points for the first crystallization (Hugot, 1986), the typical value for the purity of A-molasses should have been about 65%.

The weight percent of crystals in the *massecuite* is computed as follows (Chen and Chou, 1993; Hugot, 1986):

$$x = P_s \cdot \frac{B_m}{100} \cdot \frac{P_m - P_e}{P_s - P_e} \tag{3.3}$$

where

x	=	% Crystals, g sugar crystals/100 g *massecuite*, %
P_s	=	Sugar crystals purity, g sucrose/100 g sugar crystals, %
B_m	=	*Massecuite* brix, g soluble solids/100 g *massecuite*, %
P_m	=	*Massecuite* purity, g sucrose/100 g soluble solids in *massecuite*, %
P_e	=	Molasses purity, g sucrose/100 g soluble solids in molasses, %

Thus, the *massecuite* was formed of 37.0% (w/w) crystals and 63.0% (w/w) molasses; or, expressed on a brix of *massecuite* basis, it becomes 43% crystals on brix of *massecuite.* This number is low compared with typical values, which are in the order of 45 to 65% on brix for the A-*massecuite* (Hugot, 1986).

The *massecuite* exhaustion (Hugot, 1986) also measures the crystallization efficiency expressed as weight of crystals recovered per amount of sucrose present (i.e., yield). This parameter is calculated as follows:

$$E_m = P_s \cdot \frac{100}{P_m} \cdot \frac{P_m - P_e}{P_s - P_e} \tag{3.4}$$

where

E_m = *Massecuite* exhaustion, g crystal/100 g sucrose in *massecuite*, %

The value for E_m was 49.9%, which is also low because it should be 60 to 65% for the A-*massecuite*.

The small purity drop in the molasses and, consequently, the low *massecuite* exhaustion can be attributed to the crystallizer conditions, mainly to the poor control and the spontaneous crystallization. In addition, as it was shown, due to carbonation inefficiencies, the pH rose during evaporation, which also makes crystallization more difficult and inefficient.

The destruction of reducing sugars during preservation is a concern. Reducing sugars prevent the loss of a corresponding quantity of sucrose to molasses (i.e., in the absence of reducing sugars, sucrose takes their place in the molasses) (Hugot, 1986); however, with only one strike, and the poor process conditions in the experiment, it is hard to pinpoint the extent of sucrose losses. The carbonatation must be improved and pilot studies of the crystallization process, where two or more crystallization steps are performed, must be undertaken to obtain realistic values for molasses exhaustion.

It is important to mention that the juice had a high potassium and calcium content from cane and from inefficiencies in the carbonatation, respectively, as it will be seen later in Section III.3.4.2.5. High concentration of these elements might also cause sucrose losses to molasses (Chen and Chou, 1993). Nonetheless, purity drops for the A-*massecuite* at the W.R. Cowley Sugar House (Santa Rosa TX), from where the juice was obtained, are normal (~ 20 points) in spite of their high potassium levels (Wu, 2004).

III.3.4.2.2.2 Sugar Crystals Characteristics

Because spontaneous crystallization occurred, the crystals were smaller than those obtained from the conventional process, which uses seeding. Spontaneous crystallization also caused conglomeration (Figure 3.35) and promoted the formation of twin crystals (Figure 3.36).

However, some single crystals did form (Figure 3.37) and allowed assessment of abnormalities in shape and surface that might indicate the existence of foreign substances that interfere with the crystallization or affect the quality of the crystallized sugar.

The crystals shown in Figure 3.37 presented the typical characteristic D-shape of normal sucrose crystals. They were not elongated (as in the presence of dextrans), or tapered (as in the presence of raffinose). In the presence of certain salts, the surface of the crystal is altered (e.g., potassium chloride, which enlarges the d-face of the crystal) (Mathlouthi and Reiser, 1995), but the faces of theses crystals appeared to be normal.

III.3.4.2.3 Color Assessment

As mentioned previously, the degradation of reducing sugars and their reaction with amino acids present in the juice sometimes develop colorants that are difficult to remove by conventional clarification processes. The objective of this analysis was to ascertain if the clarified juices obtained from the different batches of preserved juice,

and the products and by-products from the bench-scale crystallization, presented high colorant levels that might render the preservation process unfeasible, even when sucrose concentrations are maintained.

Color was measured at 420 nm and at neutral pH using the ICUMSA standard method (ICUMSA, 1994), which yields a uniform measure of color regardless of the concentration of the original sample.

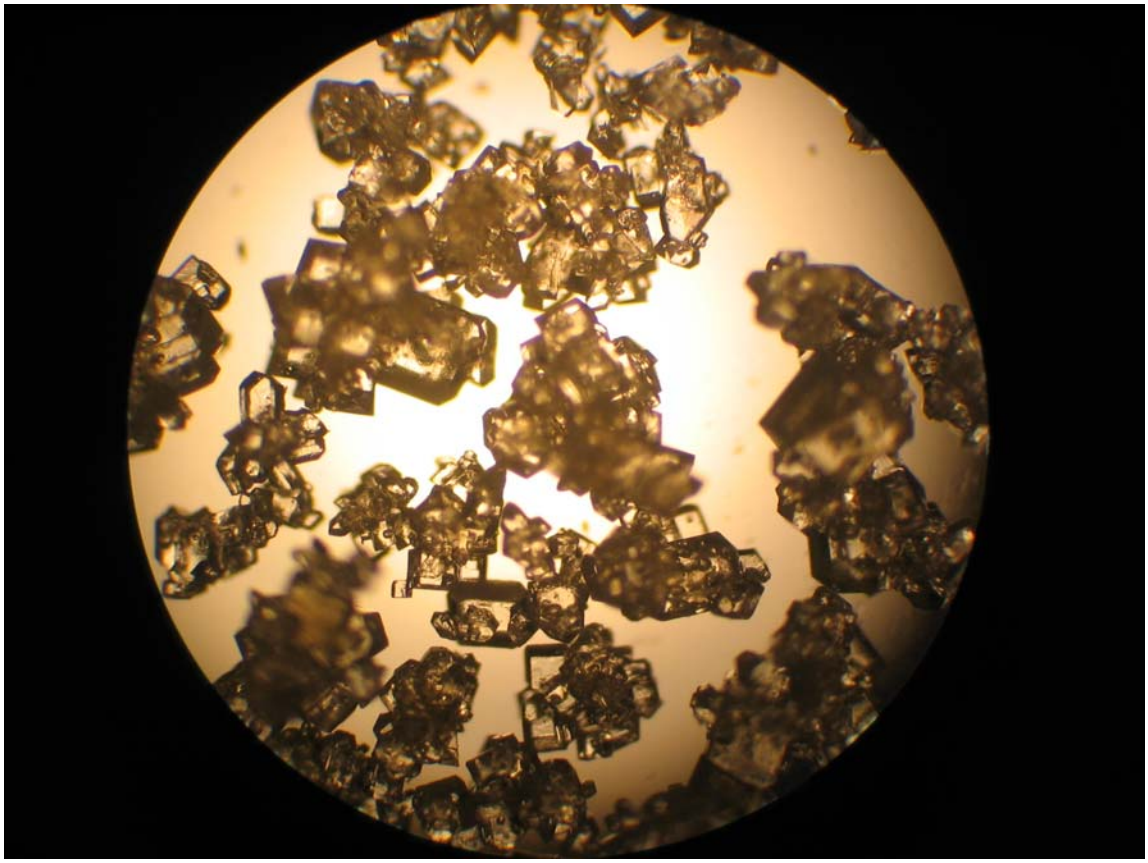


Figure 3.35 Micro-photograph of conglomerates from preserved juice crystallization. Conglomerates are typical of spontaneous crystallization.

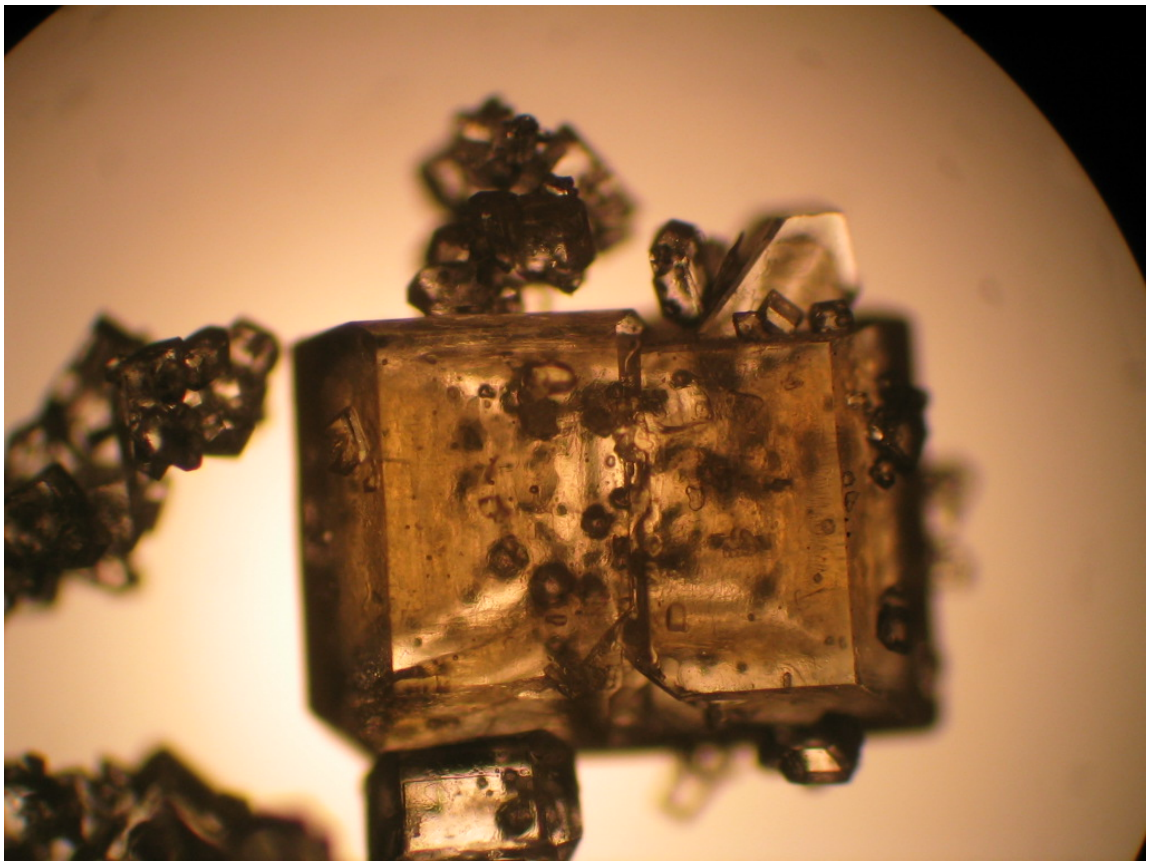


Figure 3.36 Micro-photograph of a twin crystal from preserved juice crystallization. As with conglomerates, twin crystals are common when spontaneous crystallization occurs.

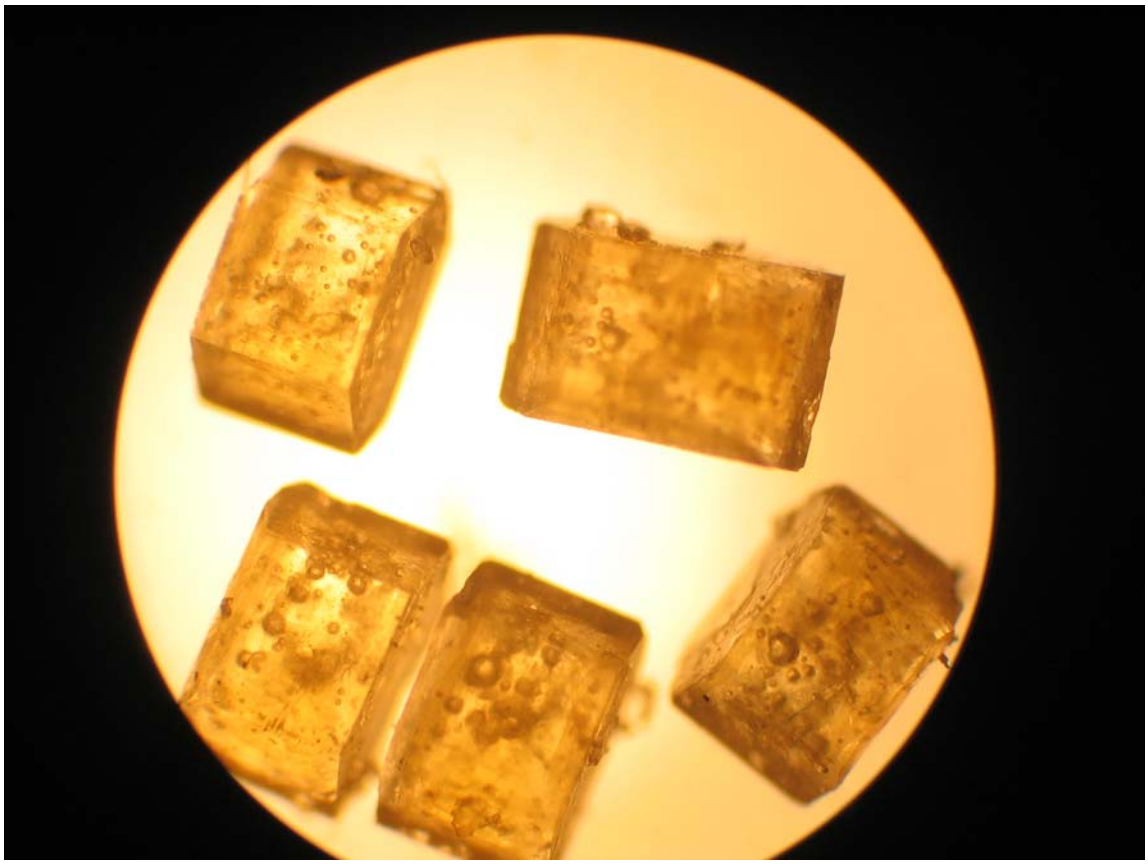


Figure 3.37 Micro-photograph of single crystals from preserved juice crystallization.

Table 3.5 shows the ICUMSA 420 color for all the batches of preserved juice after clarification. For comparison, samples of clarified juice by defecation from the W. R. Cowley Sugar House in Santa Rosa TX, the original source of juice used in the preservation, were also analyzed for color.

In general, the objective of these analyses was to show that the juice does not develop excessive color as might occur from certain undesirable conditions during sugar processing. In those cases, the juice is rendered useless, and the batch is lost. From this perspective, the color values obtained show that the preserved juice color is comparable to, or even lower than conventionally obtained clarified juice, confirming the success of the preservation.

Table 3.5 ICUMSA 420 color for all the batches of preserved juice after clarification and for clarified juice from mill.

Juice Batch	ICUMSA 420 Color*
$B_{filtered}$	N/M**
$B_{screened}$	5280
$B_{clarified}$	5100
$B_{periodic}$	7120
$P_{no\text{-}prep}$ #1	6700
$P_{no\text{-}prep}$ #2	6660
$P_{clarified}$	2570
Clarified juice from mill (time 0 for $P_{clarified}$)	10120
Clarified juice from mill	9480

* Expressed in ICUMSA units (IU)
** N/M = not measured

Nonetheless, several other observations can be made as follows:

1) $B_{screened}$ and $B_{clarified}$ show about the same color. $B_{screened}$ was preserved as raw juice and then clarified by carbonatation (i.e., carbonation followed by filtration of sludge) at the end of the preservation period, whereas $B_{clarified}$ was clarified by carbonatation before preservation, and then carbonatated again at the end of the preservation period. The results from the color measurements suggest that carbonatating twice will not decrease color significantly.
2) $B_{periodic}$ shows a higher color than $B_{screened}$ and $B_{clarified}$, which might suggest color development due to a lack of mixing. Because the purity of $B_{periodic}$ (Table 3.3) is

higher, it can be hypothesized that the rise in purity is due to the transformation of non-sucrose substances into colorants, that otherwise would contribute to the refractive index for brix measurement. Further tests are necessary to confirm this hypothesis.

3) $P_{no\text{-}prep}$ #1 and $P_{no\text{-}prep}$ #2, which were preserved under exactly the same conditions (i.e., outdoors, no preparation before preservation, etc.), have virtually the same value for color, which suggests good repeatability.
4) $P_{no\text{-}prep}$ #1 and $P_{no\text{-}prep}$ #2, which were preserved with the *bagacillo* or *cush cush* as obtained from the mill and were preserved outdoors, have slightly higher color than the bench scale batches. This suggests that the degradation of *bagacillo* causes a slight increase in color and its removal must be considered. This is standard practice in the sugar industry, where screens separate the *bagacillo* or *cush cush*. Based on these results, the difference in color cannot be attributed to temperature. $P_{no\text{-}prep}$ #1 was preserved during the winter. Its average temperatures were lower than the bench-scale batches, which were preserved indoors at an average temperature of 23°C, and much lower temperatures than $P_{no\text{-}prep}$ #2, which went through a Texas summer.
5) $P_{clarified}$ shows the lowest color (2570 IU), with a tremendous decrease from its starting juice, which was clarified by defecation at the mill (10120 IU). This suggests that defecation followed by carbonatation is a very efficient way to clarify juice.
6) From the color values, it is obvious, that even though our carbonatation of preserved juice was not optimized, it is more efficient than conventional defecation. The difference was in average about 3300 IU.

Table 3.6 shows the ICUMSA 420 colors for the products and by-products of the bench-scale crystallization of $B_{screened}$, for the syrup of $B_{periodic}$, and from a sample of typical sugar crystals obtained from defecation-clarified juice at the W.R. Cowley Sugar House.

Table 3.6 ICUMSA 420 color for the products and by-products of the bench-scale crystallization and of conventional raw sugar.

Crystallization Product or By-product	ICUMSA 420 Color*
$B_{screened}$-syrup	5900
$B_{periodic}$-syrup	7830
$B_{screened}$- A *massecuite*	N/M**
$B_{screened}$- A molasses	11340
$B_{screened}$-crystals	1820
Mill raw sugar crystals	2770

* Expressed in ICUMSA units (IU)
** N/M = not measured

The colors of the syrups are normal, although they increased slightly during concentration, as it can be seen when comparing the color values for the juices in Table 3.5, and syrups in Table 3.6 for both $B_{screened}$ and $B_{periodic}$.

The sugar crystals from $B_{screened}$ have a lower color than conventionally obtained raw sugar from juice clarified by defecation. This could be attributed mostly to the clarification process employed (i.e., carbonatation), which, even when it is inefficient, is more effective. When compared to a conventional efficient carbonatation process, which is standard practice for producing white sugars directly from cane (ICUMSA 420 color of 50 – 150 IU), then, obviously, the sugar color obtained from $B_{screened}$ is high.

There are several reasons why the sugar color from the bench-scale crystallization is considerably higher than that obtained in conventional carbonatation.

1) As mentioned, the carbonatation process is not optimized and it was performed in a slightly different way. The carbonatation for these studies occurred at ambient temperature by carbonating to a pH of 9.0±0.2, which is the pH at which calcium

carbonate recovery is maximized, then filtering and carbonating to neutrality. In conventional carbonatation, sometimes there are two or more steps in which the juice is carbonated, filtered, and then limed again (Chapter I). The filtration sometimes occurs around pH 10, and then again around pH 8.5. The process is highly controlled, and it occurs at higher temperatures to make it more efficient (Hugot, 1995; Chen and Chou, 1993; Honig, 1953). In fact, cold juice carbonatation used in these studies was the original single carbonatation, which can now be considered ancient, and was discontinued around 1915 due to its inefficiencies (Honig, 1953). Also, sometimes carbonatation is combined with sulphitation, which does an excellent job in removing color (Valdes Delgado and de Armas Casanova, 2001**)**.

2) The pH increase during evaporation, due to inefficiencies in the final carbonation to neutrality, could have also caused color development. As shown in Tables 3.5 and 3.6, the color increased slightly in the syrups, but the temperature during that part of the evaporation was only 55^{o}C. The questionable evaporation occurred in the Rotavapor® at 70^{o}C. To confirm this, the color of the *massecuite* is required. Although this color was not measured, an approximation can come from the fraction of crystals and molasses present in the *massecuite*. From the purities, the *massecuite* was found to be 0.37 g crystals/g *massecuite* and 0.63 g molasses/g *massecuite*. Multiplying each fraction by the color found in the sugar and the molasses, respectively, we get a value of 8960 IU, which does in fact represent an increase from clarified juice and syrup.
3) The high pH (~8), which existed during the preserved juice crystallization, makes crystallization more difficult and inefficient.
4) Spontaneous crystallization, which occurred in these studies, promoted the excessive formation of conglomerates and twin crystals. Conglomerates and twin crystals entrap impurities where they fuse and do not allow for proper purification of sucrose. In contrast, when good seeding is provided, only single crystals form, which do not entrap impurities (Mathlouthi and Reiser, 1995).

5) Because the crystals were small, they were not washed after centrifugation; therefore, some of the molasses was not removed from the surface, as would occur in an industrial setting. In fact, without washing it is not possible to produce commercial sugar of acceptable quality (Hugot, 1995).

Figure 3.38 shows conventional raw sugar from the W. R. Cowley Sugar House (juice clarification by defecation) and the sugar obtained from the bench-scale crystallization of $B_{screened}$ (juice clarification by carbonatation at ambient temperature). Visual inspection clearly shows that the color is lower for the crystals from $B_{screened}$.

Figure 3.38 Photograph of conventional mill raw sugar, ICUMSA 2770 (left) and sugar from preserved juice, ICUMSA 1820 (right).

Most sugar plants that use conventional carbonatation as their juice clarification method produce white sugar directly from cane (skipping raw sugar). In our case, as

mentioned, although the color is lower than raw sugars obtained from clarification by conventional defecation, the sugar crystals are not considered white sugar as obtained from optimized carbonatation processes. The higher color in the sugar crystals from $B_{screened}$ compared to the white sugar obtained from conventional carbonatation processes cannot be attributed only to one of the reasons mentioned above, but it is rather a combination of all of at least most of them.

III.3.4.2.4 Dextran Levels

Dextran, also known as α-1,6 polyglucose, is a soluble polymer of glucose. It is produced by microorganisms during most stages of sugar production, especially within the cane itself and extracted juices. In juice, it is normally formed from sucrose degradation by microorganisms, such as *Leuconostoc mesenteroides*. This results in the loss of sucrose and an increase in molasses (Chen and Chou, 1993).

Table 3.7 shows the dextran concentrations in two different bench-scale batches, $B_{screened}$ and $B_{periodic}$, as determined by monoclonal antibody immunoassay at the Audubon Sugar Institute (Baton Rouge LA).

Table 3.7 Dextran concentrations for bench scale batches $B_{screened}$ and $B_{periodic}$.

Sample	Brix	Dextran (ppm)	Dextran (ppm/brix)
$B_{screened}$	13.3	53	401
$B_{periodic}$	16.1	5.0	31

Dextran levels are normally reported as ppm on brix. Typical dextran levels in sugar mills are 500 to 1000 ppm/brix and they can go as high as 20,000 ppm/brix (Chen and Chou, 1993). The values reported in Table 3.7 show that the dextran concentrations in the preserved batches are very low. This is an expected result for two reasons: 1) The

high pH inhibits microorganisms, including those that produce dextran, 2) The high pH degrades reducing sugars, including polymers of reducing sugars, such as dextran. In fact, the preservation will actually decrease the amount of dextran that comes from cane itself.

III.3.4.2.5 Mineral Profiles

The mineral profile of the juices is important because some elements can adversely affect crystallization, recovery, and sugar quality. In general, high concentrations of inorganic non-sugars (particularly potassium) have a melassigenic effect, that is, they will take sucrose to molasses causing losses (Chen and Chou, 1995). Also, certain minerals (e.g., high concentrations of magnesium) will increase the molasses viscosity, which causes mechanical problems in the crystallizer and can also lead to losses (Mathlouthi and Reiser, 1995).

Table 3.8 gives the mineral constituents of the batches of juice preserved at pilot scale after clarification by carbonatation as determined by inductively coupled plasma emission spectrophotometry (ICP) (Soil Testing Laboratory, College Station TX). As a comparison, Table 3.8 also shows the mineral profiles of juice samples as obtained from the mill (W. R. Cowley Sugar House, Santa Rosa TX). These samples were as follows: 1) raw juice, 2) juice clarified by conventional defecation by the mill, and 3) the juice also clarified by conventional defecation by the mill, which was time 0 for $P_{clarified}$. The average typical ranges of certain minerals for juice clarified by defecation, as cited by Chen and Chou (1993), are also included in Table 3.8.

Table 3.8 Mineral constituents of preserved juice pilot batches, raw juice and clarified juice by defecation[†].

Batch	Brix	Na	Mg	P	S	K	Ca	Mn	Fe	Cu	Zn
$P_{no\text{-}prep}$ #1	12.8	977	445	39.1	4172	15805	12320	0.7	12.3	0.7	2.0
$P_{no\text{-}prep}$ #2	15.0	560	793	33.3	3820	15213	9527	0.3	6.7	1.4	1.7
$P_{clarified}$	8.5	1988	765	23.5	3489	14435	23471	0.4	2.5	4.7	0.4
Juice clarified by defecation from mill (time 0 for $P_{clarified}$)	8.5	2471	729	235	4886	12576	3938	3.1	8.6	0.5	3.4
Juice clarified by defecation from mill	14.6	671	507	295	5055	13616	1299	1.2	2.1	0.2	1.6
Raw juice from mill	16.0	594	475	1350	3925	11506	1275	9.8	17.9	1.8	12.1
Range in clarified juice by defecation*		200 –700	1200 –2400	100 –400	600 –1800	2500 –8300	1900 –3900	N/R	70 –200	N/R[††]	N/R

[†] Values reported in ppm/brix, (mg element/1000 g total juice)/(g soluble solids/g total juice)
[††] N/R ≡ Not reported
* From Chen and Chou (1993)

All the soluble minerals are ionic (e.g., Ca^{++}, PO_4^{3-}, $SO_4^{=}$, Na^{+}, etc.). However, ICP reports the concentration of the elements themselves present in the ions (e.g., Ca, P, S, Na, etc.). The ICP element concentration is the same as the ion concentration for metals (i.e., Ca^{++}, Na^{+} and other cations) and some non-metals such as chlorine and its ion, Chloride (Cl^{-}), but for other non-metals (e.g., phosphorus, etc.), stoichiometric computations must be done to find the actual ion concentration (i.e., PO_4^{3-}, and other anions). In the case of some anions, such as those sulfur-based (i.e., sulfate ($SO_4^{=}$) and sulfite ($SO_3^{=}$)), ICP cannot distinguish between them. In addition, ICP will also account for the sulfur present in other compounds, such as the amino acid cysteine.

It can be observed that the mineral concentrations behave as expected. Phosphorus (i.e., phosphate (PO_4^{3-})), magnesium, manganese, and zinc are partially removed by the clarification as reported by Chen and Chou (1993). The preservation and subsequent carbonatation is more effective than the conventional defecation process, especially in removing phosphate and manganese.

The concentrations of potassium and sodium are maintained because these compounds are not removed by the clarification process (Chen and Chou, 1993). The concentration of sulfur (i.e., sulfate and/or sulfite and/or cysteine) is high compared to the values reported from Chen and Chou (1993) in Table 3.8. This is expected because the values from Chen and Chou (1993) are the stochiometric levels for sulfate alone. It can be observed that the ICP sulfur levels for the preserved juices are similar to the levels from the raw and clarified juice obtained from the mill. The potassium concentration is high, but this is due to the nature of the raw juice itself. The soils in the Rio Grande Valley, where the juice was obtained, are alkaline; therefore, they produce cane with high potassium content (Chen and Chou, 1993).

The calcium concentrations, as expected, are higher than those in the raw juice and the juice clarified by conventional defecation by the mill. In addition to the fact that the carbonatation was not optimized, some carbonatation and sulphitation processes yield higher calcium concentrations. For instance, Ghosh et al. (2000) report calcium concentrations in juice clarified by a sulphitation process of 6000 – 7000 ppm/brix.

The calcium concentration for $P_{clarified}$ is higher than that of $P_{no\text{-}prep}$ #1, and this is higher than that of $P_{no\text{-}prep}$ #2. This disparity can be explained by two reasons: 1) the results are reported on a brix basis and their brix concentration (Table 3.8) was different (i.e., $P_{clarified} < P_{no\text{-}prep}$ #1 $< P_{no\text{-}prep}$ #2), but all of them were saturated solutions of calcium carbonate, and 2) the solubility of calcium carbonate varies with sugar concentration, reaching a peak at about 10% (10 g sucrose/100 g of juice) (Chen and Chou, 1993). Of the three batches, $P_{clarified}$ is closest to this sucrose concentration, which explains why it has the highest calcium concentration. $P_{no\text{-}prep}$ #1 sucrose concentration is closer to 10% than $P_{no\text{-}prep}$ #2, which explains why the former has a higher calcium concentration than the latter.

Except for calcium, the concentrations of all mineral constituents were comparable to, or lower than, those found in the juice clarified by conventional defecation from the W. R. Cowley Sugar House (Santa Rosa TX).

Table 3.9 shows several mineral constituents found in the syrups concentrated from the bench-scale batches $B_{screened}$ and $B_{periodic}$ as determined by HPLC using a Dionex IonPac CS12 column and a pulse electrochemical detector at the Audubon Sugar Institute (Baton Rouge LA). The observations are essentially the same. Potassium and calcium concentrations are higher than normal due to the nature of the sugarcane from which the juice was obtained, and the use of the unoptimized carbonatation as the clarification method, respectively.

The ammonium levels are below detectable limits. This is not surprising because at the alkaline pH the juice was preserved, all the ammonium ions become ammonia, which easily evaporates. Ammonia would also be produced from protein degradation, which also occurs at high pH. This effect was observed in the pilot-scale batches, where sometimes ammonia smells were detected.

It is important to mention that the melassigenic effect due to the high concentrations of potassium and calcium (especially potassium, which is considerably excessive) could have also contributed to the low purity drop and the low *massecuite* exhaustion of the preserved juice crystallization (Section III.3.4.2.2.1).

Table 3.9 Mineral constituents for the syrups from $B_{screened}$ and $B_{periodic}$[†].

Batch	Brix	Sodium	Ammonium	Potassium	Magnesium	Calcium
$B_{screened}$-Syrup	60.5	869	<0.8	19637	501	9289
$B_{periodic}$-Syrup	67.8	583	<0.7	22026	428	6737
Syrup from juice clarified by defecation*		150 –300	N/R[††]	5810 –8300	180 –1930	2500 –2640

[†] Values reported in ppm/brix, (mg element/1000 g total juice)/(g soluble solids/g total juice)
[††] N/R ≡ Not reported
* From Chen and Chou (1993)

III.3.4.3 Carbonatation Sludge Recovery and Treatment

III.3.4.3.1 Experiences with sucro-carbonate of lime

When a solution containing sucrose is limed to pH > 11, and then is carbonated to decrease its pH to recover the lime as calcium carbonate, there is a pH range that forms a complex called the sucro-carbonate of lime. Its chemical formula follows:

$$C_{12}H_{12}O_{11} \cdot 3\,CaCO_3 \cdot 2\,Ca(OH)_2$$

According to Chen and Chou (1993), in a carbonatation process, liming should not exceed pH 11 to avoid this insoluble and viscous complex, which can cause sucrose losses in the carbonatation sludge filter cake. However, Hugot (1986) suggests that the sucro-carbonate of lime dissolves after a period of time as pH is decreased during carbonation; thus avoiding losses.

Due to this seemingly contradictory information, a simple test was performed to simulate the carbonatation conditions employed in these studies to determine if sucrose was lost to the carbonatation sludge at the filtration pH.

For this study, ACS reagent-grade sucrose (EM Science, Gibbstown NJ) was used to prepare a sucrose solution of approximately 15^{o} Brix. A sample was taken for HPLC analysis of the sucrose concentration.

The solution was transferred to a beaker and placed on a magnetic stirrer for constant mixing. Certified 99.3% calcium hydroxide (Fisher Scientific Co., Pittsburgh PA) was added to the solution in about the same proportion as it was added in the preservations studies (i.e., ~0.29 lb/gal or 35 kg/m^3). At this point, another sample was taken for HPLC analysis. A pH meter (ORION™, Orion, Inc., Boston MA) was used to monitor the pH. The starting pH of the solution was 12.30.

A small diffuser stone (Fisher Scientific Co., Pittsburgh PA) was used to bubble carbon dioxide into the solution. At the beginning, the pH decreased slowly. The solution was not viscous, attaining good mixing. At pH ~ 11.5, a gel-like, viscous substance formed. The viscosity of the solution increased and stirring became difficult. This substance is known as sucro-carbonate of lime. It was also observed in all the carbonatations performed in these studies, at both bench and pilot scale. At pH 11.40, while this substance was still present, another sample was withdrawn for HPLC analysis.

The substance seemed to dissolve around pH 11 and, at that moment, the pH decreased rapidly. The viscosity decreased and good stirring resulted. For HPLC analysis, another sample was taken at pH 10.23 and another at the end of the carbonatation at pH 9.01.

The objective of this study was to assess whether sucrose is lost in the form of sucro-carbonate of lime if filtration is performed at pH 9.0. This would be indicated by a decrease in sucrose concentration in the solution.

Figure 3.39 shows the HPLC sucrose concentrations (run in duplicates) for all the samples taken at different pH during the carbonation process. Only the sample taken at 11.40 showed a significant decrease in the sucrose concentration, which indicates that sucrose had been sequestered by the sucro-carbonate of lime. This agrees with the observation during the carbonation; between pH 11.5 and 11.0, the lime suspension took the characteristic viscosity and appearance of the sucro-carbonate complex.

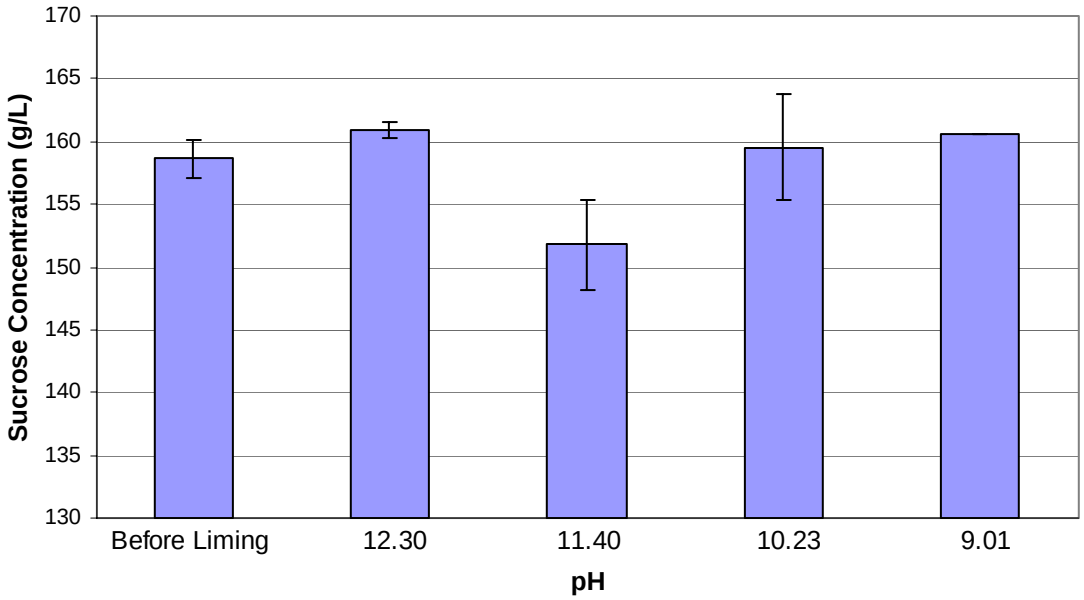


Figure 3.39 Sucrose concentrations at different pH during the carbonation process (error bars =± 1 standard deviation).

At pH 10.23 and at pH 9.01, which is the pH at which filtration was performed in these studies, the sucrose concentration had returned to normal, indicating that the sucro-carbonate of lime had decomposed.

III.3.4.3.2 Assessment of Lime Recovery from the Carbonatation Sludge

Substances in the *bagacillo* or *cush cush* (e.g., proteins, lignin, cellulose, reducing sugars, and polymers of reducing sugars such as starch and dextran,) degrade during preservation. They produce acids that decrease pH and form calcium salts, which may or may not be soluble. If the calcium salts are soluble, they end up in the juice. This calcium cannot be recovered in the carbonatation process, which increases the calcium concentration in the juice and decreases the overall lime recovery after calcination in a kiln. This situation is detrimental both because too high levels of inorganic non-sugars in the juice, in this case calcium, decrease sugar recovery from

molasses and because lime would be consumed without the possibility of regeneration. The calcium concentrations shown in Tables 3.8 and 3.9 indicate how much calcium is in the juice and, therefore, how much lime is lost. However, actual measurements of lime recovery yield a more palpable assessment of this parameter because it also considers the efficiency of the calcination process; thus, giving results more comparable to those obtained in a lime kiln.

The objective of these studies is to determine the amount of lime that can be recovered by a lime kiln from carbonatation sludge collected after preservation. These calculations could only be performed on the bench-scale batches. In the pilot-scale studies, there was a lot of material lost in handling; therefore, a quantitative analysis could not be performed.

The lime recovery after preservation was approximated as follows:

$$L_{rec} = \frac{S_{col} \cdot D_s \cdot C_s \left(\frac{M_{HL}}{M_{QL}} \right)}{(L_{added} \cdot D_L)} \cdot 100 \qquad (3.5)$$

where

L_{rec} = Lime recovery, g $Ca(OH)_2$ recovered /100 g $Ca(OH)_2$ added, %

S_{col} = Amount of carbonatation sludge collected , g

D_s = Sludge dry weight fraction, g dry sludge/g sludge

C_s = Calcination solids fraction (915^{o}C), g calcination solids/g sludge

M_{HL} = Molecular weight of calcium hydroxide, 74.1 g/mol

M_{QL} = Molecular weight of calcium oxide, 56.1 g/mol

L_{added} = Lime added for preservation, g

D_L = Lime dry weight fraction, g dry lime/g lime

Equation 3.5 is only an approximation of the lime recovery because it assumes that the carbonatation sludge is 100% calcium carbonate and/or calcium bicarbonate

and/or calcium hydroxide, which, after calcination, completely become calcium oxide. This assumption is reasonable because analysis of carbonatation sludge by inductively coupled plasma emission spectrophotometry (ICP) at the Soil Testing Laboratory (College Station TX) (Table 3.10) indicated that the calcium content in the sludge was 25 g/100 g total sludge. The sludge had an organic content of 32 g/100 g total sludge; therefore, the calcium content in the organics-free solids was 37 g/100 g organic-free sludge. This value is very close to 40 g/100 g organic-free solids, the fraction of calcium in pure calcium carbonate. Other components levels are very small (Table 3.10).

As explained in Table 3.2, $B_{filtered}$ was prepared before preservation by vacuum filtration through a trigger-type cloth, the same type used in the filtration of carbonatation sludge in the pilot-scale experiments. The concentration of filterable solids left in the juice after filtration, as determined by filtration through a 0.45-μm membrane, was 2.58 g/L.

At the mill (W. R. Cowley Sugar House, Santa Rosa TX), 4 gal of juice were collected and 0.202 kg lime (92% by weight calcium hydroxide, Chemical Lime Co, New Braunfels TX) was added for preservation during transportation. The juice had a sucrose concentration of 11.6% (g sucrose/100 g of juice). According to Chen and Chou (1993), at this concentration, the amount of $Ca(OH)_2$ dissolved is 2.3% (g of $Ca(OH)_2$/100 g of solution), which means that 4 gal (~15 L) of juice could contain up to 0.38 kg in solution; thus, this would indicate that all the lime added at the mill would be in solution. Nonetheless, other substances present also affect lime solubility in juice. In addition, some ions present, such as phosphate (Chen and Chou, 1993), precipitate when the lime is added, even at this high pH without carbonating. It is conclude, therefore, that some of the lime was removed by the filtration. Because of the uncertain amount of lime removed by the filtration prior to preservation, the recovery was reported as a range including and excluding the lime added at the mill.

Both $B_{screened}$ and $B_{periodic}$ were prepared in the same way, where the *bagacillo* was removed at the mill by screening with ~20-mesh strainer before 0.227 kg of lime were added for preservation during transportation; thus, the lime added at the mill had to

also be considered in the recovery calculations. Screening the juice to remove the *bagacillo* is a common practice in the sugar industry (Hugot, 1986; Chen and Chou, 1993).

Table 3.10 Carbonatation sludge composition.

Component	Content
Nitrogen (% w/w)	0.26
Phosphorus (% w/w)	0.21
Potassium (% w/w)	0.78
Calcium (% w/w)	24.9
Magnesium (% w/w)	0.25
Sodium (ppm)	1845
Zinc (ppm)	26
Iron (ppm)	1463
Copper (ppm)	10
Manganese (ppm)	88
Sulfur (ppm)	3947
Boron (ppm)	16
Organic Contents, from ashing at 550^{o}C (% w/w)	32

In the case of $B_{clarified}$, 0.113 kg of lime was added at the mill for preservation during transportation. Once in the laboratory, it was carbonated to pH 9.0 and then

vacuum filtered; thus, the juice was saturated with calcium carbonate, to which lime was added for long-term preservation. The amount of sucrose in this solution was 11.3 % (g sucrose/100 g total juice). Chen and Chou (1993) report that at this concentration, the concentration of calcium carbonate in the solution is about 0.03 g/L. In 15 L (4 gal) of juice, this is equivalent to approximately 0.45 g of calcium carbonate; therefore, it can be neglected and only the lime added in the laboratory for preservation, after the clarification, was considered for the recovery calculations.

The organic content of the carbonatation sludge must be low (i.e., < 10%) to be compatible with the stationary lime kiln. Raw juice preservation yielded a sludge too high in organic content, so the tests on the stationary lime kiln could not be performed. To obtain carbonatation sludge with lower organic contents, pre-clarified juice was preserved instead. In an industrial setting raw juice preservation is preferred because the clarifiers would not need to be oversized to handle all the cane during the short season.

The lime used to preserve $B_{clarified}$ during transportation and later for clarification prior to preservation, was converted mostly to calcium carbonate and then filtered out. This amount of lime is neglected because in the actual process, if clarification prior to preservation were required to reduce organic levels for the stationary lime kiln, this would be a separate unit operation. Likely, the clarification would occur by defecation because this method is cheaper, although less effective, than carbonatation. Also, as shown in Section III.3.4.2.3, after carbonatation, preserved juice pre-clarified by defecation has less color than preserved juice pre-clarified by carbonatation. Thus, defecation : preservation : carbonatation results in better clarification than carbonatation : preservation : carbonatation.

For the calculation, it was assumed that the lime added to preserve the juice was 100% calcium hydroxide, even though the manufacturer reports that the lime is only 92 g calcium hydroxide/100 g total solids. This assumption gives a conservative estimate of recovery because the recovered sludge was assumed to be 100% calcium carbonate/calcium bicarbonate/calcium hydroxide.

Table 3.11 shows the lime recoveries for all the batches expressed as g $Ca(OH)_2$ recovered after calcination/100 g $Ca(OH)_2$ added for preservation. The recoveries show a trend. With less impurities, the recovery increased. $B_{clarified}$, which removed most impurities by clarification prior to preservation, had the highest recovery. Comparing $B_{screened}$ to $B_{periodic}$ shows that mixing frequency had no effect on the recovery. Although for $B_{filtered}$, only a range is reported, it can be hypothesized that the recovery will be higher than $B_{screened}$, but lower than $B_{clarified}$. In general, it can safely be expected to have recoveries higher than 65 – 70% (65 – 70 g lime recovered/100 g lime added for preservation)

Table 3.11 Lime recoveries after preservation for bench-scale batches.

Batch	Lime Recovery*
$B_{filtered}$	64.8±0.4 – 91.7±0.6†
$B_{screened}$	78.5±11.6
$B_{clarified}$	89.5±0.5
$B_{periodic}$	77.6±3.5

* Values given in g $Ca(OH)_2$ recovered/100 g $Ca(OH)_2$ added
† Error = ± 1 standard deviation

Filtering of the carbonatation sludge for $B_{screened}$ and $B_{periodic}$ was difficult and took a long time; therefore, each batch was divided into three smaller batches, which were then separately carbonated and filtered. The recovery was calculated on a per volume basis for each batch. The value reported is an average recovery for the three separate batches, which explains the high standard deviations for $B_{screened}$ and $B_{periodic}$. In contrast, filtering of the carbonatation sludge for $B_{filtered}$ and $B_{clarified}$ occurred in one shot, processing all the contents of each batch at once, thus obtaining a total amount of sludge

recovered. The major variation for $B_{filtered}$ and $B_{clarified}$, from which their standard deviations are reported, were the moisture content and calcination solids, which were determined in triplicate.

III.3.4.3.3 Compatibility of Carbonatation Sludge with Stationary Lime Kiln

The compatibility of the carbonatation sludge with the stationary lime kiln (SLK) was tested by the researchers at Altex Technologies Corp. (Sunnyvale CA).

After preservation, the juice was clarified by carbonatation and the sludge of certain batches was recovered, dried, packaged and shipped to Altex Technologies Corp. for testing on the SLK.

As described in Chapter I, this kiln is more energy efficient than conventional lime kilns because it can be insulated more efficiently than a rotating lime kiln and because more lime can be loaded into the reactor per unit volume. The latter is accomplished by pelletizing the calcium-carbonate-rich raw material, in this case carbonatation sludge, and packing it inside the stationary furnace. The pellets provide interstitial void spaces that allow hot gas to pass through and calcine the material.

According to tests at Altex Technologies Corp., the SLK requires the organic content in the sludge to be less than 10 % (10 g organics/100 g total dry solids). High organic contents weaken the pellets at high temperatures because the organics burn off leaving voids that cause the pellets to disintegrate and clog the reactor.

Preserved sugarcane juice contained waxes, gums, and undegraded fiber (i.e., *bagacillo*), which precipitated in the clarification process (Chen and Chou, 1993); therefore, the carbonatation sludge from preserved raw juice ($P_{no\text{-}prep}$ #1, $P_{no\text{-}prep}$ #2, $B_{filtered}$, $B_{screened}$ and $B_{periodic}$) had a high organic content, which ranged from 26 to 32% (26 – 32 g organics/100 g total dry solids). This was incompatible with the SLK. Extensive washing of the material did little to remove the organics from these samples.

When pre-clarified juice was preserved, the organic levels in the sludge from the second post-preservation clarification decreased to 6.9% in $B_{clarified}$ and 7.3% in $P_{clarified}$.

The SLK results with sludge from the pre-clarified juice in $B_{clarified}$ and $P_{clarified}$ were satisfactory; however, as mentioned, preservation of raw juice would be preferred because it avoids oversizing the clarification equipment, which is needed to clarify the juice prior to preservation.

We propose a method that removes the first clarification step and allows the preservation of raw juice. Figure 3.40 shows the proposed method, which decreases the sludge organic contents prior to loading the stationary lime kiln.

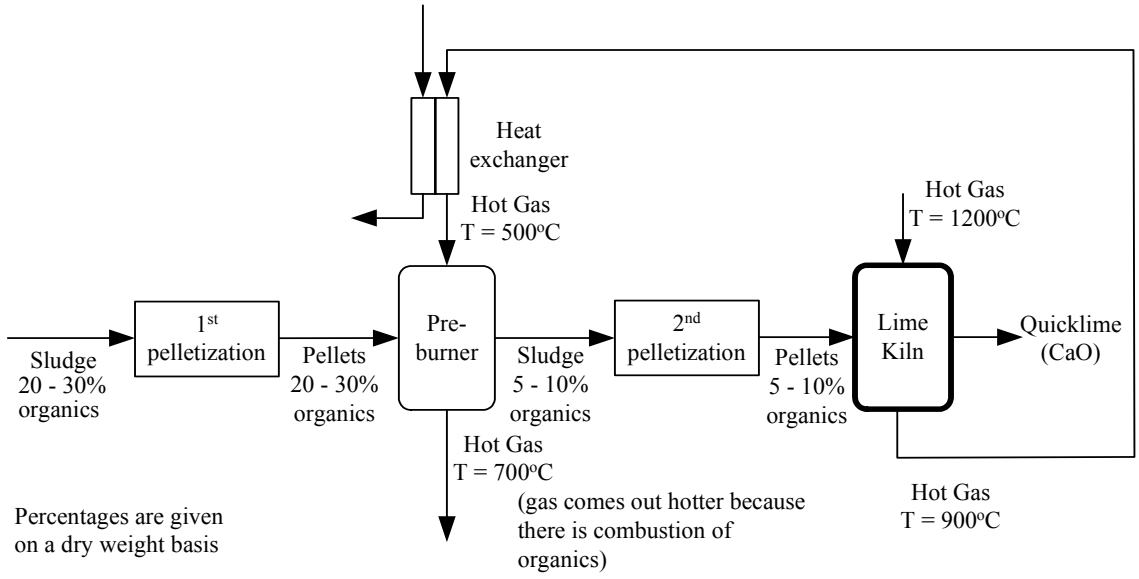


Figure 3.40 Approach to enable the use of high organic-content sludge in the stationary lime kiln process.

High organic-content sludge is pelletized and loaded in a pre-burner, where hot gas (i.e., air) (~ 500°C) contacts the pellets and burns off some organics. The gas exiting the pre-burner is hotter than the inlet gas due to the combustion of the organics. The low-organic-content sludge exiting the pre-burner is then re-pelletized and loaded into the stationary lime kiln, where it is contacted by hot gas (~1200°C) for calcination. The product of the process is mostly quicklime (CaO).

Table 3.12 reports the strength tests of pellets from different sources, temperatures, and preparation conditions tested by researchers at Altex Technologies

Corp. (Sunnyvale CA). Samples of the different materials were mixed with water to the appropriate moisture content, and then extruded to form pellets about 1 inch in length. These pellets were dried and placed in a furnace at the specified target temperatures to simulate conditions in the SLK. The pellets from each target temperature were then tested for strength using a press equipped with a dial-compression gauge. Pressure was applied gradually to the pellets until they fractured. The fracture force is shown in Table 3.12.

Table 3.12 Strength tests (force required for fracture) of carbonatation sludge pellets at different temperatures and preparation conditions. (Data from Altex Tech.Corp.)

Material	Organic Contents (g /100 g total solids)	Sodium (g /100 g total solids)	150°C (lb_f)	590°C (lb_f)	760°C (lb_f)	925°C (lb_f)
$B_{filtered}$ - Sludge	> 15	0	48	16	5	0*
$B_{filtered}$ - Sludge	> 15	1	41	18	66	20
Pre-burned $B_{filtered}$ - Sludge	4	1	140	76	26	16
$B_{clarified}$ - Sludge	7	0	73	113	48	0
$B_{clarified}$ - Sludge	7	1	116	81	236	23
Paper Mud	2	1	50	258	845	35
Paper Mud	2	2	246	345	736	48

* Force values of 0 mean that the pellets fell apart as they were removed from the furnace

Sodium was added to some pellets to a concentration of 1% (1 g/100 g total solids). Researchers at Altex Technologies Corp. report that sodium acts as a high-temperature binder and improves pellet strength (Kelly and Namazian, 1998). The source of sodium was a 45% solution of Maracell XE (Lignotech USA, Rothschild WI).

A sample from the high-organic-content sludge from $B_{filtered}$ was formed into pellets and placed in a furnace at 260°C for 3 hours, which decreased the organic content to 4% (4 g/100 g total solids). The resulting pellets were crushed, re-pelletized and heated to the target temperatures to perform the strength tests. The objective of the latter procedure was to simulate the process depicted in Figure 3.40.

For comparison, samples of residual paper mud from the Kraft pulping process in the paper industry (Weyerhauser plant, Longview WA) were also tested.

The results showed that the high-organic-content sludge from $B_{filtered}$ performed poorly, although its strength did increase when sodium was added.

$B_{clarified}$ also performed poorly when tested without added sodium, but its mechanical strength increased tremendously and had an excellent performance once sodium was provided.

The pre-burned sludge performance was acceptable, although not as good as the results obtained from the sludge of $B_{clarified}$ when sodium was added.

The pellets of paper mud from the Kraft pulping process already had a high sodium level and low organic content; thus, their mechanical strength considerably surpassed all the samples of carbonatation sludge.

The results suggest that sodium is very important, and must be added to carbonatation sludge to improve pellet strength. An increase of sodium content might represent a problem because sodium is very soluble and it will remain in the juice. Sodium has a high melassigenic effect (i.e., increases the loss of sucrose to molasses). Chen and Chou (1993) report that sodium has melassigenic coefficients (i.e., parts of sucrose that will be taken to the molasses/parts of sodium present) that range from 0.42 to 4.61 depending on the anions present in the solution.

Assume the sodium concentration in the sludge is 1%. After calcination, gases (mainly carbon dioxide) are driven off, which increases sodium concentration in the quicklime to ~ 1.8% (1.8 lb of sodium/100 lb of quicklime). Assume a 14 – 15° Brix raw juice. At the proportion that lime needs to be added for 1-year preservation (i.e., 16% slacked lime on brix or 12% quicklime on brix), and assuming that the melassigenic

effect of sodium in this juice based on the anions present is about 2 – which is the middle of the range given by Chen and Chou (1993) – then, this increase in sodium will cause a sucrose loss of about 0.07% (0.07 lb of sucrose lost to molasses/100 lb total juice). In a sugar house of the size of W.R. Cowley Sugar House, which processes about 10,000 ton cane/day and operates 6 months per year, this increase in sodium represents a loss of sucrose to molasses of about 8 tons/day. At ~ 20 cent/lb of raw sugar, this amounts to about $570,000/year in losses, which is substantial. Fortunately, the quicklime that exits the SLK, because it comes out in chunks, must be slacked. The lime slacker can be modified to remove sodium from the lime to acceptable levels.

III.4 Conclusions

The preservation of sugarcane juice with lime at normal ambient conditions successfully maintained sucrose concentrations for periods as long as 1 year. The amount of hydrated lime required to preserve the juice for 1 year is 20% on sucrose (20 lb/100 lb of sucrose present) or 16% on brix (16 lb/100 lb of soluble solids) assuming 80% purity. This is about the same amount of lime needed in the single carbonatation and the continuous double carbonatation processes (40 lb or 18 kg of quicklime/tone of cane) (Hugot, 1986).

Although mixing is imperative, constant recirculation is not necessary because periodic or intermittent mixing suffices.

The carbonatation process that clarifies the juice after preservation must be optimized and improved. Nonetheless, the juice obtained from the preservation was normal with respect to purity, color, and mineral contents, which were comparable to the values from typical clarified juice. The calcium concentrations were higher than those obtained in juices clarified by defecation, but this can be attributed to the use of the unoptimized carbonatation as the clarification procedure. The dextran concentrations were very low, which was expected, because the conditions at which the juice is

maintained do an excellent job suppressing microorganisms, including those that produce dextran. Further, any dextran present in the raw juice is destroyed by alkaline conditions.

The only potential drawback from the lime preservation procedure seems to be the destruction of reducing sugars due to the high alkalinity, but the actual effect on crystallized sugar recovery cannot be assessed until the clarification (i.e., carbonatation) procedure is improved and pilot-scale crystallization of the process is performed. The reducing sugars degradation products were not transformed into color at the preservation conditions as the color measurements suggest, and they were still optically active because they were detected by the refractometer. It is possible that these substances will simply take the place of the reducing sugars in the molasses; thus, not affecting sucrose recovery.

A bench-scale crystallization test showed that the sugar crystals produced are normal and have less color than sugar crystals obtained from a sugar mill that employs defecation as the clarification method. The exhaustibility measurements from this bench crystallization test were low. Nonetheless, it could not be concluded that this was due to the preservation procedure because there were other factors that could have affected the crystallization as well, such as inefficiencies in the carbonatation, which yielded high calcium concentrations, high potassium concentrations from the original raw juice, and inefficiencies in the crystallization itself that caused spontaneous crystallization.

If the carbonatation procedure is improved and optimized, it is believed that it would be possible to obtain white sugars directly from this process, which would contribute considerably to the economics.

The approximate lime recovery for preservation of screened (i.e., no *bagacillo*) raw juice was found to be about 80% (80 g of recovered after calcination/100 g of lime added before preservation), and it becomes as high as 90% if clarified juice is preserved.

The carbonatation sludge recovered from the clarification step after preservation of raw juice is not compatible with the energy-efficient stationary lime kiln (SLK) due to its high organic and low sodium contents. If the organic contents are decreased, either

by burning them off or by preserving clarified juice, and sodium is added, then the mechanical strength of the pellets improves, making the sludge adequate for the process. If sodium is added to help pellet integrity, it can be removed during the slacking procedure.

It is well known that carbonatation is a more efficient procedure for clarification than defecation. In fact, white sugars can be directly obtained from the carbonatation process. However, the high costs for materials and equipment make it unpopular. The cheaper lime produced by the SLK, and the savings incurred by the preservation of the juice, which would avoid oversizing the process equipment, makes this alternative to sugar manufacturing very attractive.

III.5 Future Work

With respect to the preservation procedure, tests must be made to find the actual frequency needed for mixing, bearing in mind that it is preferred to mix as infrequently as possible to save power.

Because adding excess lime to the juice raises the pH above 12, studies should also be performed with a pH controller constantly adding lime to maintain the pH at adequate levels for preservation (i.e., 11.0 – 11.5), which is the recommended procedure for the actual process. This experiment should determine more accurately the exact amount of lime needed for preservation, which was slightly overestimated in these studies.

Studies should be performed to improve the clarification procedure after preservation. The carbonatation process must be optimized to recover the highest amount of lime and to remove the highest amount of impurities and color from the juice. Parameters to be tested are temperature, number of carbonations and filtrations, pH at which the carbonations and filtrations should occur, scale formation on the equipment, and sludge filterability. The starting point should be conventional modern carbonatation

methods, which are far superior to the ancient cold-juice single carbonatation that was performed in these experiments (Honig, 1953).

Tests should also be performed to improve the mass transfer of carbon dioxide, especially at pH close to neutrality. As mentioned, agitators with high gas transfer efficiency should be tested.

Pilot-scale crystallization studies of the juice should be performed. For this purpose, the Audubon Sugar Institute (Baton Rouge LA) has adequate facilities. This test will allow a better estimation of the quality of the juice with respect to evaporator duties, molasses exhaustibility, and in general to the overall sucrose recovery in crystals from the preserved juice.

Because sodium is a necessary additive for the carbonatation sludge to ensure the proper operation of the stationary lime kiln, more studies on the downstream impact of this alteration to the mineral composition of the lime must be performed.

III.6 Questions and Answers

The following questions were made by two experts in the field, Dr. Michael Saska from the Audubon Sugar Institute (Baton Rouge LA) and Mr. Carlos de Armas from the Cuban Research Institute of Sugar Cane Derivatives (Havana Cuba).

The following are Mr. De Armas' questions:

Question:

"You store the juice but what do you think to do with the bagasse?"

Answer:

A plant such as this one will definitely have to have co-generation to produce energy to deal with the excess bagasse. The idea is to produce energy (e.g., electricity) from the bagasse as soon as it becomes available and sell it, keeping only the bagasse that is needed to operate the small boilers.

But, on another note, I have to tell you that the real incentive for the proposal of this method is the fact that our group does not want to use the bagasse to simply burn it.

Our research group has been working for the past 15 years or so in the MixAlco process, which converts biomass into a mixture of volatile fatty acids (i.e., acetic, propionic, butanoic, pentanoic, etc.) and then transforms them into a mixture of alcohols to be used as fuel.

It has been demonstrated that this is a much more efficient way of handling excess biomass (i.e., municipal solids waste, corn stover, paper waste, chicken and pig manure, etc. and of course sugarcane bagasse) than simply burning it.

The bagasse produced will be pretreated to increase digestibility and immediately fermented countercurrently with a mixture of acid-producing microbes to produce fuel by means of the MixAlco process.

The bagasse will definitely be worth more than it is worth now, and people will not want to just burn it, if they can obtain fuels more efficiently.

On the other hand, in the worst case scenario, if you opt for not implementing this process, true that you will have to store some bagasse and that costs money, but at least you now have the flexibility to find a happy medium that will minimize your cost between not oversizing your mill and not storing too much bagasse.

Question:

"As far as the juice storing is concerned, you will have to store about 4000 ton per day (100% extraction), approximately 440000 cubic meters in total, which say, at ten meters high, means 44000 square meters of tanks surface, or about 60 covered tanks of 30 meters diameter each one. Have you had thought in the R+D, plus engineering tasks and specially the investment involved?"

Answer:

People store their raw sugars now in a warehouse of a certain size. Say you store a 15^{o} Brix juice, with 80% purity, for a plant that has 87% boiling house recovery, and considering that the warehouses are not completely filled. You will need several ponds (not tanks) lined with a geomembrane whose added volume will be equal to about 7 to 8

times the size of the warehouse sugar houses now have for storing their raw sugar. A pond lined with a geomembrane is much cheaper than a warehouse of the same size.

Also, a mill like this will not need a warehouse, at least not as big as the one existing mills have, because it will sell the raw sugar (or maybe even white sugar, because of the efficiency of the clarification method) as it is produced.

Question:

"Concerning the processing of the after-stored juice, have you had done tests on its processing to sugar? What differences have you had found with fresh juice?"

Answer:

I have done some pilot and bench tests on processing and clarifying the juice. Purities are normal. The clarified juice obtained has a lower ICUMSA 420 color than the juice obtained by conventional defecation.

I have also done bench scale crystallization, and the crystals are normal, plus the ICUMSA 420 color is also lower than conventional raw sugar.

Question:

"I mean the whole problems involved, like scaling in heating and evaporation surfaces, and eventual changes in the viscosities of massecuites, how it could change the mass transfer coefficients, and consequently, boiling processing times."

Answer:

Indeed more testing at the pilot and industrial scale is needed.

Question:

"Concerning sucrose losses, you speak about reducing sugars losses, what explanation you give to the fact of having only these losses, it does not happens that when destroyed, the hydrolysis reaction does not move to new formation of more reducing sugars, which again will be destroyed, and so on (moving to the right the hydrolysis reaction)?"

Answer:

The theory is a follows:

The reducing sugars, in alkaline conditions, are converted into saccharinic acids, which are stable in alkali under normal ambient conditions; thus, also forming an equilibrium that avoids the destruction of more reducing sugars. The equilibrium reactions occur in the following way:

$$\text{Sucrose} \leftrightarrow \text{Reducing Sugars}$$

$$\text{Reducing sugar} \leftrightarrow \text{Saccharinic acids}$$

So the overall reaction, and equilibrium to be concerned with, is actually,

$$\text{Sucrose} \leftrightarrow \text{Saccharinic acids}$$

Both sucrose and saccharinic acids under normal conditions of temperature and pressure are stable in alkaline conditions. Thus, equilibrium is maintained which avoids, in the overall reaction, further destruction of sucrose towards saccharinic acids.

The following questions were made by Dr. Michael Saska:

Question:

"The amount of lime you use is at least 30 times more on juice volume that is used presently in the raw sugar process. Hence, the weight of cake some 45 times more than is presently produced, again on the same juice volume basis. With the same washing efficiency, the sugar loss in the filter cake you can expect 45 times larger than the present loss."

Answer:

The experiments show that the amount of cake produced is between about 1.3 for the raw juice preservations and about 1.5 times the lime added for the clarified juice preservation. Because the sugar industry that clarifies by defecation limes at a rate of

about 1 – 1.5 lb calcium oxide/ton cane and our liming would be about 40 lb CaO/ton cane, your estimation is about right.

But the deficiency you describe will never be worse than in the conventional single carbonatation and the continuous double carbonatation processes, because we would use the same amount of lime they do, or even less if the preservation is for less than a year.

Now if the losses are of much concern, it is worth to also consider other positive aspects such as the fact that carbonatation is a better clarification method than defecation, and that direct white sugar may be obtained from this process if the carbonatation is optimized, thus helping the economics. Also, you will have to find a happy medium to maximize your earnings. On the one hand, by being able to preserve the juice you save a lot of money in the initial investment by not having to oversize anything other than your extraction equipment, and on the other extreme you save money by not having too much cake, thus avoiding sugar losses. You have the flexibility to choose for how long you wish to preserve the juice. The longer you preserve, the smaller your equipment but the higher the amount of lime needed (and higher cake yield) and vice versa.

Question:

"The precipitate from carbonatation will be totally different than from the present defecation, much finer, and you will need filterpresses to handle the mud, not the vacuum filters existing in the mills."

Answer:

Some mills that clarify by carbonatation do use rotary vacuum drum filters. They adjust the liming and carbonating conditions to attain a “fluffier” sludge that can be picked up by the filters. Without a doubt, filtration studies need to be done too on this regard, because the sludge is different to what you normally get from carbonatation, because you have given more time for degradation of impurities which does not occur in conventional carbonatation processes.

Now, you are talking about *existing* mills. Our intended target in this research has been from the beginning new mills that would be able to benefit from the size reduction in their equipment.

The case with existing mills is different because they are already oversized; thus, they do not need to store a lot of juice. In their case, I would say, they can use the highly limed preserved juice as their lime source for the fresh juice coming in and they may continue using their defecation method for clarification. This is the conventional calcium-saccharate liming process (Hugot, 1986; Chen and Chou, 1993).

CHAPTER IV

LONG-TERM LIME PRETREATMENT OF BAGASSE

IV.1 Introduction

In sugar plants that do not produce extra power, bagasse is only used to operate the boilers. By the end of the sugarcane season, these plants must deal with all the excess bagasse that was not burned in the boilers and now lies in their backyard, which has the potential of catching fire either by accident or by spontaneous combustion. Companies must pay fees to dispose of this bagasse. By implementing the more efficient evaporation system, which decreases energy requirements, and with the preservation of thin sugarcane juice to process it along the year, it is possible that the excess bagasse will become more of a problem. However, the MixAlco process (Figure 1.2), which can produce fuels and chemicals from bagasse, solves this problem.

The MixAlco process requires that the biomass be pretreated with alkali (lime) to remove lignin, which is a key factor that inhibits microbial or enzymatic digestibility (Chang and Holtzapple, 2000). Lignin is a structural biopolymer that acts as a "glue" and binds cellulose to give rigidity to plants. It encapsulates biomass carbohydrates (cellulose and hemicellulose) and shields them from degradative enzymes. Also, alkaline pretreatment reduces the acetyl group content, which is another factor that inhibits biological digestibility, although to a lesser extent than lignin (Chang, 1999). The conventional method is the addition of 0.1 g $Ca(OH)_2$/g dry biomass, at 100^{o}C for 2 hours in an appropriate vessel (Holtzapple, 1999). This procedure, as with sugarcane juice processing, requires big vessels for processing large amounts of biomass that becomes immediately available for the fermentation.

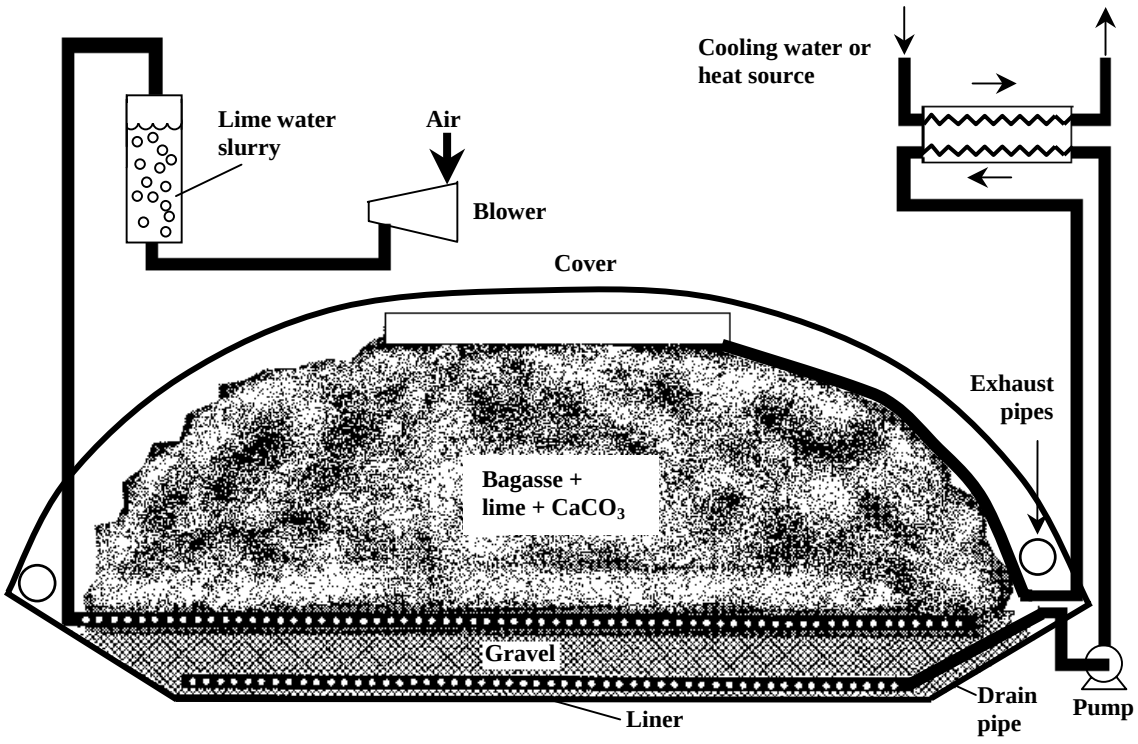


Figure 4.1 Schematic of pretreatment/fermentation pile.

The newer proposed process consists of performing both the pretreatment and fermentation in a single pile. The bagasse undergoes alkaline oxidation to increase digestibility and fermentation to produce carboxylate salts (Figure 4.1). The new pretreatment procedure will require longer times (several weeks), but the operating temperature will be lower. The process is as follows:

1) Biomass, lime, and calcium carbonate are intimately mixed and formed into a pile.
2) The pile is covered. A blower delivers carbon-dioxide-free air, obtained by pre-scrubbing with a lime-water slurry, distributing it uniformly in the pile from the bottom to induce oxidation. At the same time, water is circulated by intermittently flooding the pile to avoid channeling. The water temperature is regulated by a heat exchanger (Figure 4.1).
3) As pretreatment occurs, the pH in the pile decreases. When the pH is low enough for microorganisms to subsist, the pile is inoculated with a mixture of

marine microorganisms, which can handle high salt concentrations and thus can produce high concentrations of organic acids (Thanakoses, 2002). Water circulation continues in the same way. At this point fermentation starts.

4) The blower is now coupled to the exhaust pipes to extract the fermentation gases produced in the pile.
5) The product of this fermentation (carboxylate salts) is further treated in the MixAlco process as described by Holtzapple et al. (1999).

Paper manufacturing is another use for bagasse (Chen and Chou, 1993). In places where this process has been implemented, bagasse, which is produced during the few months of the sugarcane season, has to be stored (commonly in piles) so that it may be processed during the year (Yang et al., 2000; Ashok et al., 1986). Storage presents difficulties because there might be biochemical deterioration and loss of fiber, as well as the danger of catching fire either by accident or by spontaneous combustion (Granick, 1979). Using the same pile system, but with possibly a higher lime loading, bagasse might also be treated, while being stored, to make pulp for paper or paperboard manufacturing. Further treatment might be necessary (e.g., beating, bleaching, etc.); but savings are expected when compared to the conventional methods.

Treatment of the bagasse for paper or paperboard manufacturing might take several months with the proposed method; however, when the bagasse is to be used for fermentation, a high degree of delignification is not necessary because digestibility is not enhanced significantly below 10 g lignin/100 g total biomass (Shimizu et al., 1984; Chang, 1999). Therefore, for the MixAlco process, the pretreatment might be shorter than for pulping.

IV.2 Literature Review

IV.2.1 Alkali Pretreatment to Increase Microbial and Enzymatic Digestibility

To increase enzymatic or microbial digestibility, pretreatment of biomass with alkali (e.g., sodium hydroxide, ammonia, potassium hydroxide, and lime) has been studied extensively. However, in its majority, the pretreatment time does not exceed 24 hours at ambient temperature, and the effect of oxidation is not considered (Chang et al., 1997). One concern with long-term pretreatment is the possible destruction of carbohydrates, particularly hemicelluloses, because cellulose is more stable (Whistler and BeMiller, 1958). Even so, long-term delignification is effective. For instance, Gharib et al. (1975) treated poplar bark with lime at non-oxidative conditions for 150 days at ambient temperature, which decreased the lignin content by about 24% that of the original amount. After one day of applying the same treatment, only about 7% of delignification was achieved with about the same degree of carbohydrate destruction (~50% of hemicelluloses).

The utilization of bagasse as a substrate for biodegradation has been extensively studied (Pandey et al., 2000) and it is concluded that pretreatment to increase digestibility is imperative. Long-term lime pretreatment of bagasse has been done by Playne (1984). He obtained the best digestibility when he treated bagasse at ambient temperature for 21 days with lime and sodium carbonate under non-oxidative conditions.

Alkali pretreatment in the presence of oxygen has been shown to be more effective for bagasse delignification than alkali alone (Shimizu et al., 1984; Chang, 1999).

An important factor to consider is that because sugar plants sometimes collect bagasse during the season, it ages, which changes its properties and makes delignification more difficult (Ashok et al., 1986). A comparison of old stored bagasse and fresh bagasse must be done to establish differences on how they should be approached.

IV.2.2 Bagasse in paper manufacturing

Utilization of bagasse for paper-making is a common practice (Ashok et al., 1986). There are 20 leading countries that produce bagasse pulp for use in various grades of paper and paperboard, including bag, wrapping, printing, writing, toilet tissue, facial tissue, toweling, glassine, corrugating medium, liner board, bleached boards, coating base stock, newsprint, and mechanical-containing printing papers (Chen and Chou, 1993).

The common method for pulping bagasse is the soda process (sodium hydroxide at 160 to 170^{o}C for 10 to 90 min) (Granick, 1979; Fernández, 1995). The Kraft process (sodium hydroxide + sodium sulfide), which is popular for hardwood pulping, is not as popular for bagasse (Valdes Delgado and de Armas Casanova, 2001; Wang and Patt, 1989). Incorporating additives to the soda process, such as anthraquinone and oxygen, has improved both the properties and yields of bagasse pulps (Valdes Delgado and de Armas Casanova, 2001; El-Ashmawy, et al., 1984; Nagieb and El-Sayed, 2000; Wang and Patt, 1989). To produce good quality paper, bagasse should be depithed before pulping (Ashok et al., 1986; Granick, 1979). Bleaching with chlorine or sodium hypochlorite follows in the process after pulping (Valdes Delgado and de Armas Casanova, 2001).

Cooking bagasse with lime for paper manufacturing is not very common, although as early as 1912, lime in combination with sodium hydroxide was used in this task (Cross, 1912). On the other hand, for manufacturing strawboard or paperboard, pulping is actually very commonly done by cooking the bagasse with lime (Madan, 1981). In this case, bagasse is cooked with 5 to 15 g CaO/100 g dry bagasse at temperatures between 140 to 160^{o}C for 4 to 6 hours (Singh, 1959; Madan, 1981). To manufacture corrugating medium and cardboard, bagasse can be pulped as a whole without the extra depithing step (Ashok et al., 1986, Madan, 1981).

All the methods mentioned above pulp the bagasse using high temperatures and short time. On the other hand, Vázquez (1947) performed bagasse pulping by placing a

mixture of bagasse, lime (~10% dry basis) and water in appropriate containers and covering them to exclude air because lime consumption by carbon dioxide was a concern. The bagasse was kept under these conditions for 2 months at ambient temperature; then, the contents underwent physical analysis. The material presented excellent conditions to be reduced to paperboard pulp. Sheets of paper (0.009 inches in thickness) were made and corrugated. It was observed that in regards to the rigidity, elasticity, and the ease of binding with sodium silicate, the characteristics were similar to that of strawboards obtained by conventional methods.

Interestingly enough, long-term treatment of plant tissue with lime at ambient conditions to obtain paper pulp is said to have been used for the first time in China by T'sai Lun in the year 105 A.D. This was the original recipe for making paper (Vázquez, 1947).

IV.2.3 Long-Term Lime Treatment of Bagasse under Oxidative Conditions

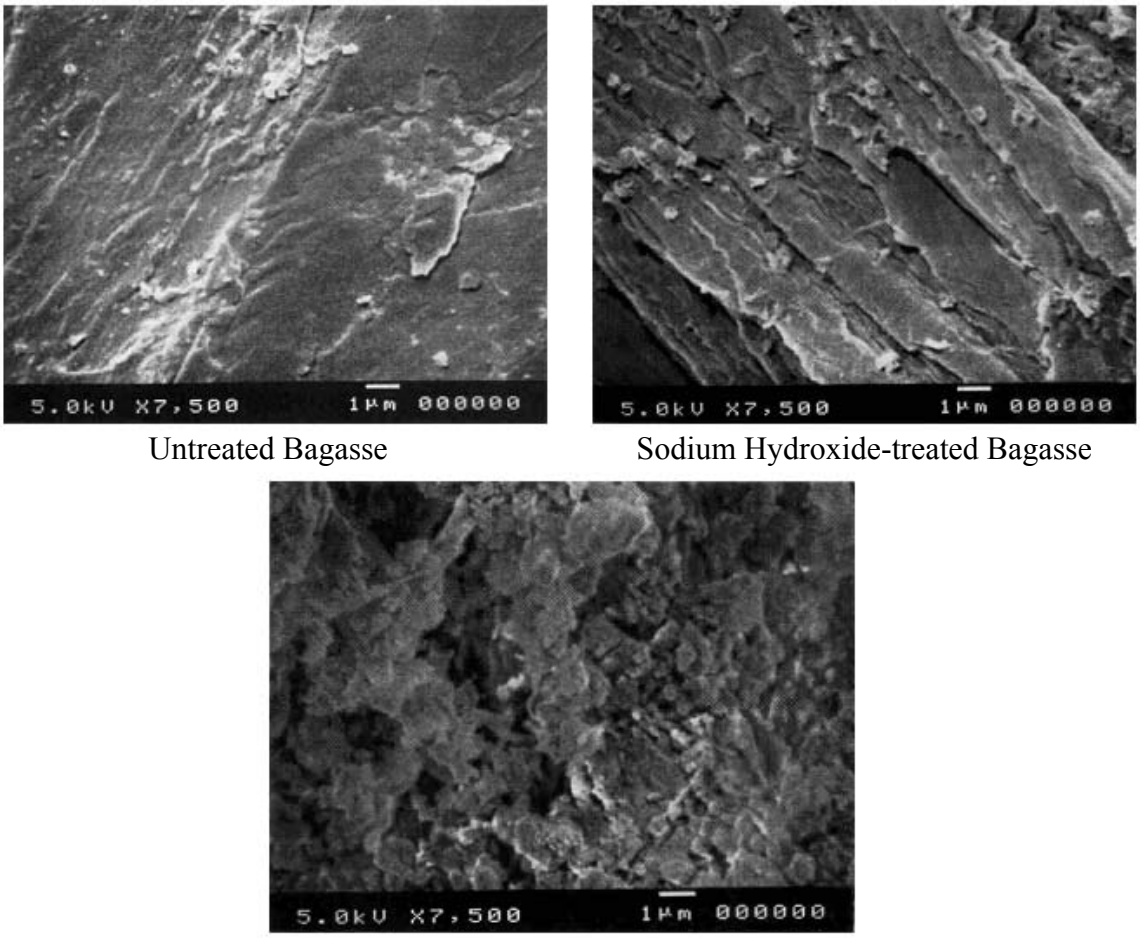
Oxygen/alkali pulping is known to produce the desired pulp yield and quality for paper manufacturing, but also it brings advantages to the process, such as lower chemical requirements in the subsequent bleaching process, higher brightness with equivalent amount of chemicals, lower amounts of rejects and, less pollution because it avoids the use of sulfur chemicals (Nagieb and El-Sayed, 2000; Asgari and Argyropoulos, 1997). However, the drawback of oxygen delignification is its poor selectivity and enhanced carbohydrate degradation (Ljunggren and Johansson, 1990), which reduces the strength properties of pulps (Trivedi and Murthy, 1982). At the end of the bleaching process, such as in conventional oxygen bleaching, only 40 to 50% delignification can be achieved without deteriorating pulp quality (Ljunggren, 1990).

Nonetheless, in sodium hydroxide/oxygen pulping of bagasse, it has been noticed that good pulp quality and yields can be attained by using small amounts of alkali earth carbonates, phosphates, silicates and oxides, which protect cellulose thus diminishing its degradation during pulping (Trivedi and Murthy, 1982; Nagieb and El-Sayed, 2000).

Magnesium carbonate is preferably used, but good results can also be obtained with other inorganic compounds, all having a water solubility of less than 0.1 g/100 g total solution at 25^{o}C, such as calcium carbonate (Robert et al., 1968). Even more convenient is the fact that better cellulose protection has been achieved by treating the lignocellulosic material with an aqueous solution of soluble salts of alkali earth, particularly magnesium chloride, before undergoing sodium hydroxide/oxygen pulping (Aung and Boyle, 1973).

López et al. (2000) evaluated surface alterations of sugarcane bagasse by treatments with both calcium hydroxide and sodium hydroxide. The evaluation was done with scanning electron microscopy, X-ray microanalysis, Fourier transform infrared spectroscopy, and thermogravimetric analysis. Their results show that calcium hydroxide treatment modifies the surface of bagasse by forming calcium carbonate deposits, whereas sodium hydroxide does not form such deposits and therefore does not modify the surface (Figure 4.2). Thermal stability of bagasse is thus increased when compared with untreated and sodium-hydroxide-treated bagasse, providing further evidence of surface modification. Lignin and carbohydrate degradation products from alkaline treatment tend to degrade all the way to carbon dioxide (Klinke et al., 2002) forming carbonates in the alkaline medium. This reaction is more likely to occur under oxidative conditions. When sodium hydroxide alone is used, no deposits are formed because sodium carbonate is soluble, but when calcium or magnesium ions are found in the solution, the carbonates of these alkali earths form insoluble deposits on the surface of the biomass. From this observation, it may be hypothesized that magnesium chloride used by Aung and Boyle (1973) or carbonate salts (Robert et al., 1968) protect cellulose by forming insoluble carbonate deposits in the places where there has already been degradation, thus forming a protective layer which prevents further attack of carbohydrates. Although for short treatment times, sodium hydroxide might do a better job delignifying biomass, these promising results with the alkali earths salts mentioned above are important because they show the advantage of calcium hydroxide over sodium

hydroxide for long-term delignification with oxygen. Further, lime is much cheaper and safer, making it the preferred source of alkali for the pretreatment.



Untreated Bagasse Sodium Hydroxide-treated Bagasse

Lime-treated Bagasse

Figure 4.2 Scanning electron microscope images of bagasse (López et al., 2000). Printed with permission of VSP International Science Publishers.

Another drawback of the alkali/oxygen treatment is the difficulty of oxygen penetrating into wood chips, but in the case of bagasse, its loose and open structure makes it more suitable (Nagieb and El-Sayed, 2000; Trivedi and Murthy, 1982).

IV.2.4 Delignification Model

Alkaline delignification is known to occur in three separate simultaneous phases: initial (rapid) phase, bulk (dominant) phase, and the final residual (slow) phase (Dolk et al., 1989; Chiang and Yu, 1990; Lindgren and Lindström, 1996); thus, from the kinetic viewpoint, lignin can be classified into these three different classes according to the phase where it degrades.

Gierer (1980) ascribes the breakage of phenolic α and β-aryl ether bonds in lignin to the initial phase; non-phenolic β-aryl ether bonds cleavage governs the bulk phase, which is the dominant phase; and cleavage of carbon-carbon linkages are thought to cause lignin degradation in the residual phase. Dolk et al. (1989) considered the possibility that the initial phase, because of its speed, might sometimes not be controlled by chemical reaction, but by diffusion. Li and Mui (1999) confirmed these findings and suggested a decrease in particle size and temperature to measure the chemical kinetics of this phase. In wood, the initial delignification stage involves a considerable amount of hemicellulose degradation with little lignin removal, the bulk stage removes most of the lignin polymers and remaining hemicelluloses and, finally, in the residual stage, cellulose and remaining hemicelluloses are decomposed further while lignin removal proceeds very slowly (de Groot et al., 1995).

In alkaline pulping (soda or Kraft), when the hydroxide and hydrosulfide ion concentrations are kept constant, the delignification of each phase is described by first-order kinetics with respect to the lignin content (Chiang and Yu, 1990). Thus, the rate equations for each phase are as follows:

$$L_i = L_{0i} \cdot e^{-k_i \cdot t} \tag{4.1}$$

$$L_b = L_{0b} \cdot e^{-k_b \cdot t} \tag{4.2}$$

$$L_r = L_{0r} \cdot e^{-k_r \cdot t} \tag{4.3}$$

where

i	=	Initial phase
b	=	Bulk phase
r	=	Residual phase
L	=	Specified phase lignin content at time t, g lignin from specified phase at time t/g total dry solids
L_0	=	Specified phase lignin content at time 0, g lignin from specified phase at time 0/g total dry solids
k	=	Specified phase rate constant, 1/unit of time

Because these reactions occur simultaneously, the total lignin, as measured by analytical methods, is the sum of all three phases; therefore, the entire delignification process is expressed as the sum of Equations 4.1, 4.2 and 4.3.

$$L_T = L_{0i} \cdot e^{-k_i \cdot t} + L_{0b} \cdot e^{-k_b \cdot t} + L_{0r} \cdot e^{-k_r \cdot t} \tag{4.4}$$

$$\frac{L_T}{L_{0T}} = a_i \cdot e^{-k_i \cdot t} + a_b \cdot e^{-k_b \cdot t} + a_r \cdot e^{-k_r \cdot t} \tag{4.5}$$

where

L_T	=	Total lignin content at time t, g lignin at time t/g total dry solids
L_{0T}	=	Total lignin content at time 0, g lignin at time 0/g total dry solids
a	=	The fraction of L_{0T} that can be removed in the specified phase, g lignin from specified phase at time 0/g lignin at time 0

Equation 4.5 correlates data remarkably well, and the Arrhenius equation may be used to correlate the rate constants with respect to temperature (Dolk et al., 1989; Chiang and Yu, 1990). However, this model is only empirical because a theoretical approach to this mechanism requires that the lignin content be expressed in moles. As a polymer, lignin has a varying molecular weight during delignification (Yan and Johnson, 1981),

so it is not possible to express the lignin content on a molar basis; thus, lignin has to be fictitiously considered as being "dissolved" in the cell wall matrix (Gierer, 1980).

Bagasse lignin is more reactive and accessible than wood lignin (Fernández et al., 1985). In the case of soda pulping of bagasse at high temperatures (100 – 165^{o}C), Sabatier et al. (1993) found that bagasse lacks an initial delignification phase and considers Equation 4.5 as the sum of only the first-order expressions for the bulk and the residual phases. They support their claim by showing that bagasse alkaline delignification proceeds, from the very beginning with a high degree of lignin removal compared to carbohydrate removal, which in woods is not characteristic of the initial phase, but of the bulk phase (de Groot et al., 1995).

Another method for modeling is to treat delignification as a degelation process, also known as reverse-gelation (Yan and Johnson, 1981; Smith et al., 1988). This is a more theoretical approach, however, Lange et al. (1989) and Smith et al. (1988) suggest that the structure and behavior of lignin cannot be described by the available gelation theories.

IV.3 Experimental Methods

IV.3.1 Objectives

The objectives of this study follow:

- Assess the effect of temperature, time, and oxygen on delignification and biological digestibility in long-term lime pretreatment of bagasse,
- Develop a delignification model, and
- Evaluate the potential of this process as a pulping technology for paper or paperboard manufacturing

IV.3.2 Bagasse Pretreatment to Increase Enzymatic Digestibility

IV.3.2.1 Equipment Description and Methodology

Old stored Louisiana sugarcane bagasse (Raceland LA) (Table 4.1) was hammermilled (Wiley Mill standard model No. 3, Arthur H. Thomas Co., Philadelphia PA) and sieved to 40 mesh with the aid of a sieve shaker (Ro-Tap model B, W. S. Tyler, Inc./Combustion Engineering, Inc., Mentor OH). The bagasse was then washed by adding distilled water and mixing for 15 min in several 1-L centrifuge bottles, then centrifuging at 4000 rpm for 15 min, and finally dumping the water taking care not to lose any solids. This washing procedure was repeated several times to rid the bagasse of water-soluble substances so that the true effect of the pretreatment may be observed, because water-soluble substances are not truly part of the biomass. The bagasse was then dried for 2 to 3 days in an oven at 45^{o}C, and then allowed to achieve equilibrium ambient moisture for 2 to 3 days. The resulting 40-mesh washed bagasse was treated with calcium hydroxide (99.3% certified, Fisher Scientific Co., Pittsburgh PA) in a shaking air bath at different temperatures (i.e., 57, 50, 40, 30, and 23^{o}C). For this purpose, several 125-mL Erlenmeyer bottles were filled with 3 g (dry weight basis) of bagasse and calcium hydroxide (0.5 g/g of dry of bagasse). Distilled water was added to the bottles in a proportion of 9 mL/g dry bagasse, which is the water loading suggested by Chang (1999). The number of bottles depended on how long the treatment was planned to last so that its effect may be monitored as a function of time. Bottles were taken offline once a week during the first month, and then once a month for the rest of the treatment. For the treatment at 57^{o}C, samples were also taken during the first week at 1, 2, 3, 5, and 6 days. Half the bottles were constantly purged with air and the other half were simply capped to exclude oxygen as a control. The air flow rate through the air-purged bottles was regulated by submerging the outlet in a small flask with water to a depth of about 2.5 cm, and adjusting the outlet flow to obtain about one bubble per second. This was approximately equivalent to an inlet flow rate, at standard temperature

and pressure, somewhere between 3.6 cm^3/min, the inlet flow rate obtained if no oxygen was consumed, and 4.6 cm^3/min, the inlet flow rate obtained if all oxygen was consumed. This flow rate was kept for the treatments at all temperatures, except for the treatment at ambient temperature (23^{o}C). At 23^{o}C, the air flow rate started at the same rate as the others, but at some point it was increased to flush condensation from the lines. Figure 4.3 shows the details on how the air purging was done and Figure 4.4 shows a photograph of the system. The air, before it was distributed to the bottles, was bubbled through a column of water at the appropriate temperature to saturate it so that water loss in the bottles could be prevented. Later, it was discovered that the carbon dioxide present in the air was consuming the lime, thus yielding higher values for lime consumption. However, for the sake of consistency, no attempt to scrub the carbon dioxide from the air was made at this point.

Table 4.1 Composition of the old stored bagasse used in these studies.

Component	% in a dry-weight basis
Lignin (g/100 g dry bagasse)	21.9 – 23.8
Acid-insoluble ash (g/100 g dry bagasse)	12.2 – 20.8
Ash (g/100 g dry bagasse)	15.8 – 22.8
Water-soluble solids (g/100 g dry bagasse)	2.36±1.81*
Crude protein (g/100 g dry bagasse)	5.0†

* Error = ±1 standard deviation

† Protein analysis was done by the Soil Testing Laboratory (College Station TX), using a LECO system (Dumas combustion procedure)

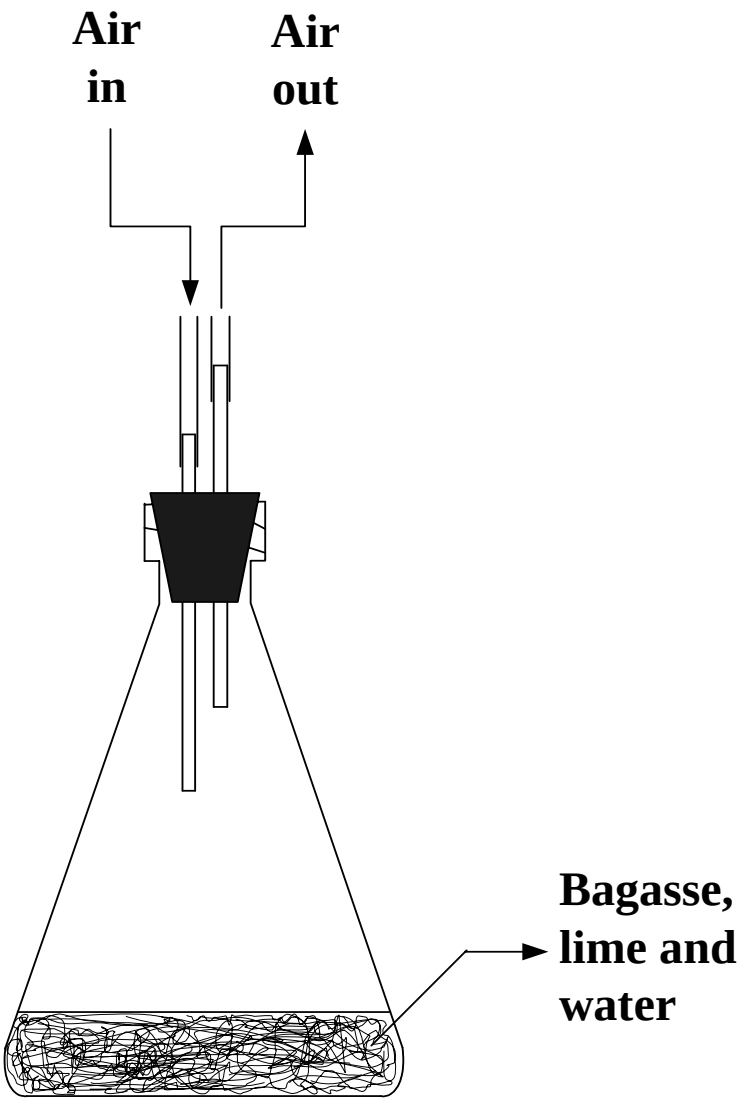


Figure 4.3 Schematic of the lime/air pretreatment of bagasse experimental setup.

Figure 4.4 Photograph of the lime/air pretreatment of bagasse experimental setup.

Two sets of bottles (i.e., A and B) were assigned to each condition of time and air or no-air treatment. Set A was used to perform a mass balance, which was done by extensively washing the biomass with water to report how much material the pretreatment had solubilized, and Set B was used to perform hydrochloric acid titrations to a pH of 7.0±0.2 to assess the amount of lime consumed by the pretreatment. After titration, the bagasse from Set B was also extensively washed and then combined with the bagasse left from Set A. This biomass was then used to determine Klason lignin content and 3-day digestibility with cellulase enzyme. The product from the digestibility was analyzed for glucose and xylose yields using an HPLC system equipped with an ion-exchange lead-based resin column (HPX-87P, Bio-Rad Laboratories, Hercules CA) and a refractive index detector (Series 200, Perkin Elmer, Perkin Elmer Life and

Analytical Sciencies, Boston MA). From the same Klason lignin content analysis, determined by the NREL methods No. 003 and 004 (NREL, 1992), the sulfuric-acid insoluble ash content (not the same as the true ash content), and an approximation of the holocellulose content (cellulose + hemicellulose) in the sample, may be obtained (holocellulose = original sample analyzed – Klason lignin – acid-insoluble ash; thus, it slightly overestimates the holocellulose content because it assumes that the biomass is formed only by holocellulose, lignin, and ash. Although close, it is not necessarily true). A detailed procedure of the methods used can be found in Appendix I.

From these studies, the yield of the treatment (g treated bagasse/g untreated bagasse), the degree of delignification, the approximate degree of carbohydrate loss, the amount of lime consumed, and the digestibility of the biomass were reported.

Because lime dissolves as the reaction occurs and because constant air purging was implemented, the hydroxide ion concentration and the oxygen levels were kept constant. This condition allowed the application of the delignification model (Equation 4.5) to our treatment.

IV.3.2.2 Preliminary Studies

Oxidative pretreatment is more effective at high oxygen pressures (Chang, 1999); however, because of the long-term conditions, it was expected that the concentration of oxygen required would be less. For the economics of the process, the use of air would be preferred over pure oxygen. To assess if there is a significant advantage that would justify the use of pure oxygen over air, a preliminary study was performed to establish a comparison.

Bottles were set up as described in Section IV.3.2.1 and kept under pure oxygen obtained from an oxygen tank (Praxair Inc., Bryan TX) and air from the building compressor. Lime was added as necessary when pH decreased; first 10 g /100 g dry untreated bagasse was added at time 0, 15 g/100 g dry untreated bagasse after 33 days, and finally 15 g/100 g dry untreated bagasse after 67 days.

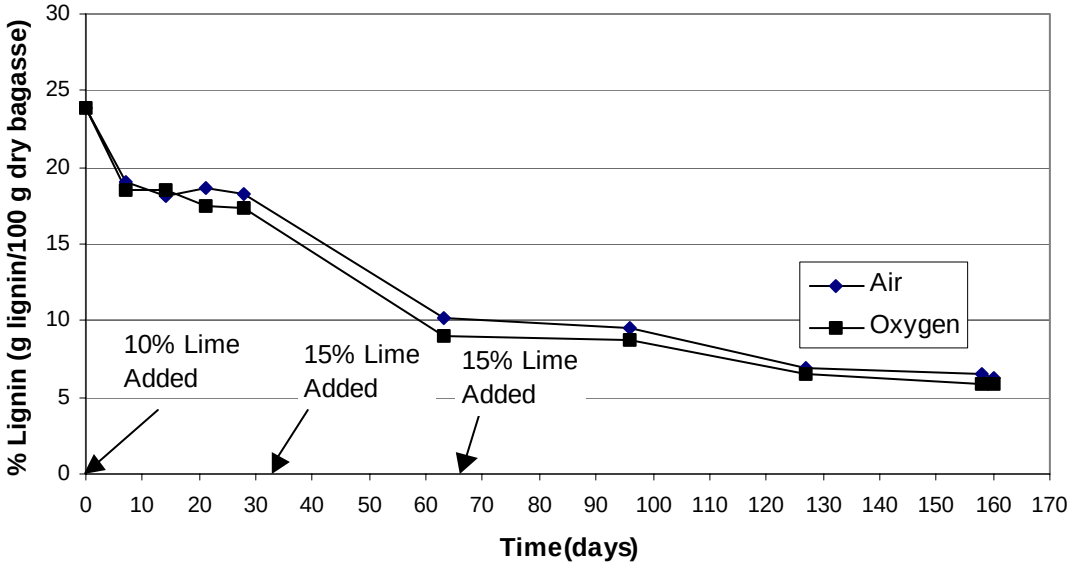


Figure 4.5 Comparison of the delignification process for air and pure oxygen (57°C).

Figure 4.5 compares the delignification process at 57°C. At the beginning of the process, there is virtually no difference between the use of oxygen and air. As delignification progressed, the process was enhanced by pure oxygen only by an average difference of 0.61±0.47% (g lignin/100 g dry bagasse) (± 1 standard deviation). In comparison, lignin content decreased from 23.9 g lignin/100 g dry bagasse to an average of 9.6 g lignin/100 dry bagasse, which is equivalent to a total decrease of 14.3 g lignin removed/100 g dry bagasse in only about 2 months. These results indicate that oxygen is an average of 4.3% (4.3 g lignin/100 g lignin removed) more effective than oxygen after 2 months. This value decreases as the reaction continues further.

This result, shows that there is no significant advantage that would justify the use of pure oxygen instead of simply using air, at least at temperatures lower than 57°C, where the oxygen partial pressure is adequately high due to the low water vapor pressure; therefore, the following experiments were performed using air only. As a control, samples were also run excluding air.

IV.3.2.3 Results and Discussions

All the procedures for the analysis of the treated bagasse described in Appendix I were also performed on untreated bagasse, and this value was then taken as time 0. All the results presented in this report are on a dry weight basis.

IV.3.2.3.1 Loss of Total Mass, Holocellulose, Lignin and Ash in Sample

Figures 4.6 through 4.15 depict holocellulose, lignin, and ash as function of time, and total yield (g total treated material/g of untreated material) as the sum of all three components. For all cases, there is a rapid decrease of holocellulose and lignin, and thus of total mass in the first 7 days. After the first 7 days, for the material treated without air at all temperatures (Figures 4.6 through 4.10), holocellulose removal levels off, and lignin elimination is very minor.

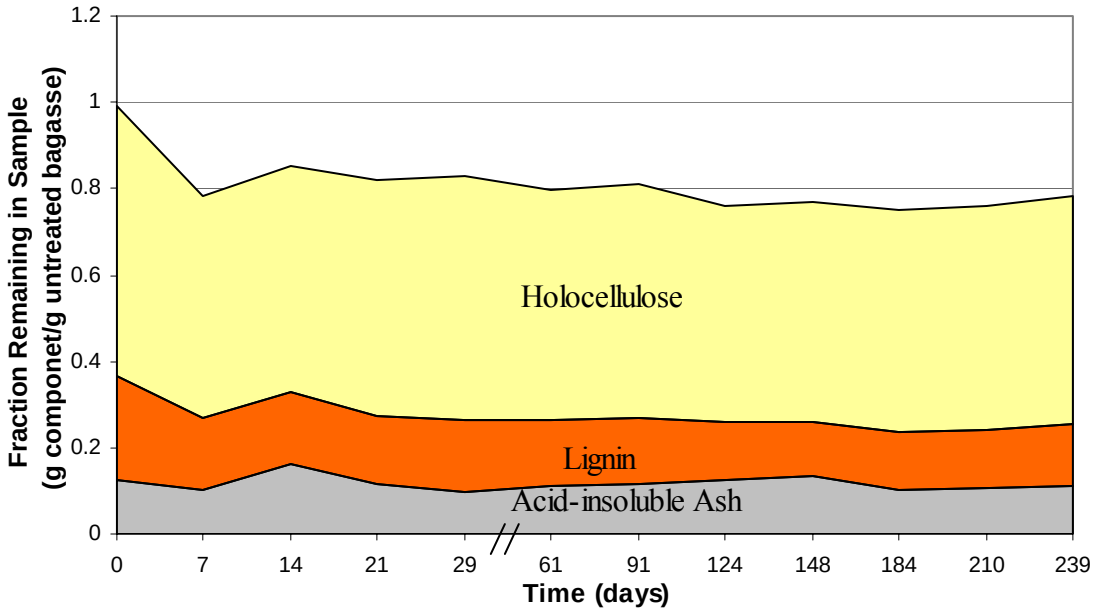


Figure 4.6 Total mass, holocellulose, lignin and ash for treatment without air purging at 23°C.

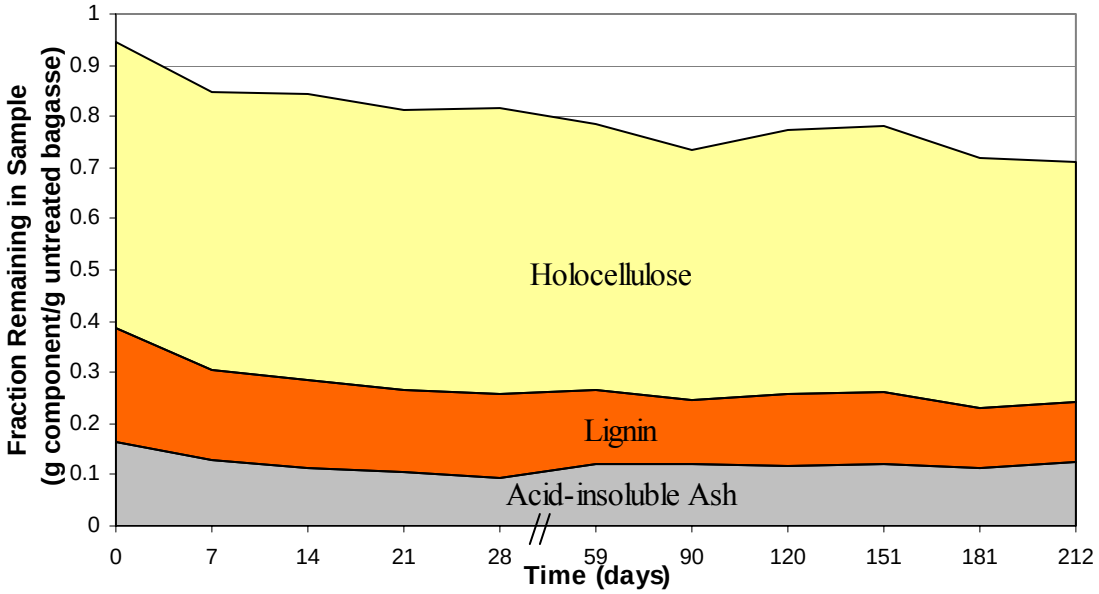


Figure 4.7 Total mass, holocellulose, lignin and ash for treatment without air purging at 30°C.

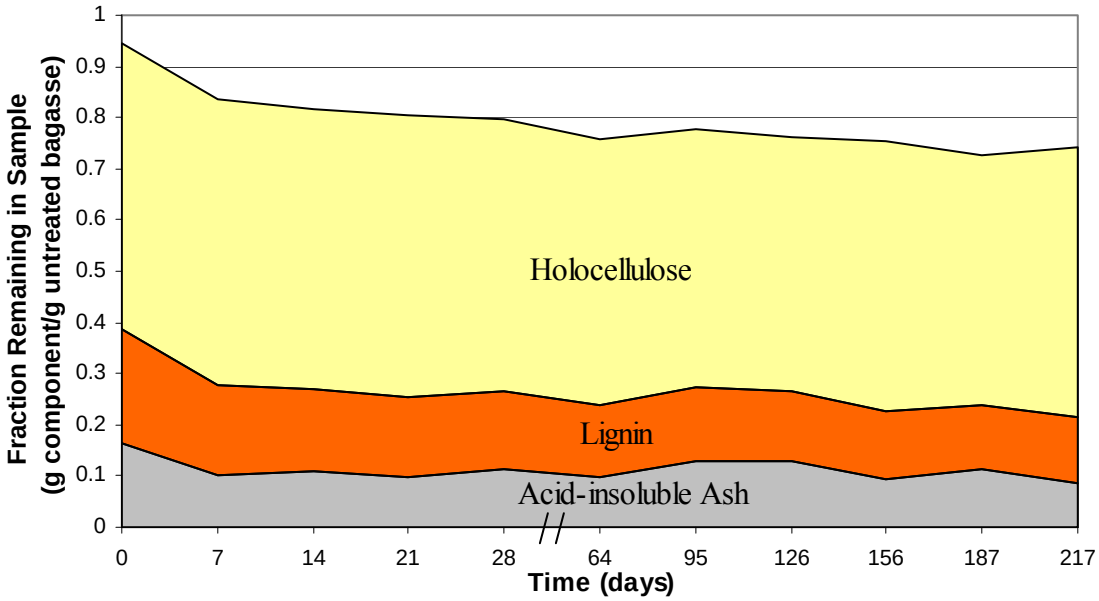


Figure 4.8 Total mass, holocellulose, lignin and ash for treatment without air purging at 40°C.

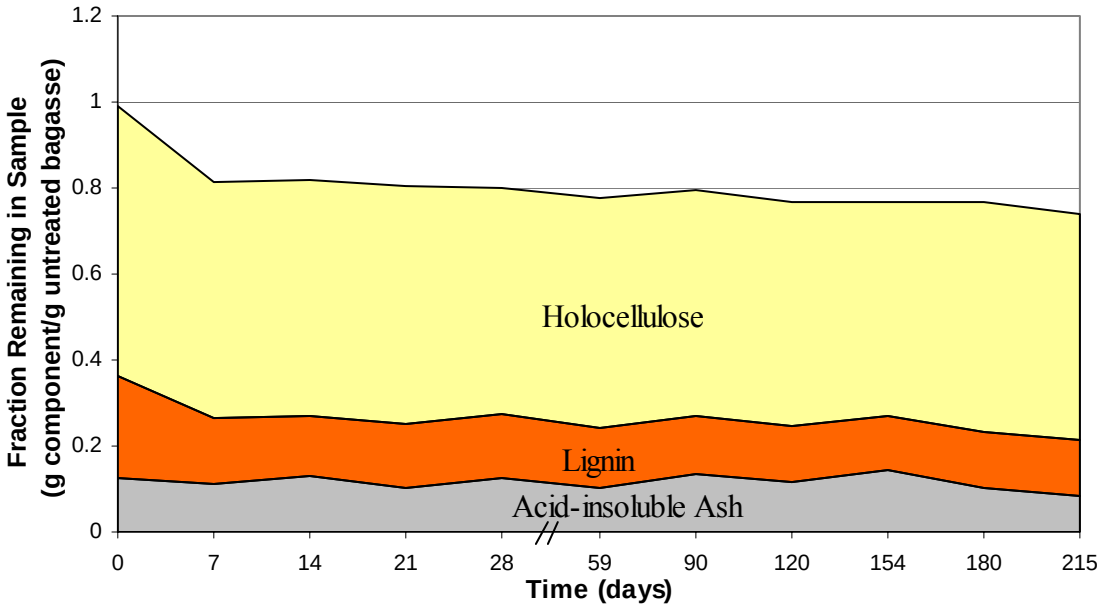


Figure 4.9 Total mass, holocellulose, lignin and ash for treatment without air purging at 50°C.

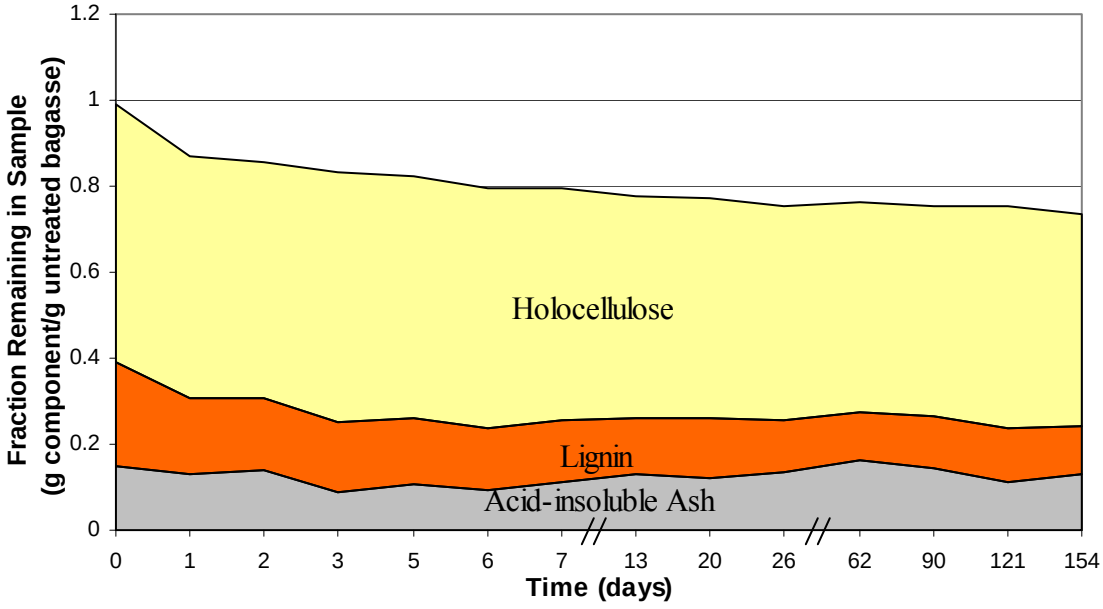


Figure 4.10 Total mass, holocellulose, lignin and ash for treatment without air purging at 57°C.

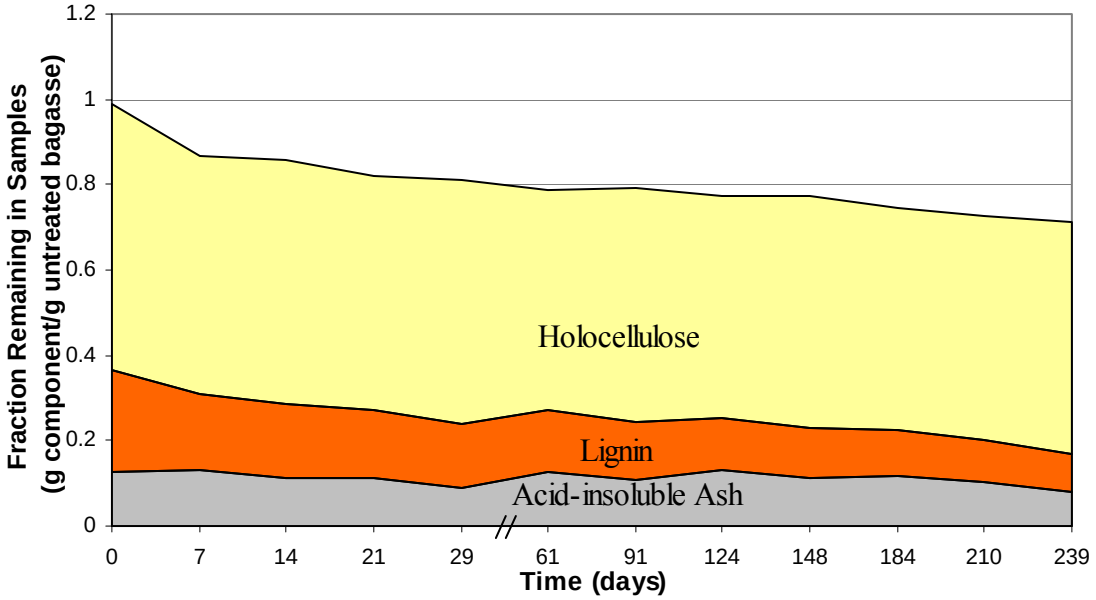


Figure 4.11 Total mass, holocellulose, lignin and ash for treatment with air purging at 23°C.

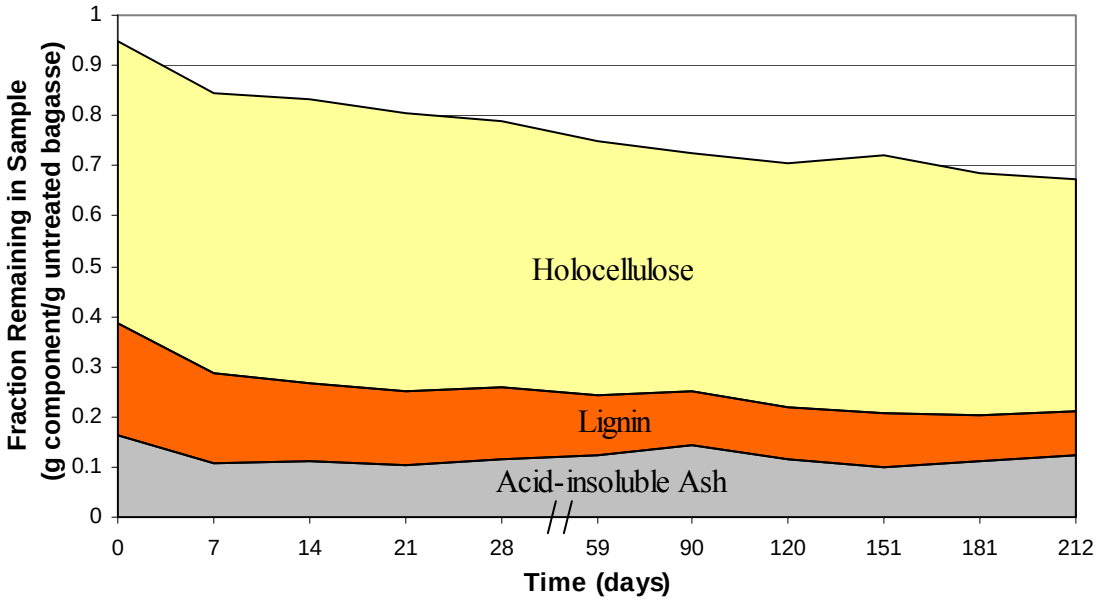


Figure 4.12 Total mass, holocellulose, lignin and ash for treatment with air purging at 30°C.

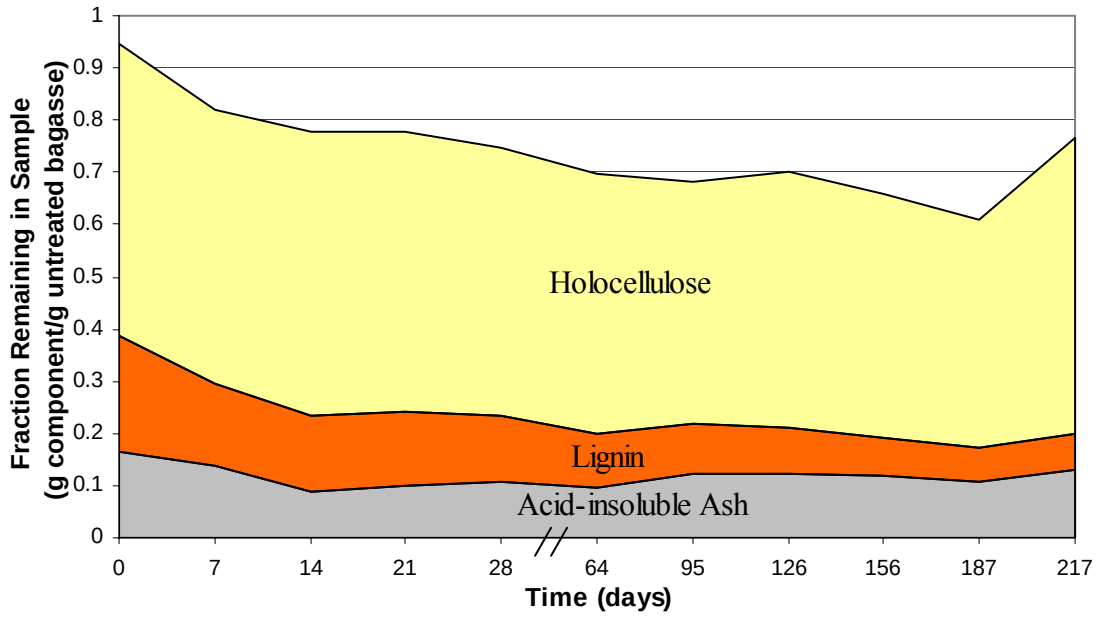


Figure 4.13 Total mass, holocellulose, lignin and ash for treatment with air purging at 40°C.

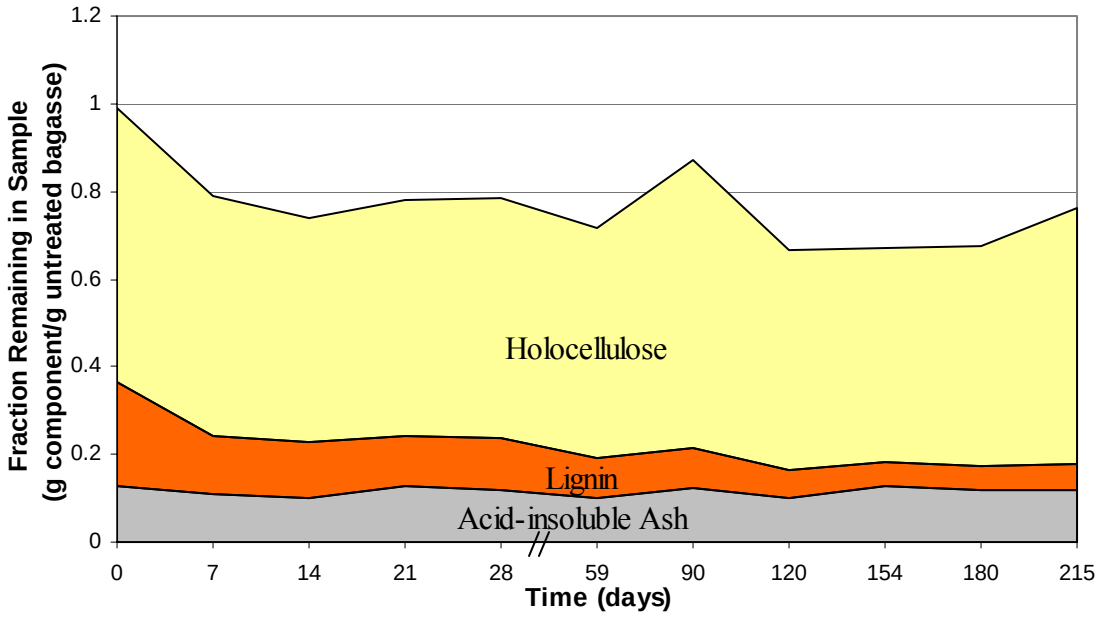


Figure 4.14 Total mass, holocellulose, lignin and ash for treatment with air purging at 50°C.

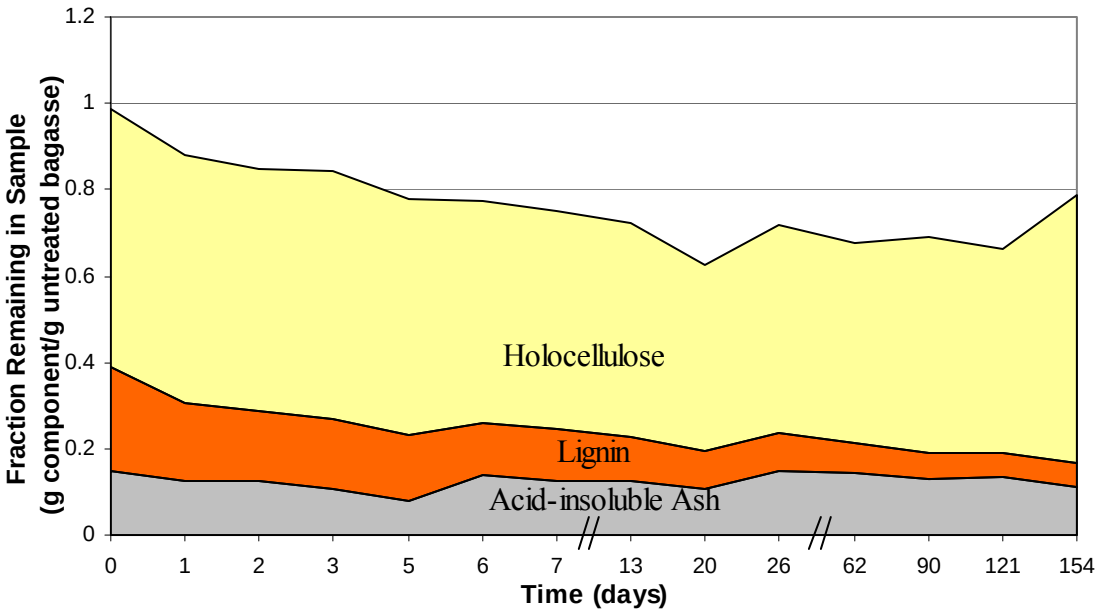


Figure 4.15 Total mass, holocellulose, lignin and ash for treatment with air purging at 57°C.

In the case of the treatment with air purging (Figures 4.11 through 4.15), holocellulose loss and lignin removal, and thus total mass loss, continues faster than in the treatments without air, although the rate of degradation is lower than during the first week. Also, a more rapid removal of lignin is observed at higher temperatures.

IV.3.2.3.2 Treatment Selectivity towards Holocellulose and Lignin

The holocellulose-to-lignin selectivity (g of holocellulose lost/g lignin removed) is a parameter of vital importance because it describes the effectiveness of our process. Ideally, a good delignification process should remove lignin without a significant loss of holocellulose; therefore, small values are desired for this parameter.

Figures 4.16 through 4.25 show the holocellulose loss as a function of lignin removed in terms of the original untreated bagasse for the final delignification stage of the treatments in the presence and absence of oxygen (i.e., air) at the different temperatures.

Linear regression was employed to obtain the slope of the curve, which is the selectivity. The statistical analysis applied to the correlations for both treatments at all the temperatures, including the criteria used to detect outliers, is discussed in Appendix J.

The values for lignin removed and holocellulose loss – in terms of the original untreated bagasse – were calculated from the lignin and holocellulose contents as ascertained by Klason lignin determination (procedures No. 003 and 004, NREL, 1992) and the total yield as found from the mass balance studies described in Appendix I. The calculation is as follows:

$$X = x_0^{Klason} Y_0 - x_t^{Klason} Y_t \tag{4.6}$$

where

X	=	Holocellulose loss or lignin removal in terms of the original untreated bagasse, g /g untreated bagasse
x_0^{Klason}	=	Holocellulose or lignin content in sample at time 0, g/g untreated bagasse
x_t^{Klason}	=	Holocellulose or lignin content in sample at any given time *t*, g/g untreated bagasse
Y_0	=	Yield at time 0, g untreated bagasse/g original untreated bagasse.
Y_t	=	Yield at time *t*, g treated bagasse/g original untreated bagasse.

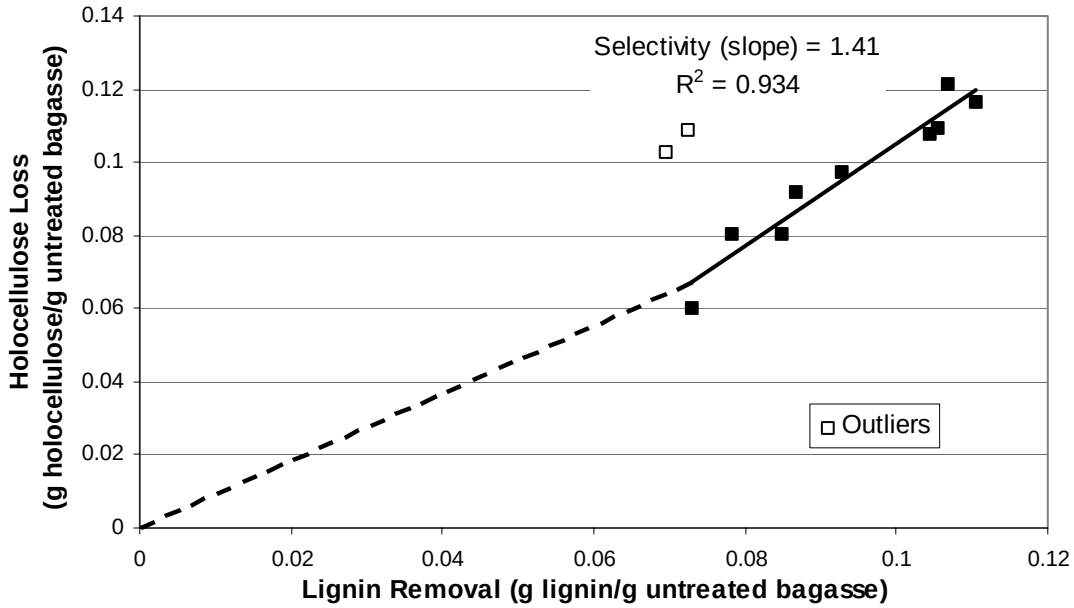


Figure 4.16 Holocellulose loss as a function of lignin removal for the final stage of lime pretreatment of bagasse without air purging at 23°C.

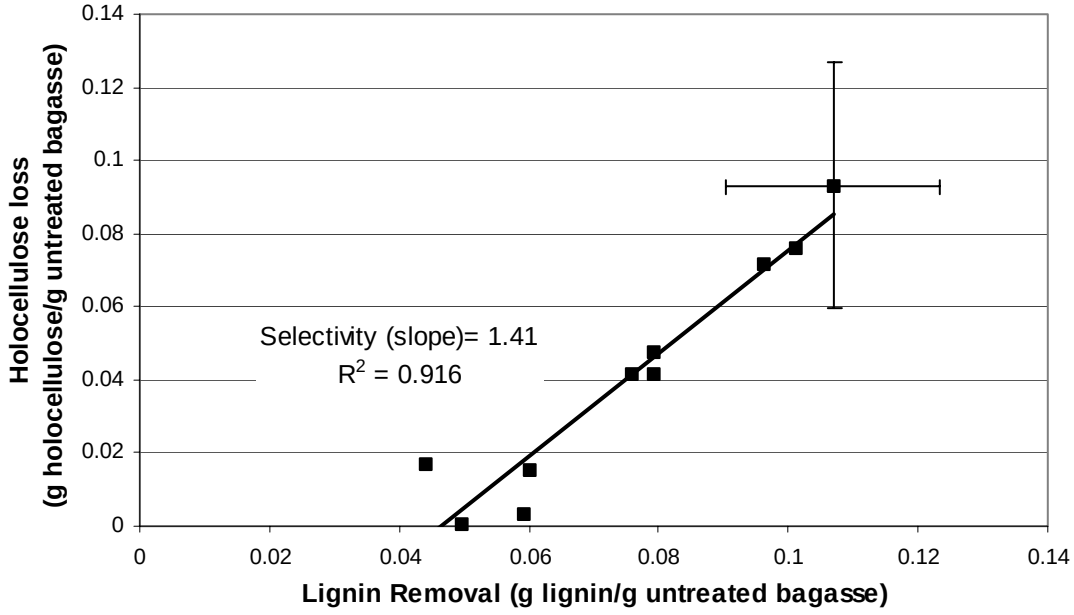


Figure 4.17 Holocellulose loss as a function of lignin removal for the final stage of lime pretreatment of bagasse without air purging at 30°C (error bars = ± 1 standard deviation).

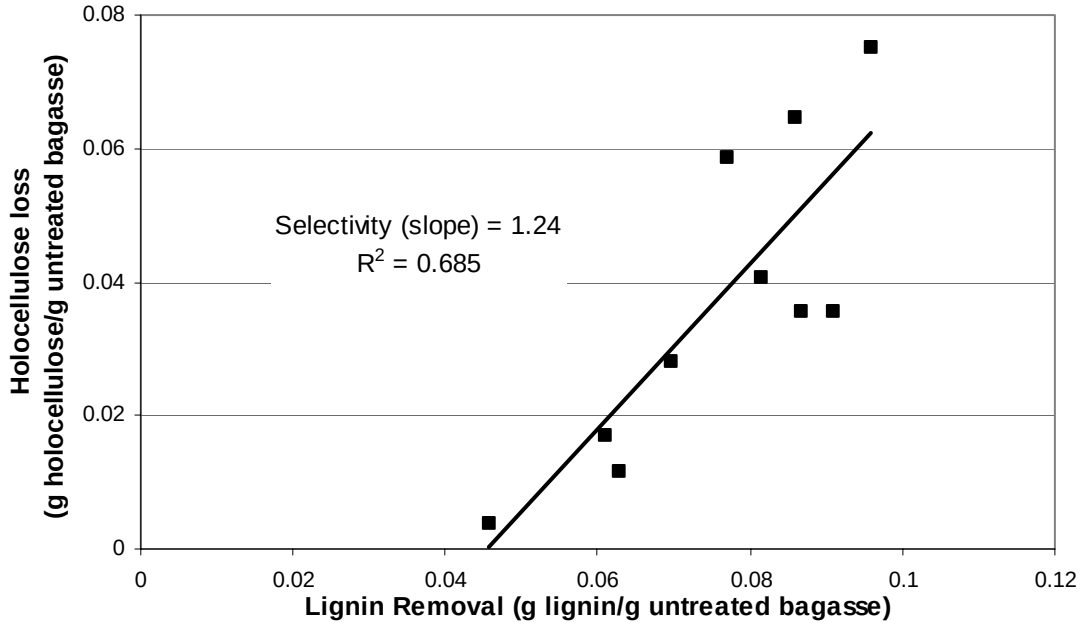


Figure 4.18 Holocellulose loss as a function of lignin removal for the final stage of lime pretreatment of bagasse without air purging at 40°C.

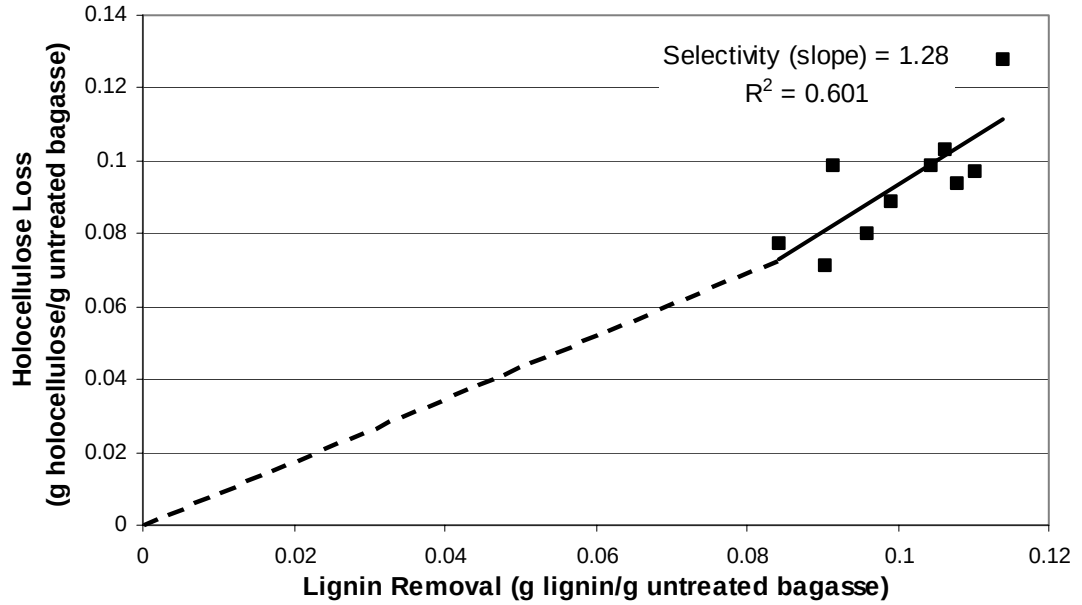


Figure 4.19 Holocellulose loss as a function of lignin removal for the final stage of lime pretreatment of bagasse without air purging at 50°C.

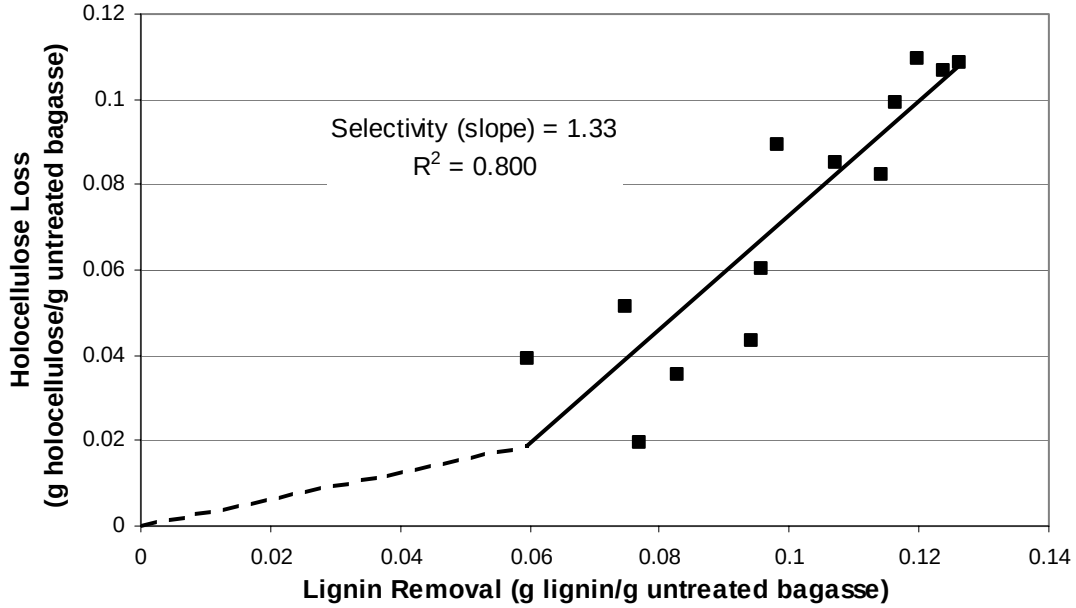


Figure 4.20 Holocellulose loss as a function of lignin removal for the final stage of lime pretreatment of bagasse without air purging at 57°C.

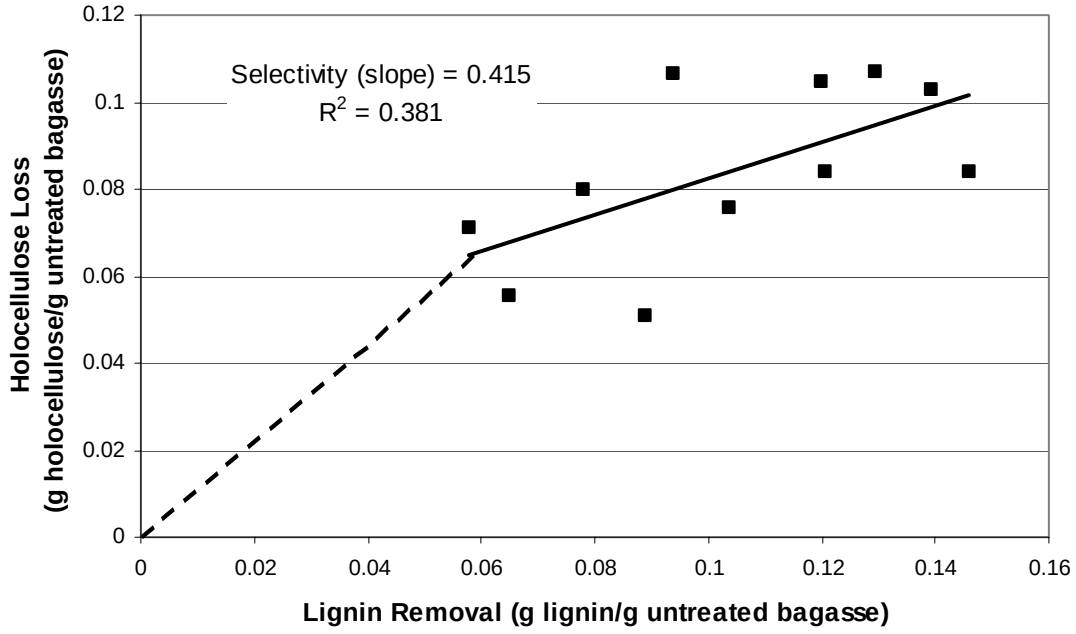


Figure 4.21 Holocellulose loss as a function of lignin removal for the final stage of lime pretreatment of bagasse with air purging at 23°C.

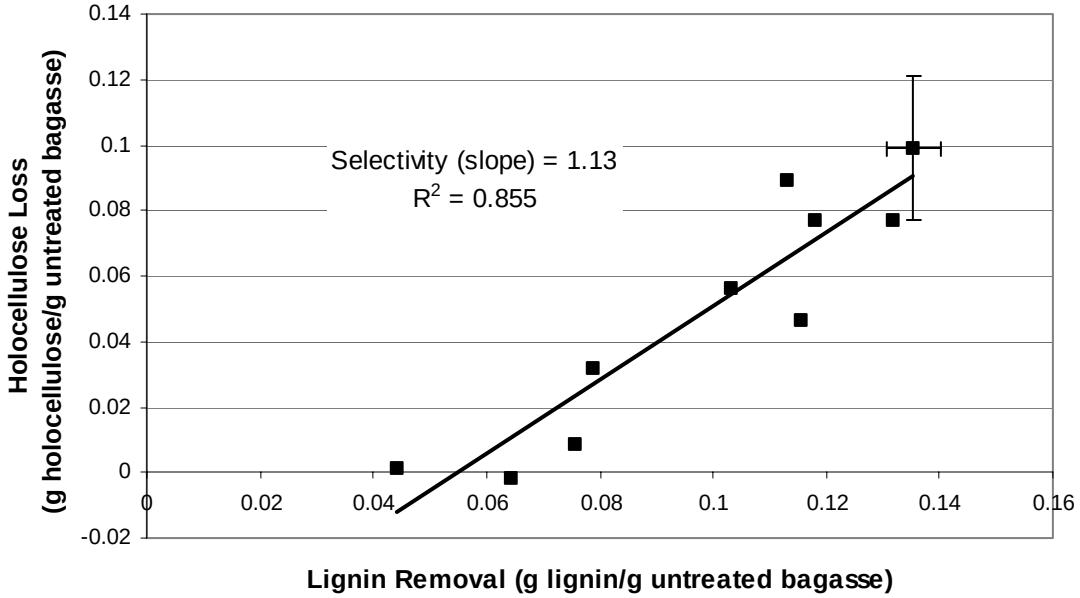


Figure 4.22 Holocellulose loss as a function of lignin removal for the final stage of lime pretreatment of bagasse with air purging at 30°C (error bars = ± 1 standard deviation).

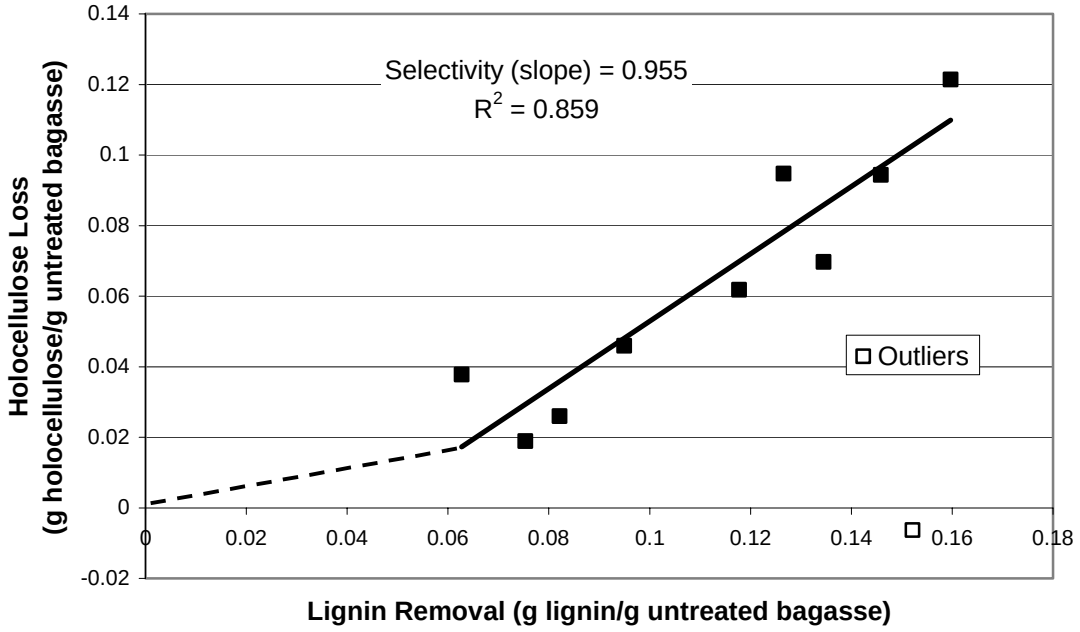


Figure 4.23 Holocellulose loss as a function of lignin removal for the final stage of lime pretreatment of bagasse with air purging at 40°C.

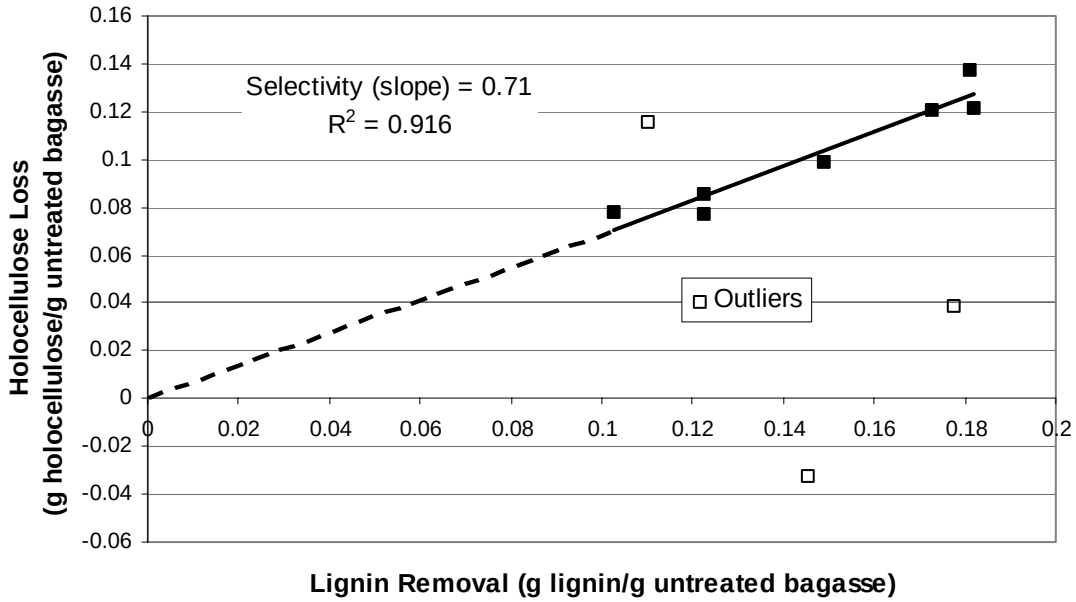


Figure 4.24 Holocellulose loss as a function of lignin removal for the final stage of lime pretreatment of bagasse with air purging at 50°C.

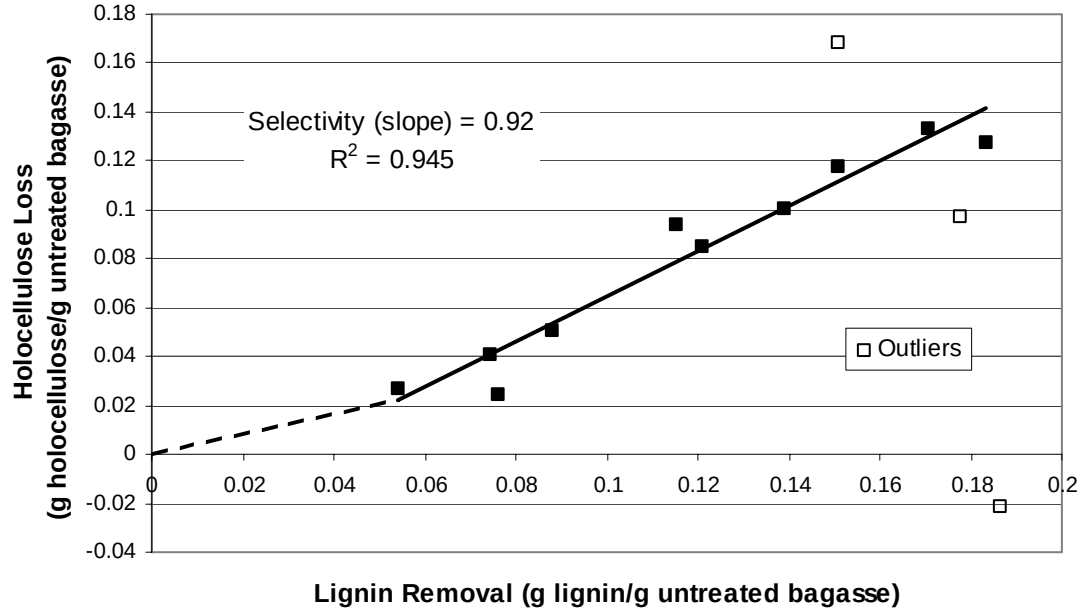


Figure 4.25 Holocellulose loss as a function of lignin removal for the final stage of lime pretreatment of bagasse with air purging at 57°C.

The overall yield at time 0 should ideally be equal to 1 g untreated bagasse/g original untreated bagasse; however, when the material balance procedure (Appendix I) was performed on the original untreated bagasse, this value was actually on the order of 0.94–0.98.

The correlations in Figures 4.16 through 4.25 do not include the initial point for the holocellulose loss and lignin removal at time 0 (i.e., 0 g of holocellulose lost or lignin removed/g of original untreated bagasse). This point, which belongs to the first delignification stage, shows a different response. Such condition was realized because, when the observation at time 0 is included in the regressions, this point is detected as an extreme outlier by the statistical influence diagnostics described in Appendix J, which was performed with SAS®.

Although more data are necessary near the beginning to obtain the selectivity for the first delignification stage, the treatment seems more selective towards lignin in the first hours or days of the pretreatment yielding a lower holocellulose-to-lignin selectivity. This would agree with the literature, which suggests that bagasse delignification occurs at the beginning with a high lignin removal rate compared to holocellulose or carbohydrate loss, and this rate changes as the treatment continues (Sabatier et al., 1993).

Figure 4.26 shows the selectivity parameters (i.e., slopes of the correlations in Figures 4.16 through 4.25) as a function of temperature. It is observed that the selectivies for the final delignification stage are virtually the same for all the temperatures for the treatment without air (i.e., non-oxidative conditions). On the other hand, there is some variability for the treatment in the presence of air. Comparing the two treatments, it is seen that the treatment with air is consistently more selective towards lignin than the treatment without air.

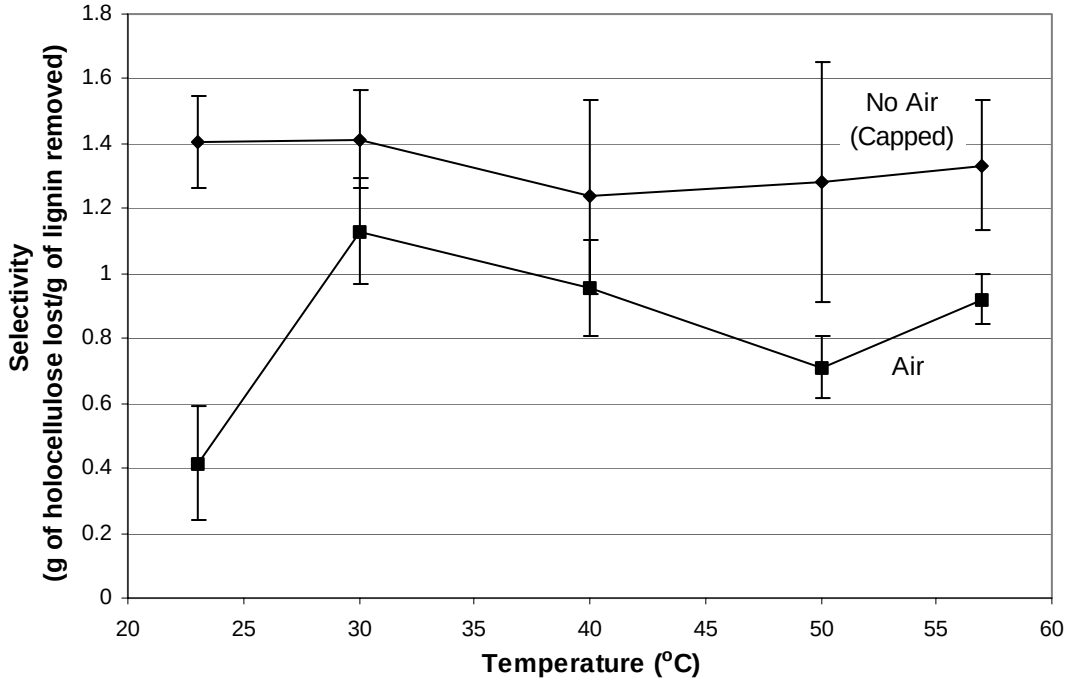


Figure 4.26 Holocellulose-to-lignin selectivities as a function of temperature for the treatments with and without air purging (error bars = ±1 standard error).

IV.3.2.3.3 Effect of Temperature and Oxygen Presence on Delignification

Figures 4.27 through 4.33 present lignin content (expressed in g remaining lignin/100 g treated bagasse on a dry weight basis) as a function of time for all the treatments at the different temperatures tested and in the presence and absence of air (i.e., oxygen).

The last observation and the original untreated bagasse for the 30°C treatment were run in triplicate; therefore standard deviations for these points could be reported. Figures 4.27 through 4.33 suggest that delignification is directly related to temperature. The delignification was more pronounced when oxygen was present. Figure 4.32 shows that when oxygen is not present, temperature does not have a significant effect on delignification. On the other hand, Figure 4.33 shows that when oxygen was present, delignification increased with temperature.

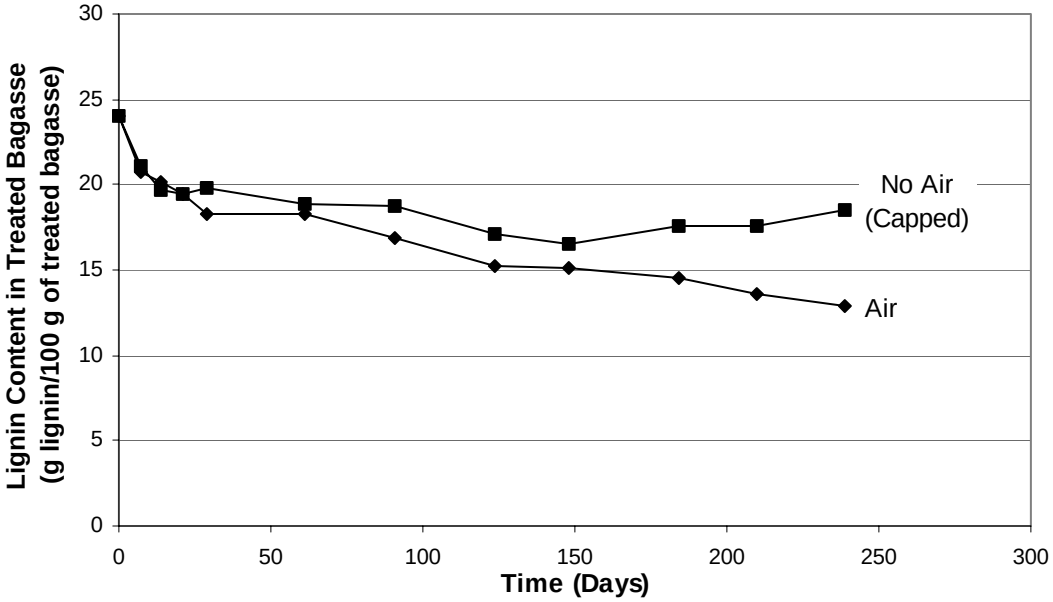


Figure 4.27 Lignin content as a function of time in lime-treated bagasse (23°C).

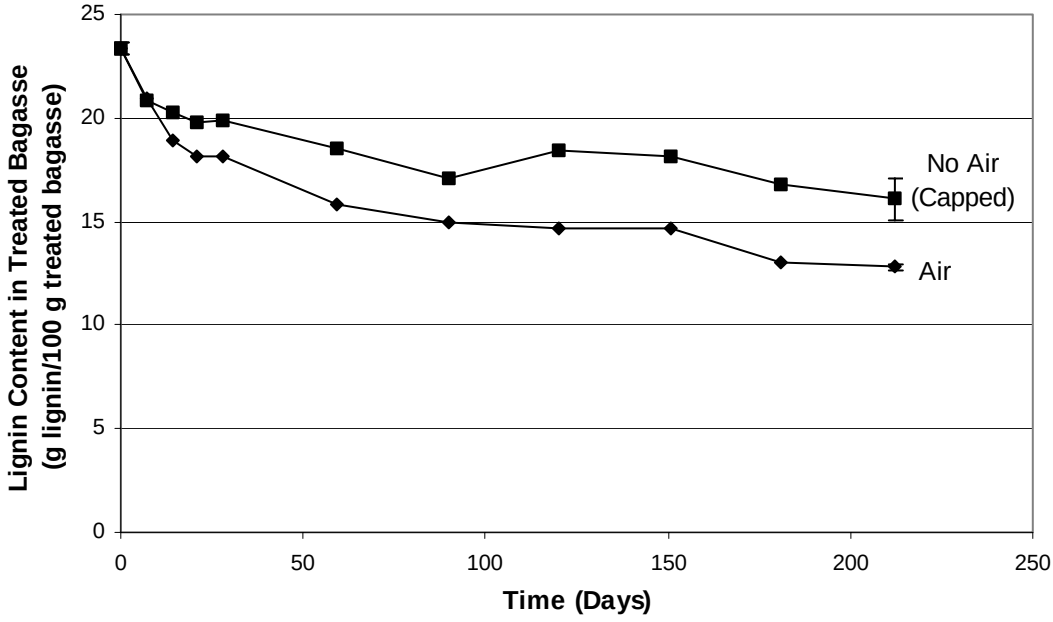


Figure 4.28 Lignin content as a function of time in lime-treated bagasse (30°C) (error bars = ±1 standard deviation).

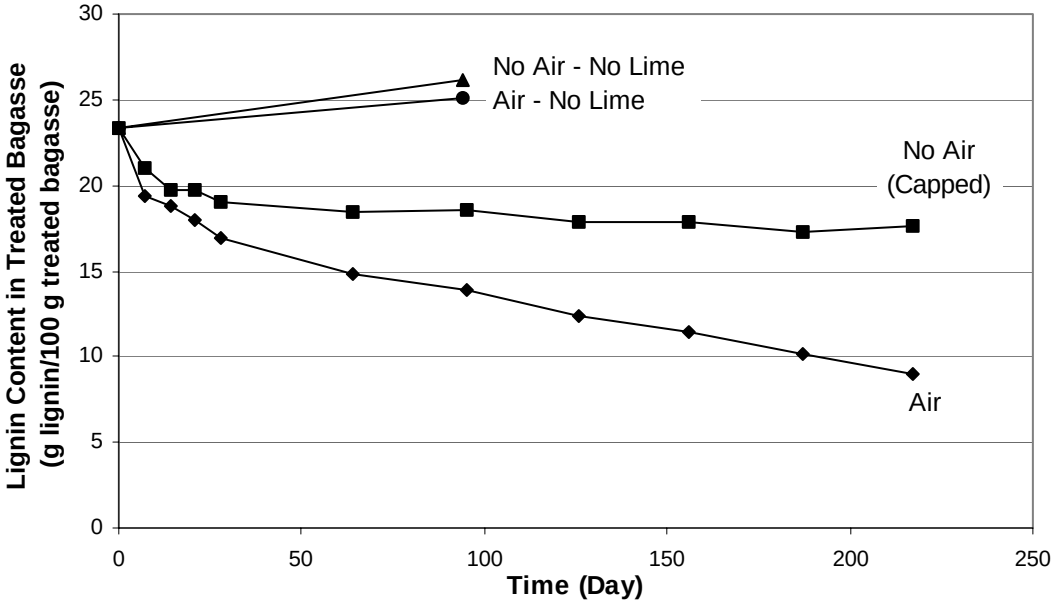


Figure 4.29 Lignin content as a function of time in lime-treated bagasse (40^{o}C).

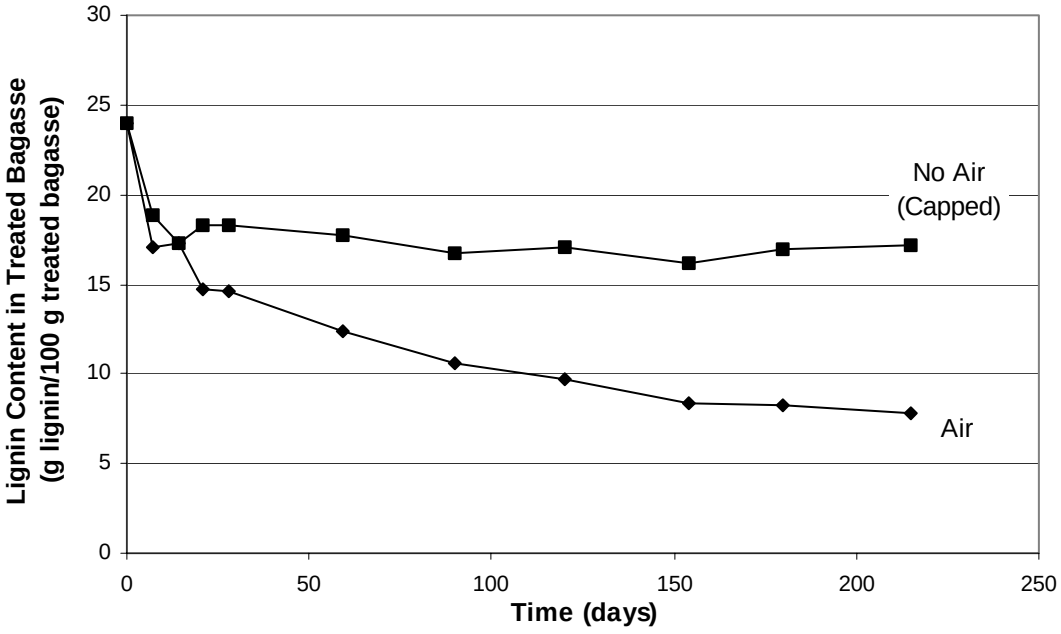


Figure 4.30 Lignin content as a function of time in lime-treated bagasse (50^{o}C).

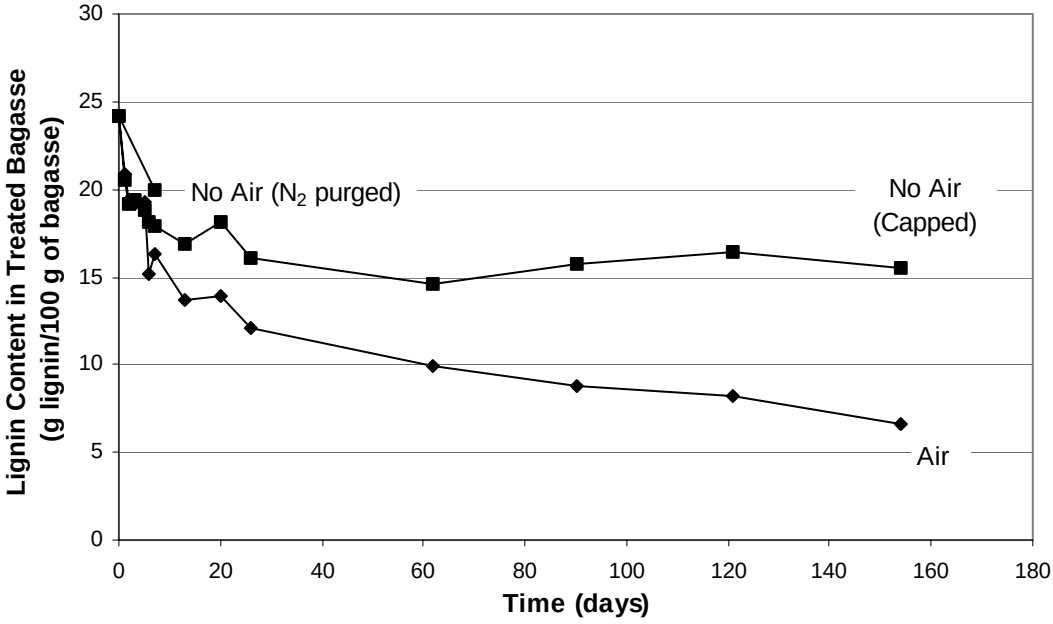


Figure 4.31 Lignin content as a function of time in lime-treated bagasse (57°C).

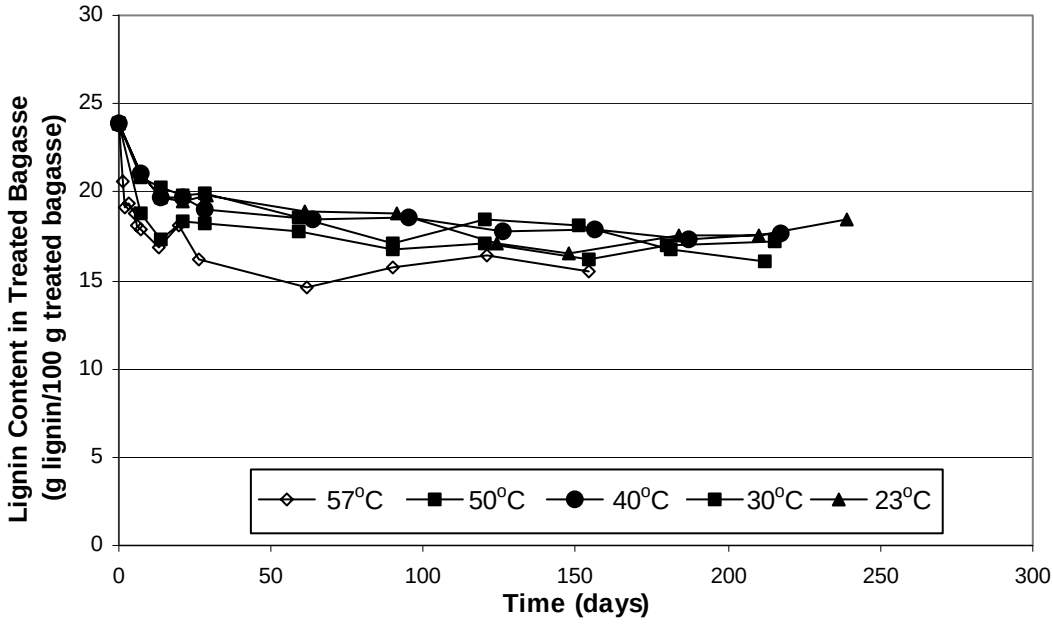


Figure 4.32 Lignin content as a function of time in bagasse lime-treated without air purging.

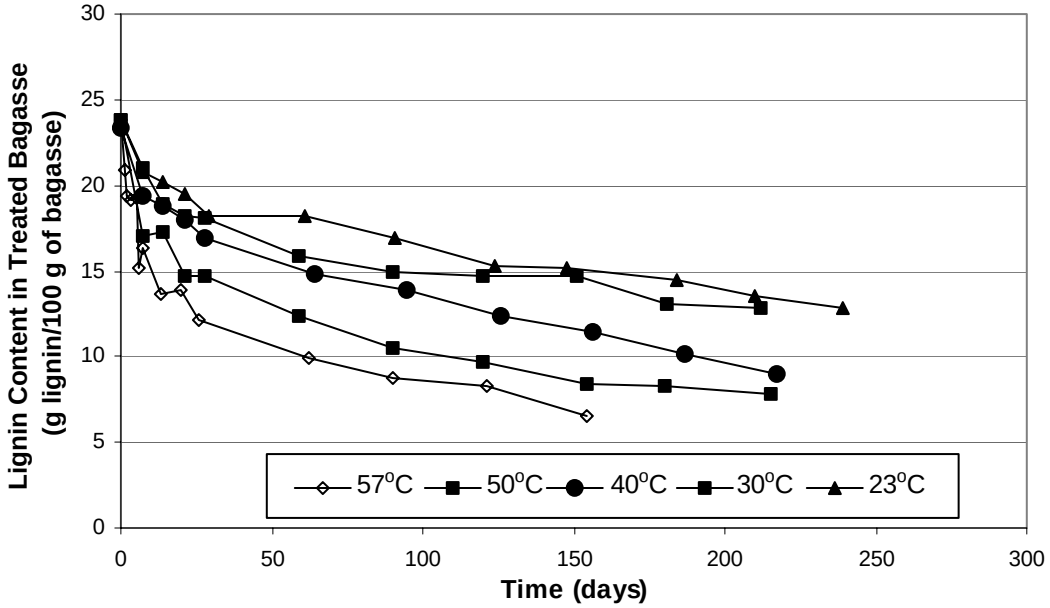


Figure 4.33 Lignin content as a function of time in bagasse lime-treated with air purging.

Even when there is no oxygen present (Figures 4.27 through 4.32), delignification occurs very rapidly during the first week and continues to level off after about a month. Because the samples that were run without air were in capped bottles, these bottles contained a head of air, which could provide some oxygen and give a high delignification rate during the first week. To test this hypothesis, a sample was first purged with nitrogen for 10 minutes and then capped. The result, shown in Figure 4.31, indicated the delignification rate was similar to the capped bottles, so the small amount of oxygen in the head space was insignificant; this first delignification stage is, indeed, independent from oxygen presence.

Controls were established to determine the following: 1) Is the first delignification stage, which is independent from oxygen presence, due to alkaline conditions? 2) Is air alone, under neutral-pH conditions, able to delignify bagasse? In the controls, no lime was added to two bottles. One bottle was capped to exclude oxygen and the other was kept under air purge. To inhibit microbial growth in these

neutral-pH bottles, 0.01-g/mL sodium azide solution was added. The results are shown in Figure 4.29. After 3 months of treatment, there was no evident lignin-content decrease in either control. It was concluded that, under these conditions, some of the lignin in the bagasse is labile to lime alone and does not require oxygen, and that in either the presence or absence of oxygen, delignification does not significantly occur unless lime (or some other alkali) is also present.

Another way of expressing delignification data is the fraction of lignin removed or lignin conversion as a function of time, which is calculated as follows:

$$L_C = \frac{L_{0T} - L_T}{L_{0T}} \tag{4.7}$$

where

L_C = Lignin conversion, g lignin removed/g lignin in untreated bagasse

L_T = Total lignin content at time t, g lignin at time t/g treated bagasse

L_{0T} = Total lignin content at time 0, g lignin/g untreated bagasse

Figure 4.34 through Figure 4.38 show that without air, lignin conversion is only 20 to 30% (i.e., g lignin removed/100 g lignin in untreated bagasse), whereas with air purging, lignin conversion increases significantly at higher temperatures to over 70% at 57^{o}C after 150 days.

IV.3.2.3.4 Lime Consumption in the Delignification process.

Figures 4.39 through 4.43 show the estimated lime consumption as a function of time. Because carbon dioxide was not scrubbed from the air, the lime consumption was overestimated. The flow of air was kept constant for all experiments; therefore, the consumption due to carbon dioxide can be considered to be constant. This fact allows comparison of lime consumption among the different treatments.

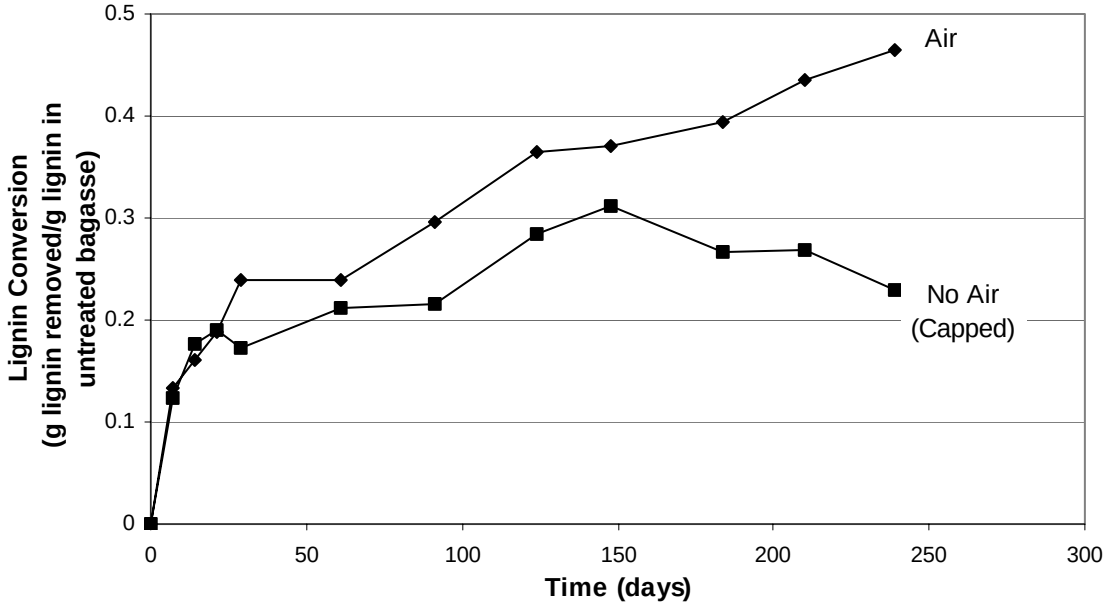


Figure 4.34 Lignin conversion of lime-treated bagasse as a function of time at 23°C.

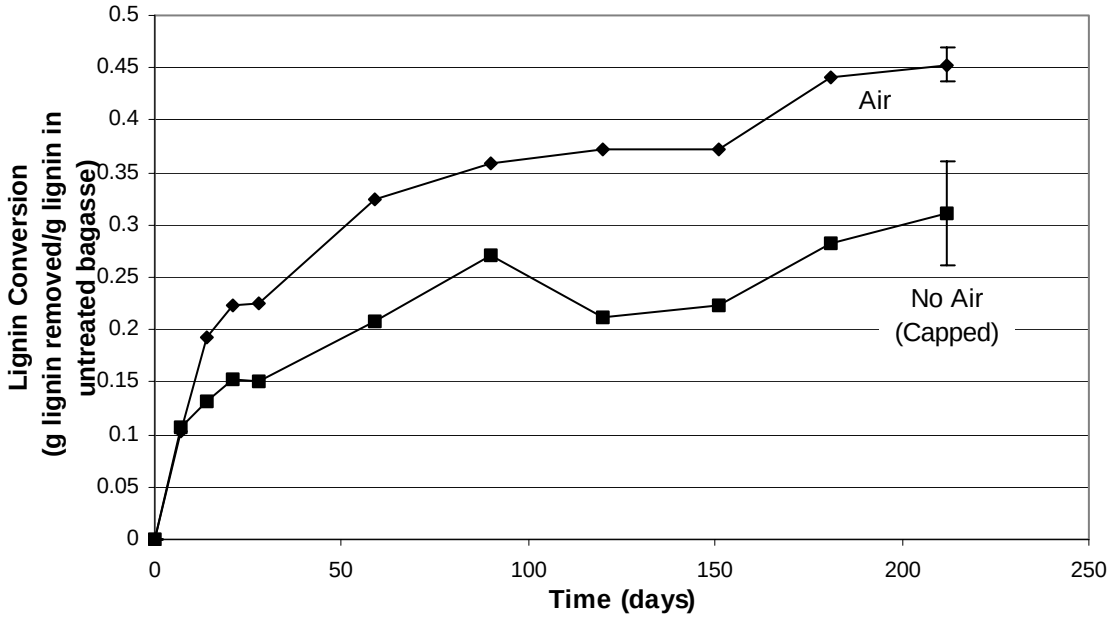


Figure 4.35 Lignin conversion of lime-treated bagasse as a function of time at 30°C (error bars = ±1 standard deviation).

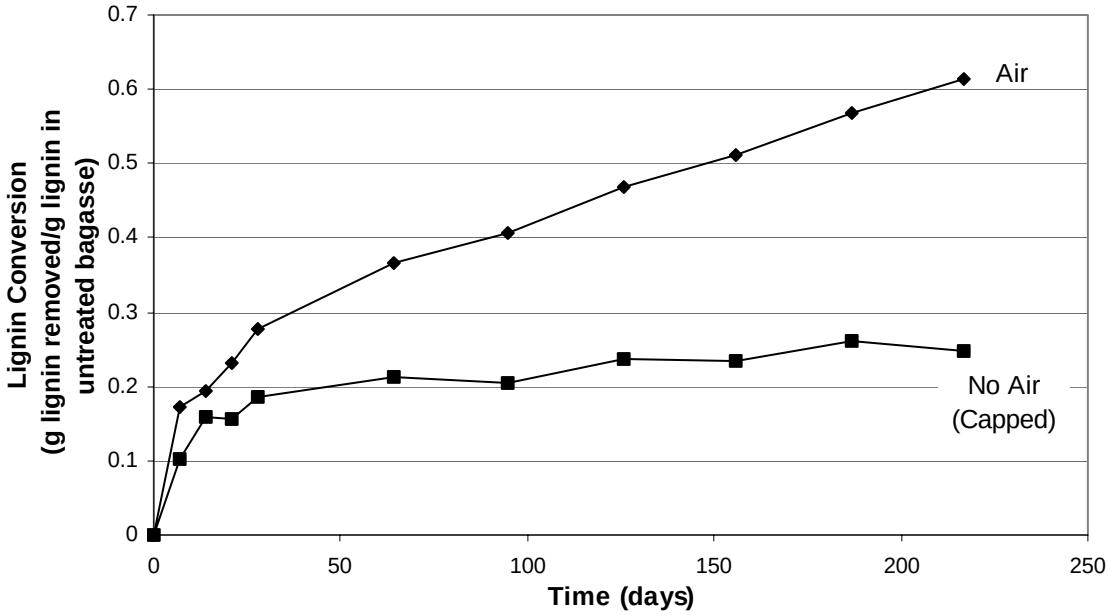


Figure 4.36 Lignin conversion of lime-treated bagasse as a function of time at 40°C.

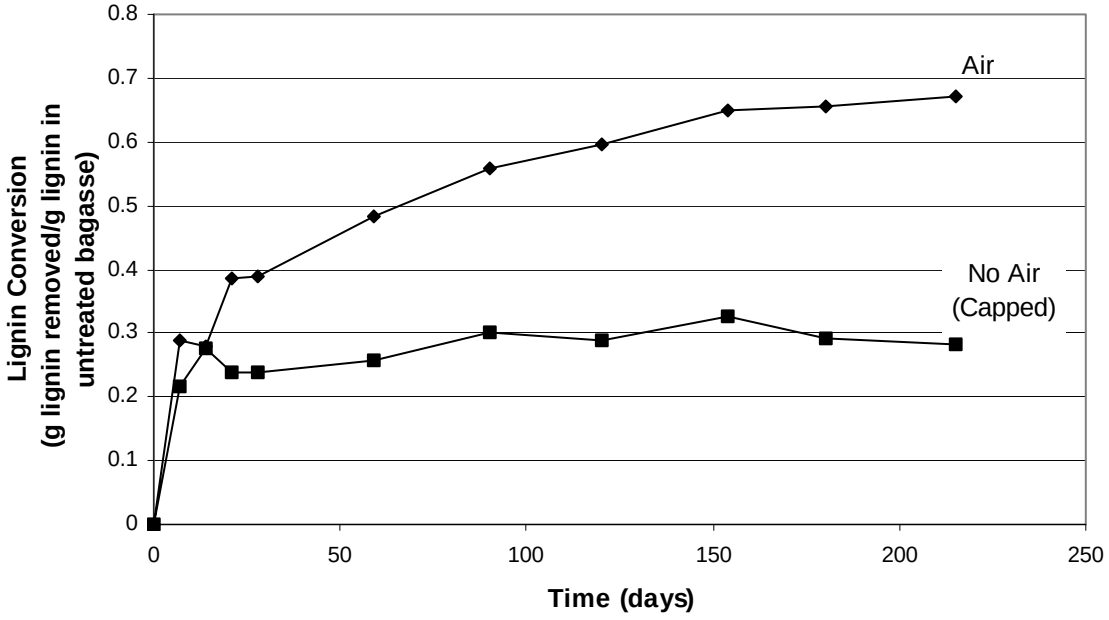


Figure 4.37 Lignin conversion of lime-treated bagasse as a function of time at 50°C.

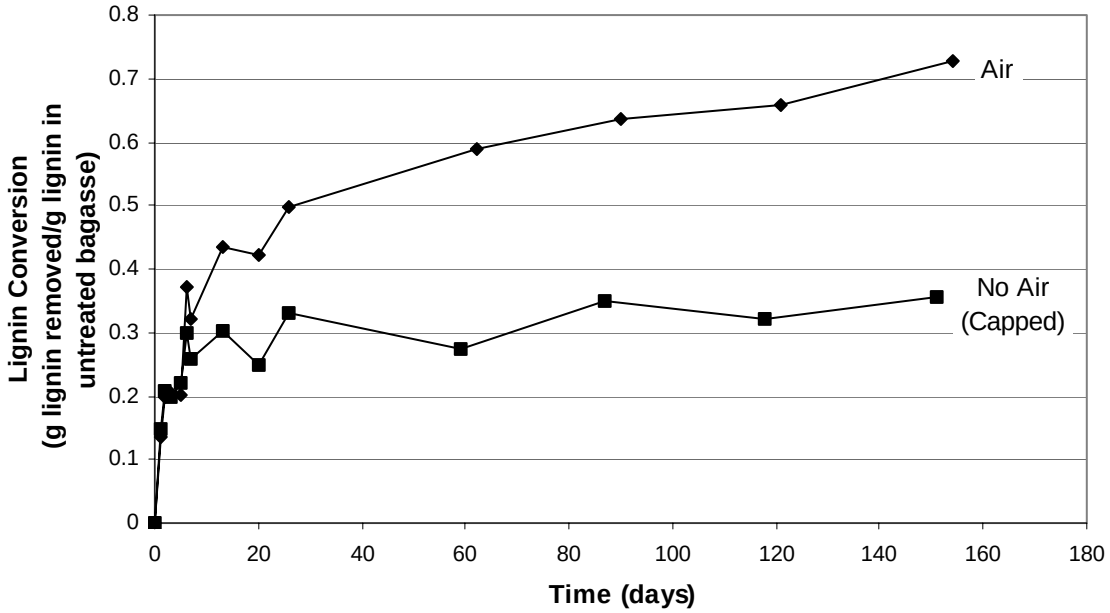


Figure 4.38 Lignin conversion of lime-treated bagasse as a function of time at 57°C.

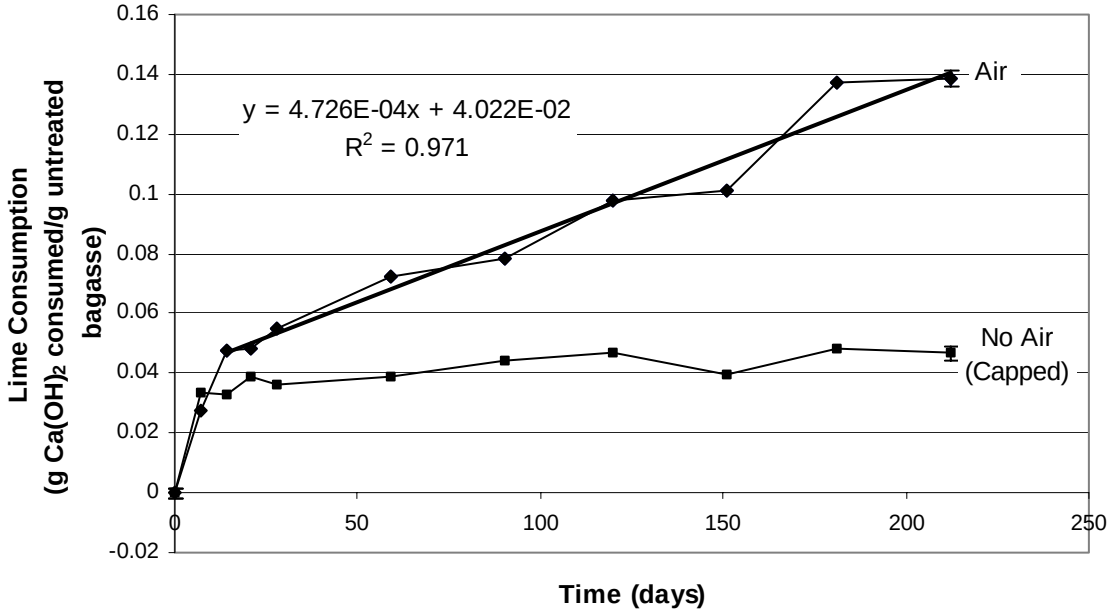


Figure 4.39 Lime consumed as a function of time in bagasse treatment at 30°C.

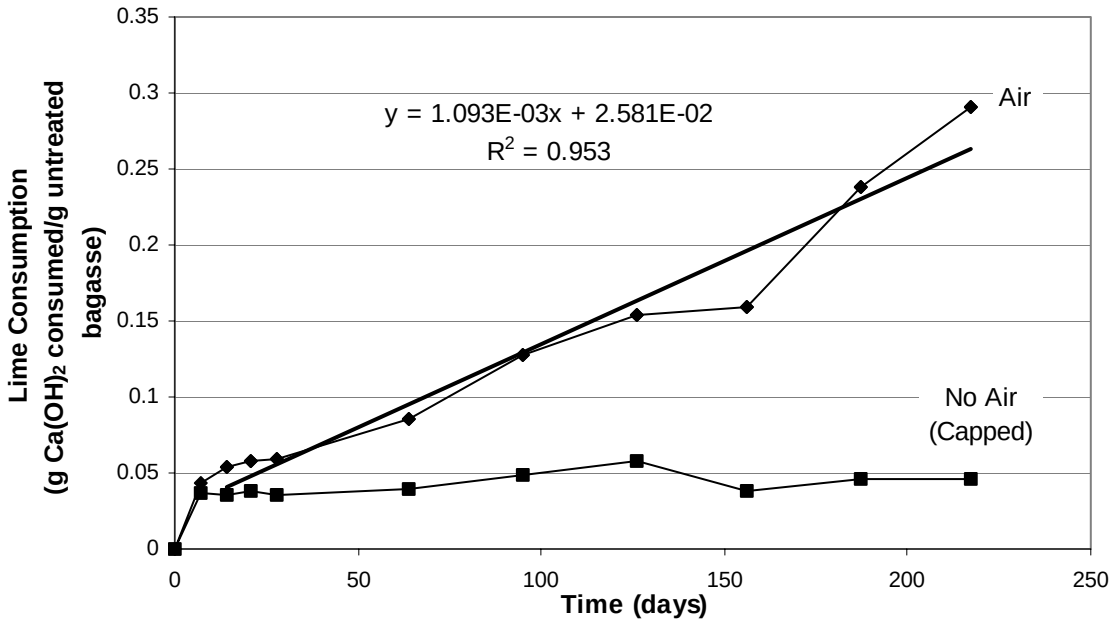


Figure 4.40 Lime consumed as a function of time in bagasse treatment at 40°C.

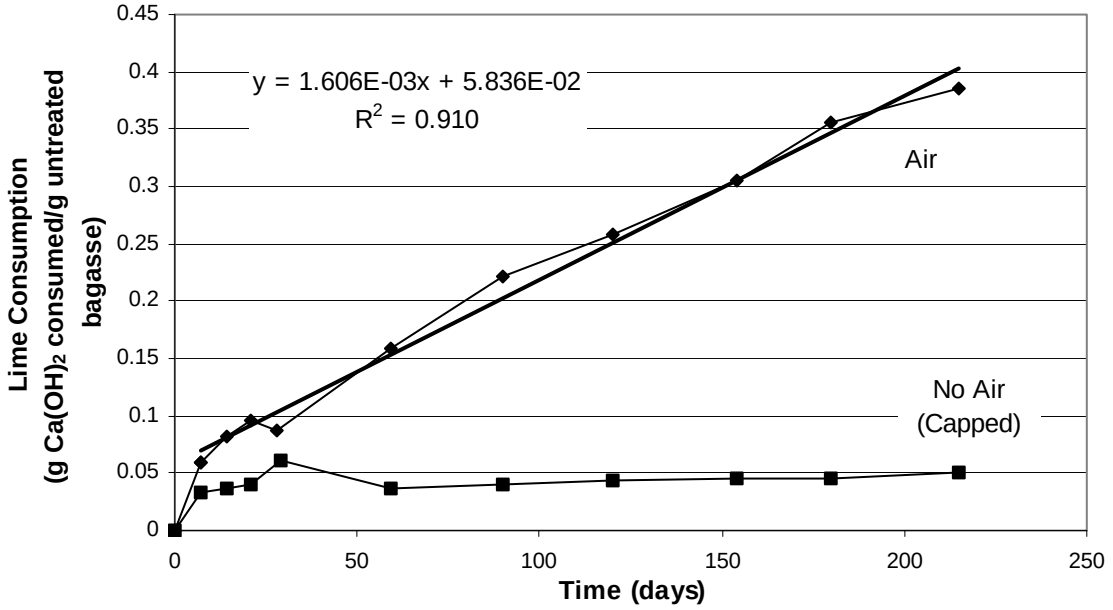


Figure 4.41 Lime consumed as a function of time in bagasse treatment at 50°C.

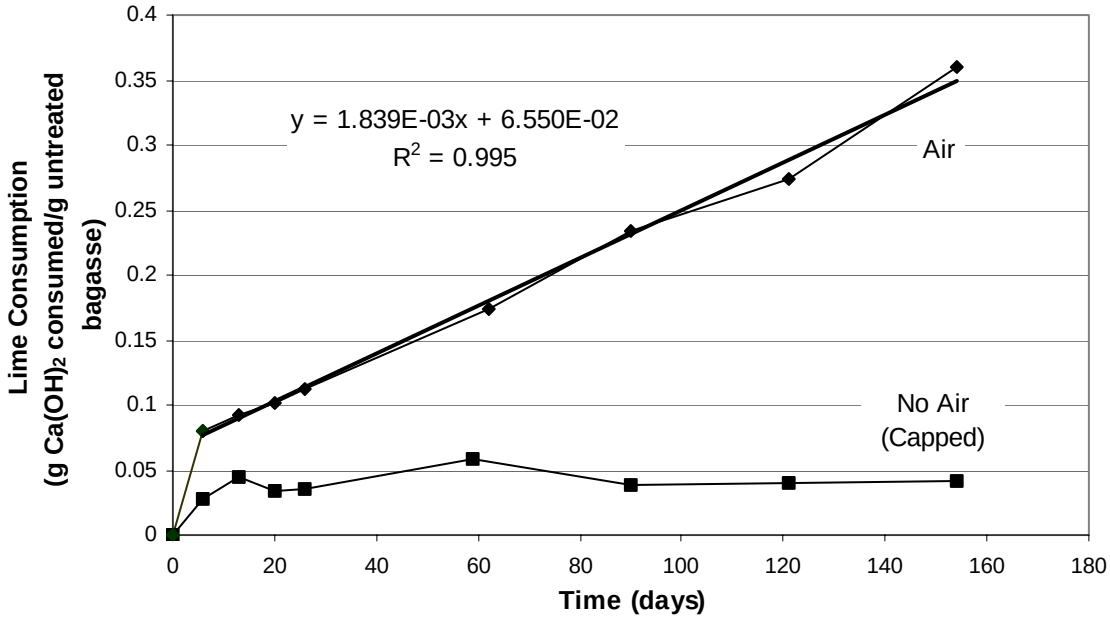


Figure 4.42 Lime consumed as a function of time in bagasse treatment at 57°C.

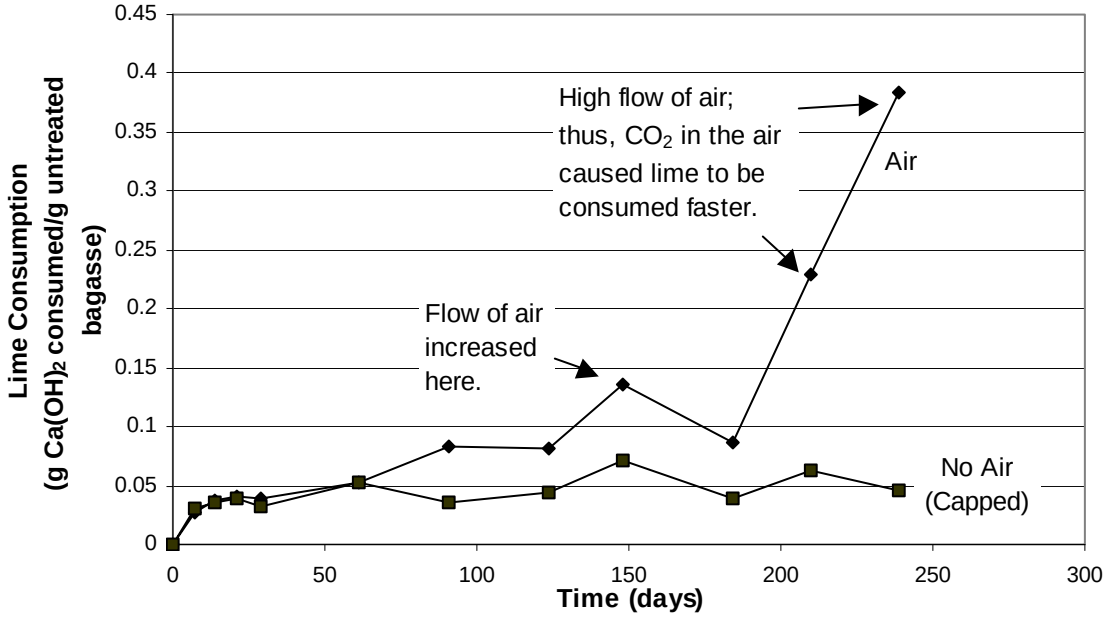


Figure 4.43 Lime consumed as a function of time in bagasse treatment at 23°C.

Lime consumption was determined by titration as described in Appendix I. The last observation and the original untreated bagasse for the treatment at 30°C were run in triplicate; thus, standard deviations could be reported for these points.

Figures 4.39 through 4.42 show that the estimated lime consumption with air is linear with respect to time after an initial 1-week phase where the lime consumption is faster. The slopes of the regressions for lime consumption as a function of time for the second phase are the lime consumption rates. Figure 4.44 shows that the relation between lime consumption rate and temperature for this second phase is not linear, but rather seems to approach an asymptote as temperature increases. This is confirmed by the fact that the data show that if lime consumption is held constant, lignin conversion is higher as temperature increases.

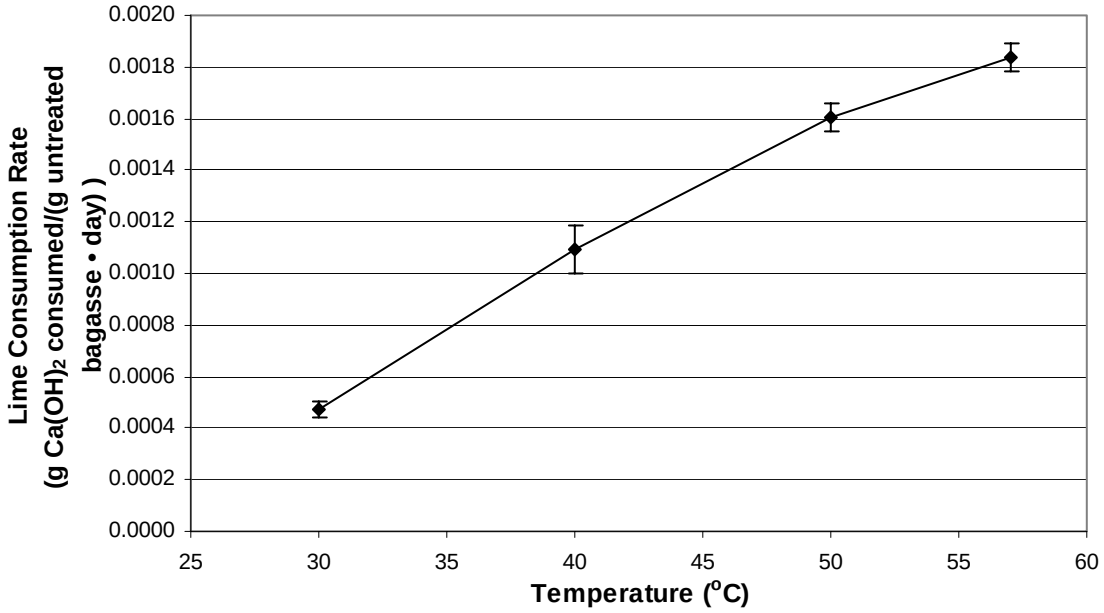


Figure 4.44 Second-phase lime consumption rate as a function of temperature for the treatment with air (error bars = ±1 standard error).

In Figure 4.43, it can be observed that the lime consumption climbed significantly after the air flow was increased for air treatment at 23°C. This situation

was attributed to carbon dioxide in the air, which consumed the lime. Those samples that were run with air purging were exposed to carbon dioxide in the air. Because the pretreatment takes several months to complete, the amount of carbon dioxide that reacts with the lime was significant; thus, the lime consumption obtained in this experiment is an overestimate. To obtain the lime consumption in the pretreatment itself, the air must be pre-scrubbed to remove carbon dioxide.

Although the values for lime consumption for the treatment with air might be overestimated, the other measurements (i.e., mass balance, lignin content and 3-day digestibility) were not affected because lime was present in excess.

Figures 4.39 through 4.43 show that the experiments without air did not display any significant lime consumption after about the first week, where it virtually settled at a lime loading of about 0.05 g $Ca(OH)_2$/g untreated bagasse. It is interesting that during the first week, the lime consumptions for both the treatment with and without air were similar. Compared to the rest of the profile for the subsequent weeks, during the first week there was a sharper lime consumption even, as mentioned, for the samples with air, which show a linear increase after the first week. Thus, it can be concluded that in lime consumption, the two-phase postulate by Sabatier et al. (1993) can also be observed.

IV.3.2.3.5 Delignification model

The delignification data were fitted to Equation 4.5 with the aid of SAS® statistical software. First, it was necessary to confirm the postulate set forth by Sabatier et al. (1993) that suggests that bagasse displays only two delignification phases instead of the common three phases observed in woody biomass to which the complete form of Equation 4.5 applies. In the selectivity studies (Section IV.3.2.3.2) it was suspected, and in the lime consumption studies (Section IV.3.2.3.4) it was clearly observed that bagasse delignification only presented two phases. Nonetheless, because the postulate says that bagasse lacks the initial phase, it was possible that this phase was so small that it would not be detected by simple visual inspection.

Although the model is semi-empirical, one of its important characteristics is that the resulting rate constants for each phase can be fitted to the well-known Arrhenius equation (Dolk et al., 1989; Chiang and Yu, 1990):

$$k = Ae^{-\frac{E_a}{RT}} \tag{4.8}$$

where

k	=	The rate constant, 1/day
A	=	The Arrhenius constant or frequency factor, 1/day
E_a	=	Activation energy, joules/mole
R	=	Universal gas constant, 8.314 joules/(mole · K)
T	=	Temperature, K

Using the three-phase model (i.e., k_i, k_b and k_r), when the rate constants obtained from the data regression were fitted to the Arrhenius equation (Equation 4.8), the fit was poor. Also, negative values for the activation energy were obtained, which is not physically possible. Therefore, it was concluded, that indeed delignification of bagasse only shows two phases, as asserted by Sabatier et al. (1993).

As suggested by Sabatier et al. (1993), the two phases in bagasse are the bulk and the residual, because the initial phase does not occur. The bulk phase is short and it controls the delignification mainly during the first week, after which the residual phase takes over. Equation 4.5 is, therefore, modified by eliminating the exponential term that belongs to the initial phase as follows:

$$\frac{L_T}{L_{0T}} = a_b \cdot e^{-k_b \cdot t} + a_r \cdot e^{-k_r \cdot t} \tag{4.9}$$

Figures 4.45 through 4.49 show the regressions of the data to the two-phase delignification model (Equation 4.9). The data fits the model remarkably well with R^2 values > 0.87. Statistical analysis for the regressions can be found in Appendix L.

The parameters a_b and a_r, as mentioned, are the fractions of lignin that are degraded in the bulk phase and the residual phase, respectively; thus, because those are the only two phases observed in bagasse, ideally, $a_b + a_r = 1$. The model regression shows, as expected, that the fraction of lignin that degrades in the residual phase is larger than the fraction that degrades in the bulk phase. Nonetheless, Figures 4.50 and 4.51 show that, as temperature increases, a_b has the tendency to slightly increase, and, consequently, a_r slightly decreases. This relation is significant, as the ANOVAS for the regressions of the curves in Figures 4.50 and 4.51 demonstrate; the P-values ranged between 0.06 and 0.13; therefore, the regressions are significant. This same response of a_b and a_r to temperature was observed by Sabatier et al. (1993) on the soda pulping of bagasse. Figures 4.50 and 4.51 also suggest that a_b is larger for the treatment with air than without air, and this difference is more pronounced as temperature increases.

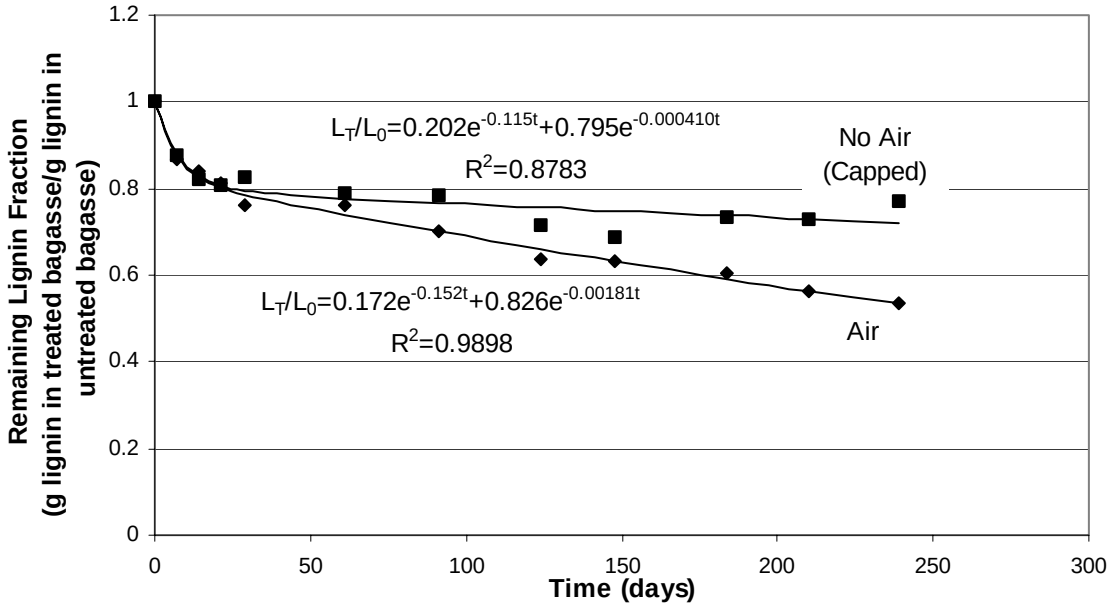


Figure 4.45 Delignification model for the treatments at 23°C.

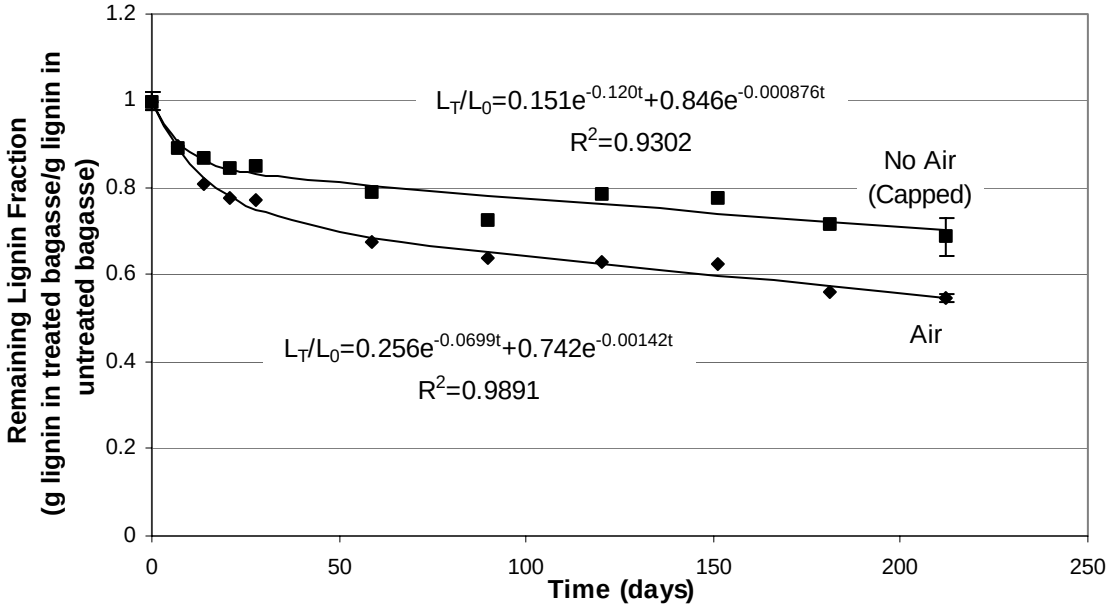


Figure 4.46 Delignification model for the treatments at 30°C (error bars = ± 1 standard deviation).

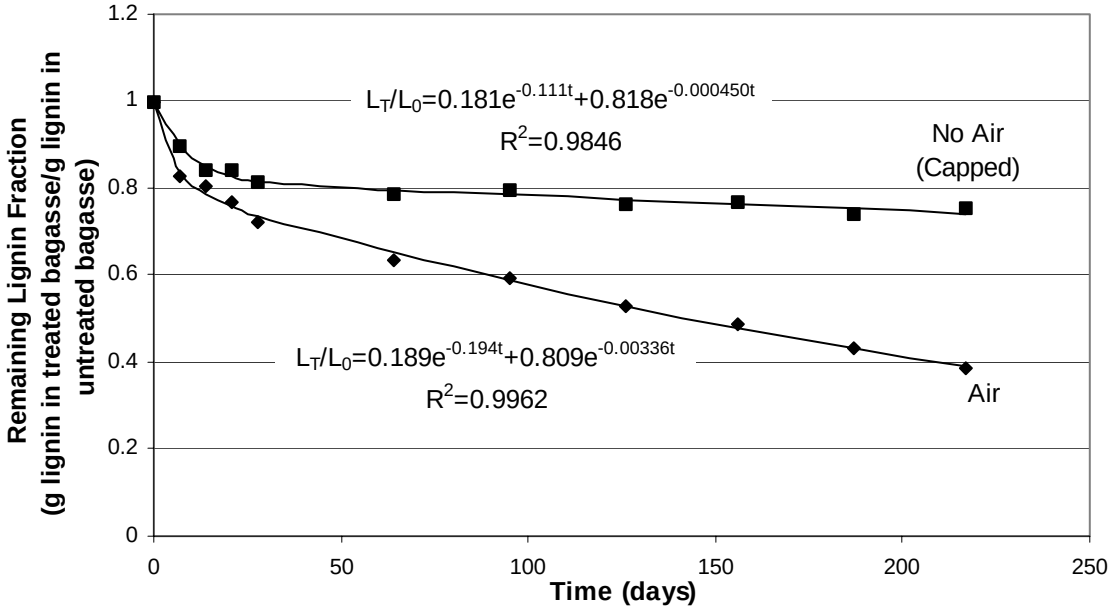


Figure 4.47 Delignification model for the treatments at 40°C.

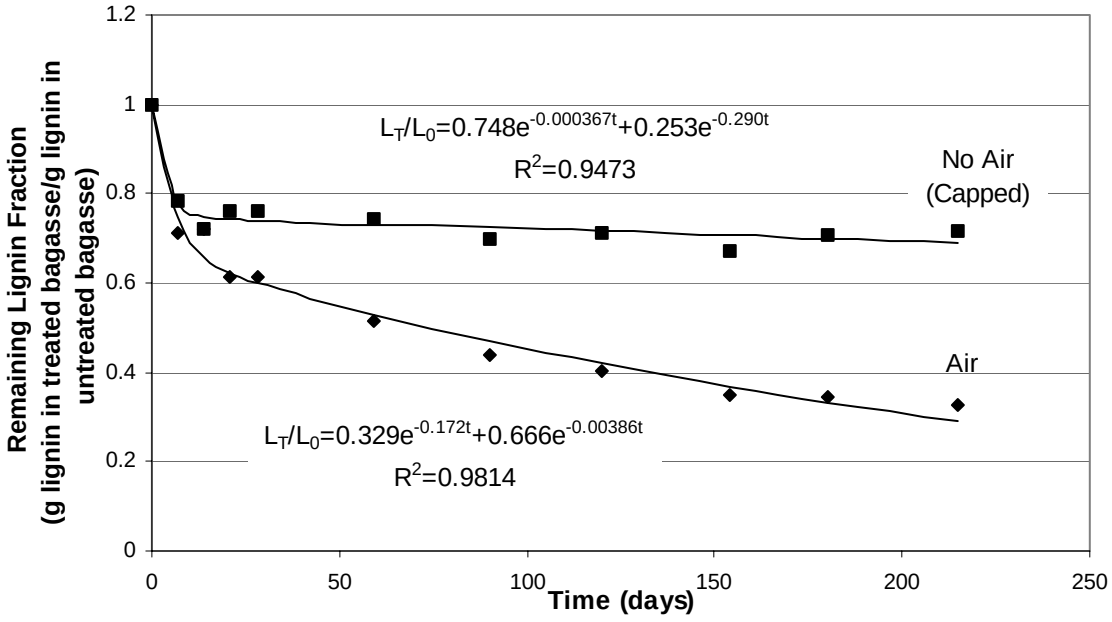


Figure 4.48 Delignification model for the treatments at 50°C.

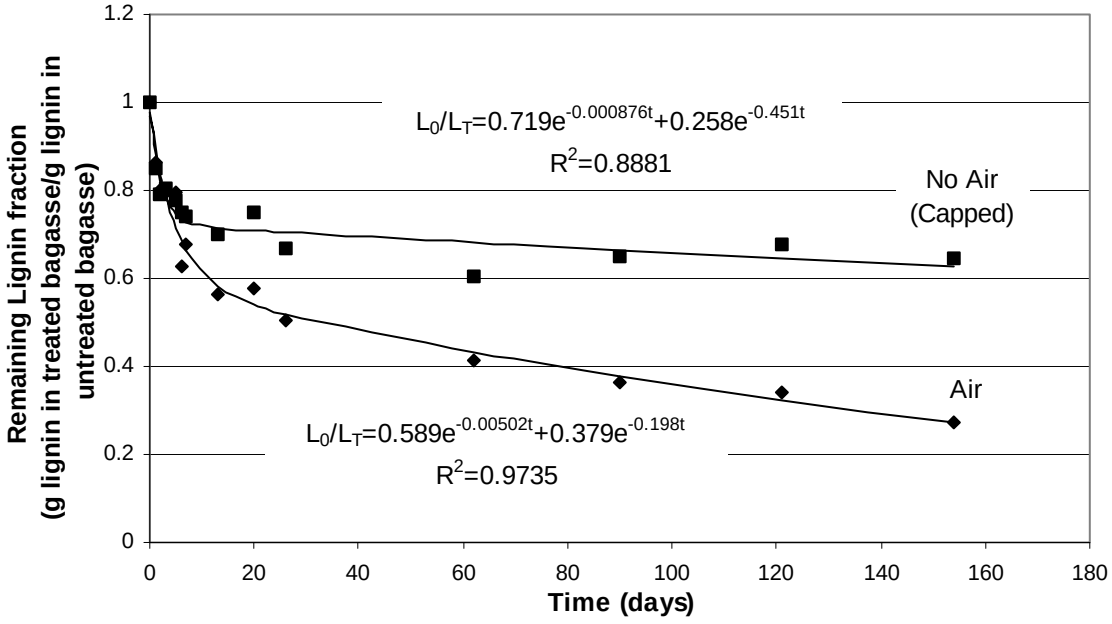


Figure 4.49 Delignification model for the treatments at 57°C.

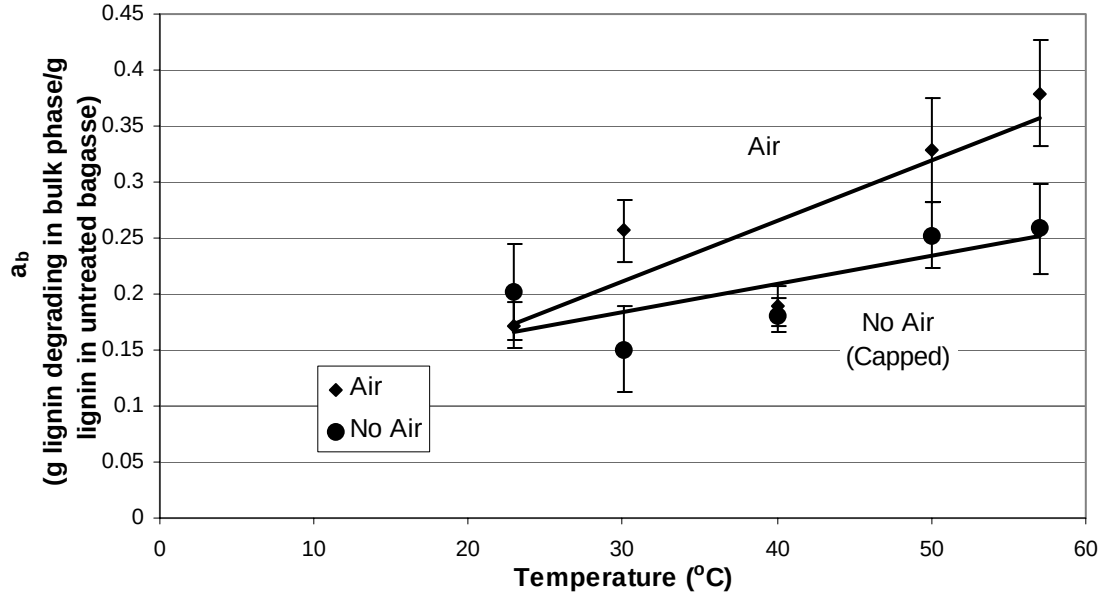


Figure 4.50 Lignin fraction that degrades in the bulk phase (a_b) as a function of temperature (error bars = ± 1 standard error).

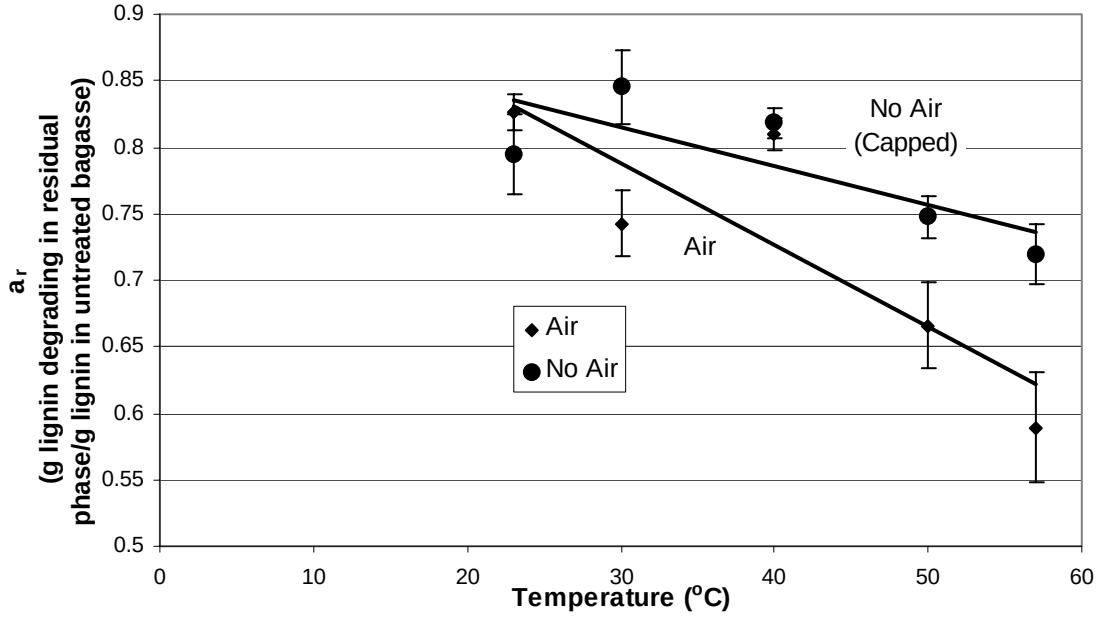


Figure 4.51 Lignin fraction that degrades in the residual phase (a_r) as function of temperature (error bars = ± 1 standard error).

This information with respect to a_b is important because, as mentioned, in the bulk phase there is high lignin removal compared to carbohydrate loss; thus, a decrease in the value of a_b also means that, overall, the process will be less selective toward lignin and therefore less efficient and vice versa. This situation suggests that, in this sense, it is advantageous to operate at higher temperatures with air. In general, any attempt to improve the delignification process should aim to increase the value of a_b.

Figures 4.52 and 4.53 show the Arrhenius plots for both phases in the presence and absence of oxygen (i.e., air). As expected, in general the values for the bulk phase rate constants (k_b) are considerably higher than for the residual phase rate constants (k_r) (by a factor of about 50 in the case of treatment with air and by a factor of about 400 in the case of treatment without air). The values for k_b for the treatments with and without air are not considerably different, but the k_r values for treatment with air are significantly higher than the k_r values for the treatment without air (by an average factor of about 6).

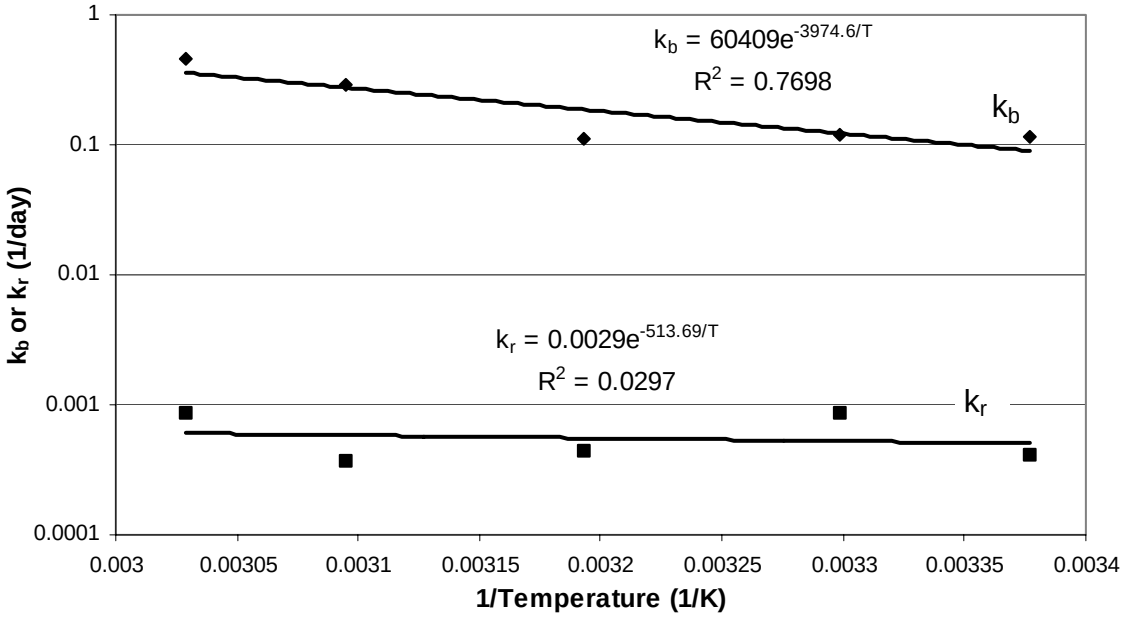


Figure 4.52 Arrhenius plot of the rate constants for the bulk (k_b) and residual (k_r) phases of the delignification for the treatment without air.

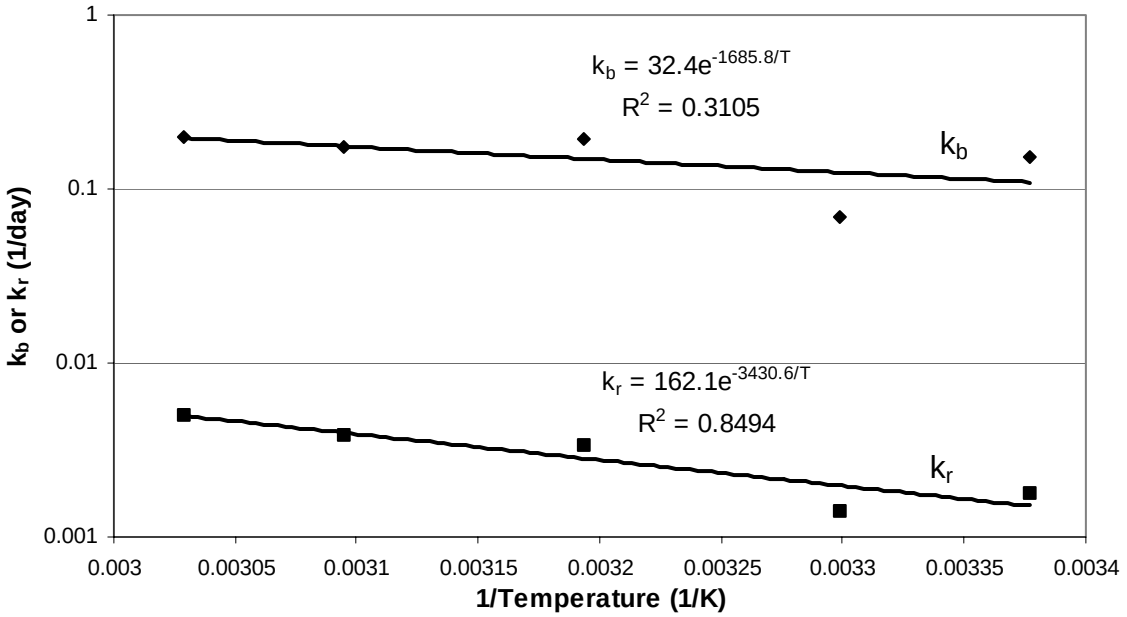


Figure 4.53 Arrhenius plot of the rate constants for the bulk (k_b) and residual (k_r) phases of the delignification for the treatment with air.

Table 4.2 shows the activation energies (E_a) and the natural log of the Arrhenius constants (ln (A)) obtained from the regressions of the Arrhenius plots. Two of the plots yielded a non-significant regression (i.e., P values > 0.1), namely the bulk phase rate constants (k_b) for the treatment with air and the residual phase rate constants (k_r) without air; thus, no conclusive values were obtained from those treatments. In the case of the activation energy for k_b, it is suggested that more data points must be taken at the beginning of the delignification process to obtain better results in the regression of the bulk phase values. In the case of the activation energy for k_r for the treatment with no air, its determination is hard under these conditions, because the values of k_r are extremely small (in the order of 0.0006 day^{-1}); thus, their measurement is overwhelmed by experimental error. The determination of the activation energy for k_r under non-oxidative conditions must be done at higher temperatures where larger values for k_r can be obtained.

Table 4.2 Activation energy (E_a) and Arrhenius constant (A) values for the specified delignification model rate constants.*

	Air	No Air (Capped)
E_a for k_b (kJ/mole)	14.0±12.1†	33.0±10.4
$\ln(A)$ for k_b (ln (1/day))	3.48±4.64†	11.0±4.02
E_a for k_r (kJ/mole)	28.5±6.9	4.27±14.10†
ln (A) for k_r (ln(1/day))	5.09±2.67	-5.86±5.43†

* Error = ± 1 standard error
† For these values the regression was not significant (see Appendix L)

Compared to the delignification of woody biomass, such as western hemlock wood with sodium hydroxide under non-oxidative conditions (Dolk et al., 1989), the activation energies and the natural logs of the Arrhenius constants were lower by a factor of about 4 and 3, respectively.

IV.3.2.3.6 Enzyme Digestibility

Iogen cellulase enzyme (Iogen Corp., Ottawa ON Canada), with an average activity of 67.9 FPU/mL, was used to run 3-day enzyme digestibility at a loading of 5 FPU/g treated bagasse as described in Appendix I. The results are shown in Figures 4.54 through 4.60.

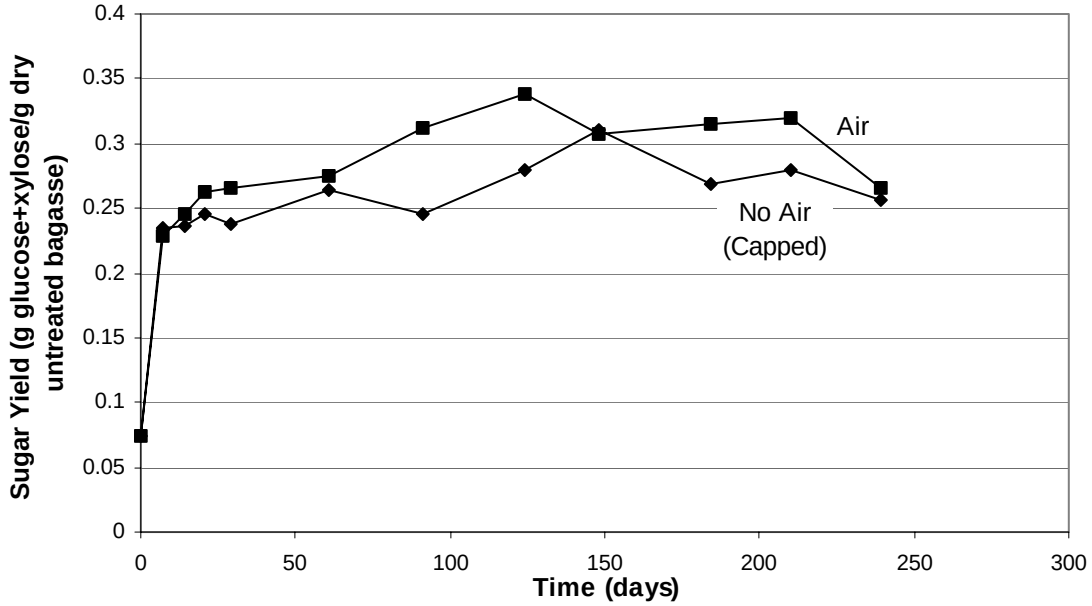


Figure 4.54 3-day enzyme digestibility of bagasse lime-treated at 23°C.

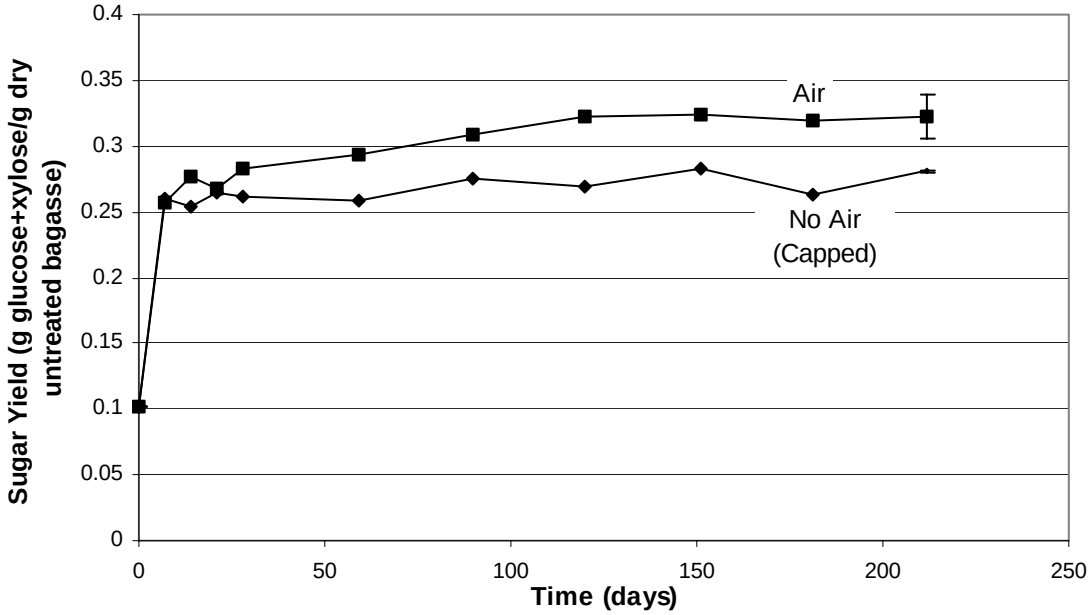


Figure 4.55 3-day enzyme digestibility of bagasse lime-treated at 30°C.

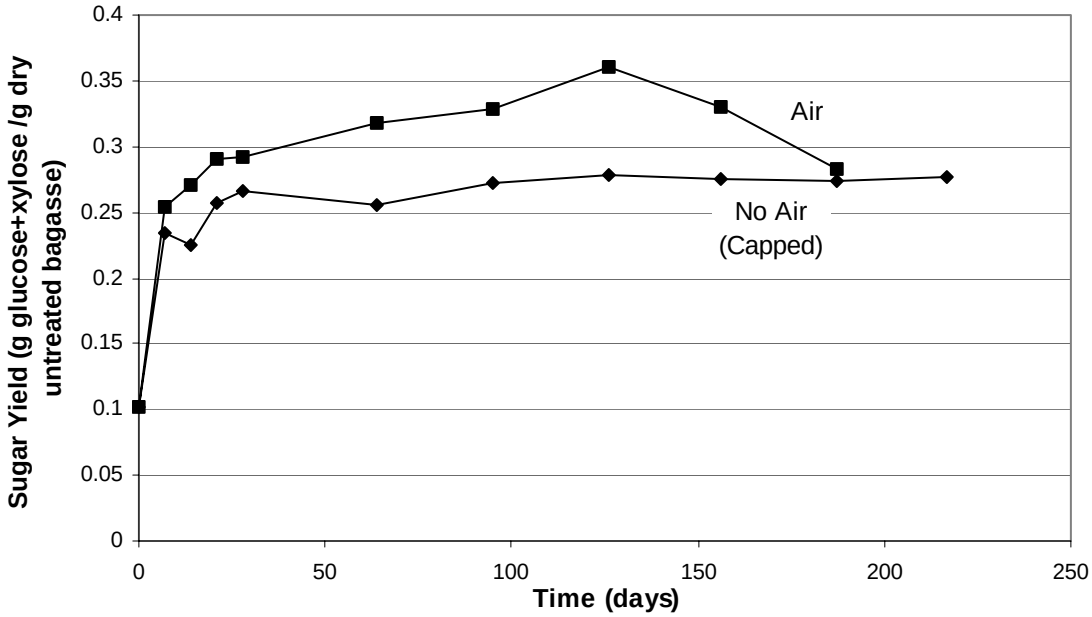


Figure 4.56 3-day enzyme digestibility of bagasse lime-treated at 40°C.

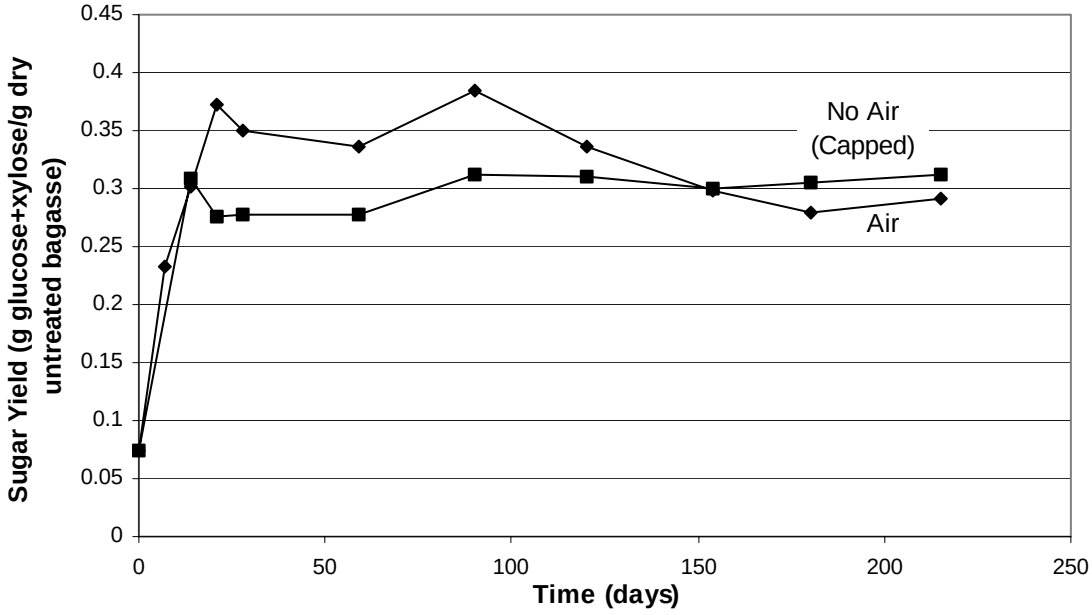


Figure 4.57 3-day enzyme digestibility of bagasse lime-treated at 50°C.

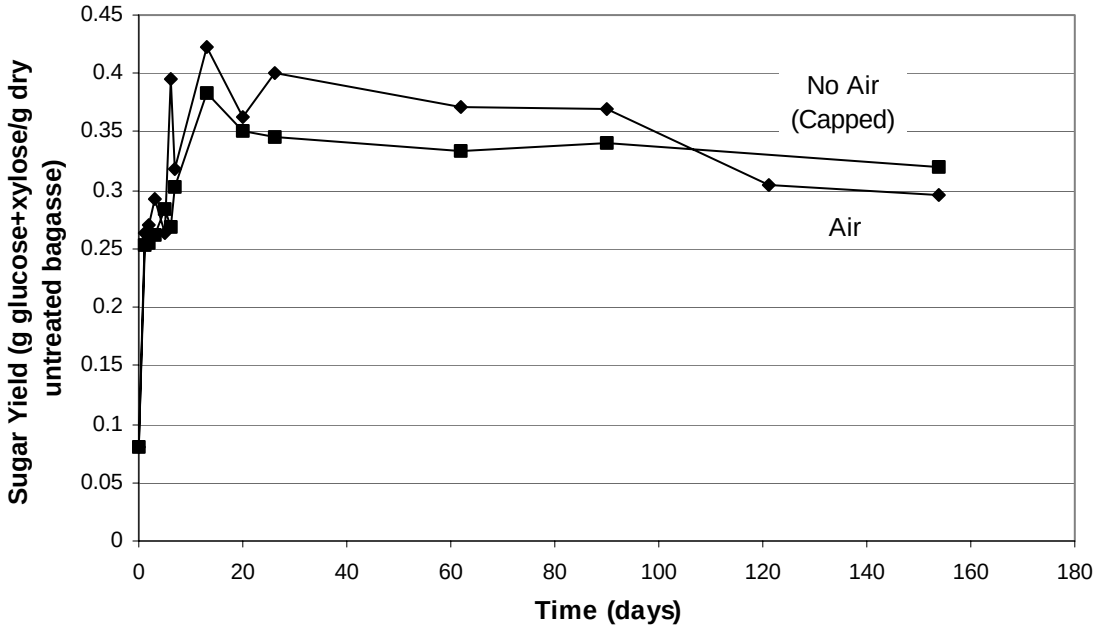


Figure 4.58 3-day enzyme digestibility of bagasse lime-treated at 57°C.

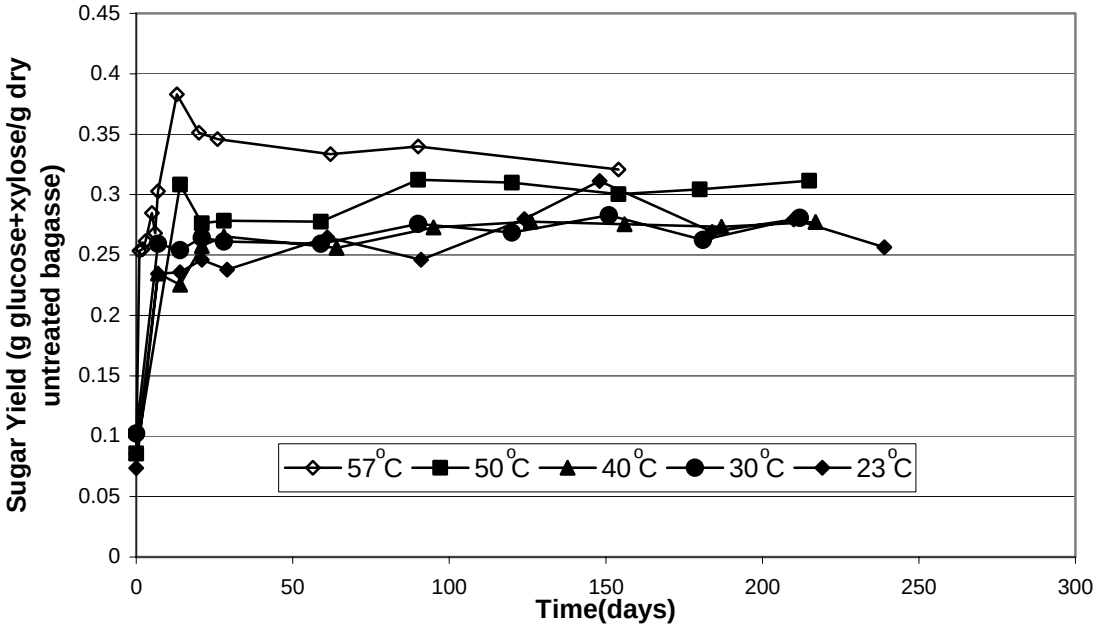


Figure 4.59 3-day enzyme digestibility of bagasse lime-treated without air.

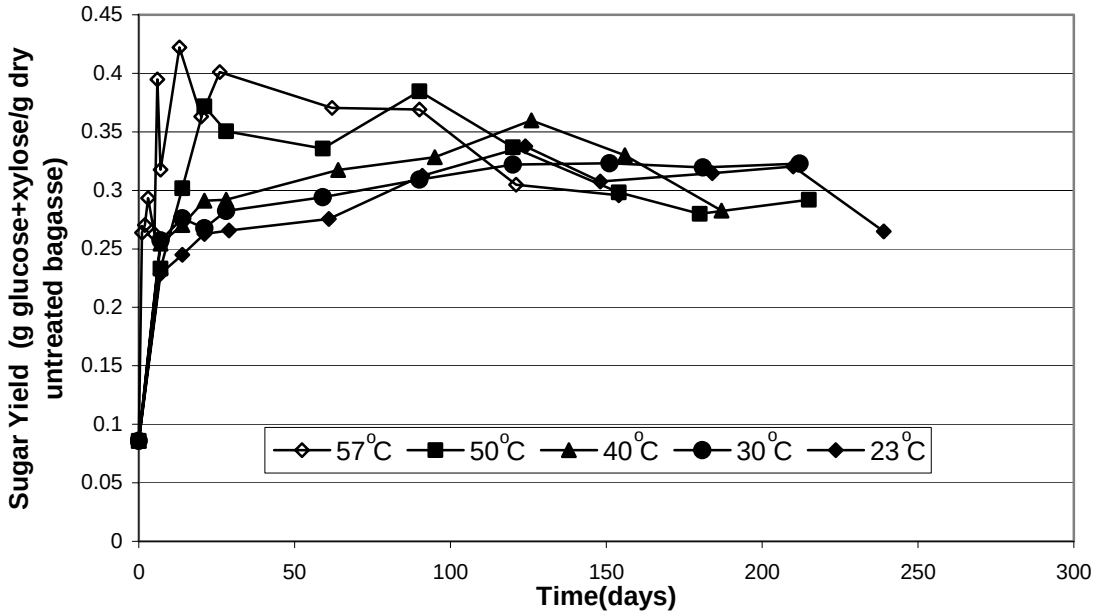


Figure 4.60 3-day enzyme digestibility of bagasse lime-treated with air.

Figures 4.54 through 4.56 show that to enhance digestibility at the lower temperatures (i.e., 23°C, 30°C and 40°C), pretreatment longer than 120 days is unnecessary. In fact, longer pretreatment times are detrimental because of carbohydrate loss; thus, a decrease in the sugar yield, based on the original untreated bagasse, is observed. In the case of the higher temperatures (i.e., 57°C and 50°C), Figures 4.57 and 4.58 show that there is no advantage in pretreatment times longer than 14 to 60 days, but rather there is a decrease in digestibility due to carbohydrate loss during pretreatment.

Figures 4.59 and 4.60 show that higher temperatures achieve higher digestibility yields, even for the samples without air (Figure 4.59).

IV.3.2.3.7 Old and Fresh Bagasse Comparison

One of the biggest sources of variation, which introduced error in these studies was the raw material (i.e., stored old bagasse). As a comparison, fresh bagasse from W.R. Cowley Sugar House (Santa Rosa TX) was used to assess the pretreatment process

at 50°C under oxidative and non-oxidative conditions for 3 months. The treatment was also done in 125-mL Erlenmeyer bottles with 3 g of fresh bagasse (dry weight basis) for each bottle. The same lime loading was used (0.5 g $Ca(OH)_2$/g dry of bagasse), but the water loading was a slightly higher (12 mL/g dry bagasse) because the texture of the fresh bagasse did not allow uniform wetting at 9 mL/g dry bagasse. (It has been shown that pretreatment, at least in the studied range of 6 – 16 mL/g dry bagasse, is independent of water loading (Chang et al., 1998).) Samples were also removed once a week during the first month and then once a month during the remaining pretreatment time. For the air-purged samples, the air was scrubbed with lime prior to delivering it to the bottles to remove carbon dioxide. The parameters measured were also the same as those measured for the old bagasse described in Appendix I (i.e., mass balance by washing, lime consumption by titration, Klason lignin and 3-day enzyme digestibility analysis). The fresh bagasse was collected within hours of having been produced from the mills. It was formed into a thin mat and dried at 45°C for 2 days. This procedure was followed by grinding in a hammer mill (Wiley Mill standard model No. 3, Arthur H. Thomas Co., Philadelphia PA) and sieving to a 40-mesh particle size. The fine bagasse was then thoroughly washed several times, as described in Appendix I, to rid it of soluble matter.

Table 4.3 compares the compositions of the old bagasse and the fresh bagasse before the washing procedure was performed. The composition of the old bagasse was not typical because it had a high dirt content (mostly sand); therefore, the values for ash are excessively high (i.e., ~15 to 22 g/100 g dry bagasse). Typical bagasse has only 1.5 to 2% ash content (1.5 to 2 g of ash/100 g total bagasse) (Chen and Chou, 1993), which is the ash content of the fresh bagasse as shown in Table 4.3.

Table 4.3 Comparison of the compositions of the old bagasse used in these studies and fresh bagasse.

Component	Old Stored Bagasse	Fresh Bagasse
Lignin (g/100 g dry bagasse)	21.9 – 3.8	21.5±0.5
Acid-insoluble Ash (g/100 g dry bagasse)	12.2 – 20.8	2.00±0.40
Ash (g/100 g dry bagasse)	15.8 – 22.8	2.08±0.02
Water-soluble solids (g/100 g dry bagasse)	2.36±1.81*	0.53
Crude Protein (g/100 g dry bagasse)	5.0†	1.8†

* Error = ± 1 standard deviation
† Protein analysis was done by the Soil Testing Laboratory (College Station TX), using a LECO system (Dumas combustion procedure)

The difference between the old bagasse and the fresh bagasse was not limited to their composition, but also to their appearance. Fresh bagasse had a white yellowish color, whereas the old stored bagasse had a dark brown color (similar to mulch) as seen in Figure 4.61.

Figures 4.62 and 4.63 show the amount of acid-insoluble ash, lignin, holocellulose, and, as the sum of the three, the total yield. As with the old bagasse (Figures 4.6 through 4.15), the two phases can be observed. First, there is a marked decrease of lignin content during the first week for both the treatment with and without air. For the treatment without air, there is almost no delignification after the first week, but for the treatment with air, delignification continues but at a slower rate than in the first week. Comparing Figures 4.62 and 4.63 to Figures 4.6 through 4.15, it can be observed that the noise level for the data has considerably decreased when using fresh bagasse. This demonstrates that the variability seen with the old bagasse is not due to procedures or methods, but rather to the material itself.

Figure 4.61 Appearance comparison of untreated ground old stored bagasse (left) and untreated ground fresh bagasse (right).

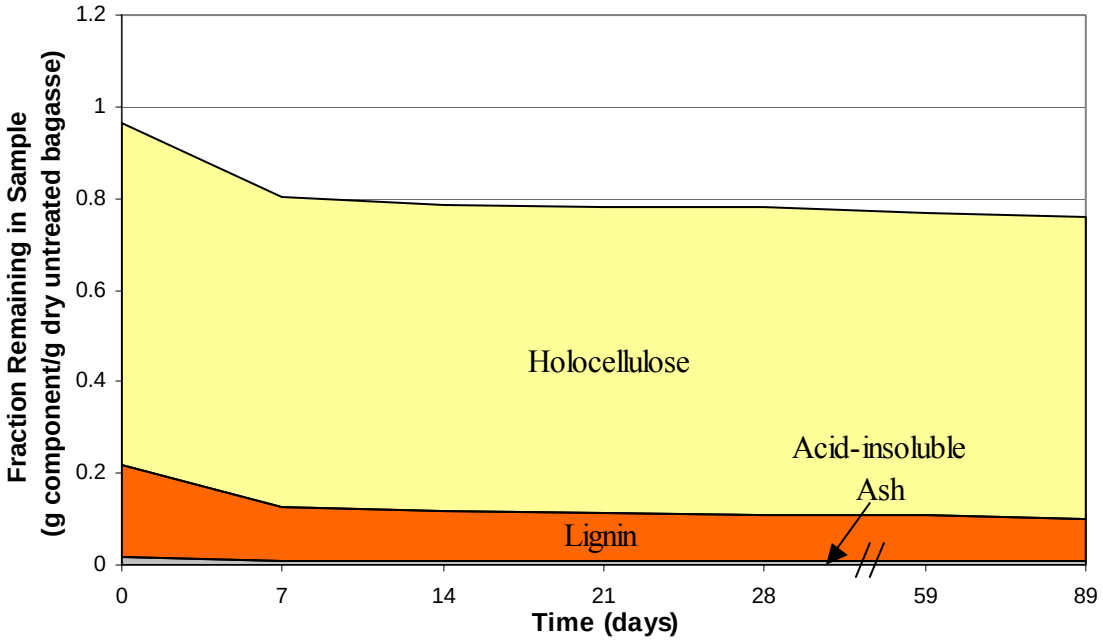


Figure 4.62 Total mass, holocellulose, lignin and ash for fresh bagasse lime-treated without air purging at 50°C.

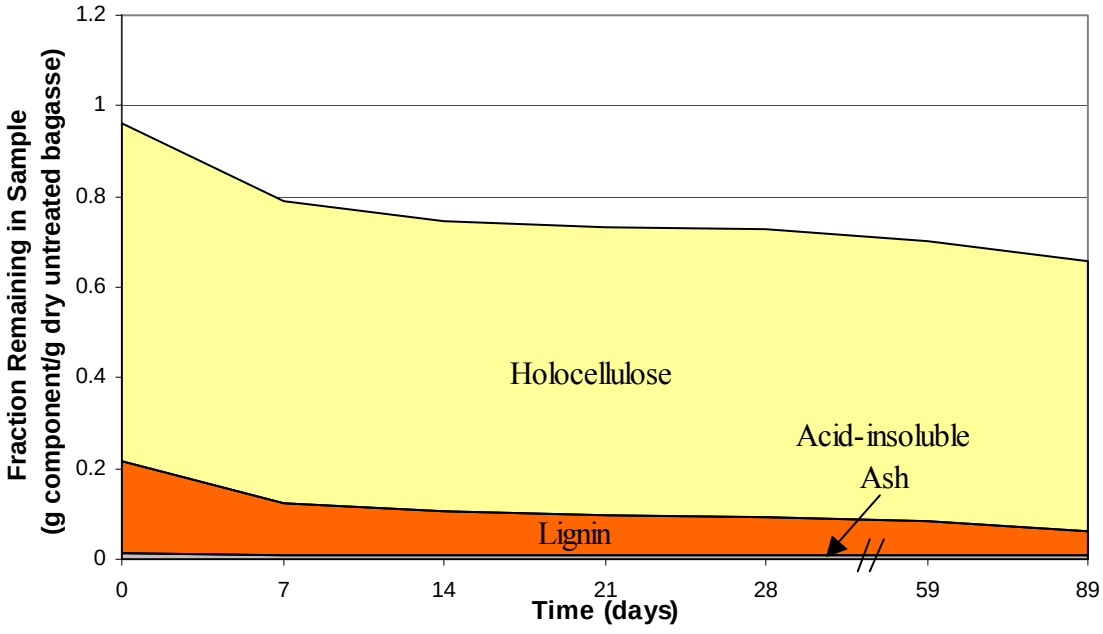


Figure 4.63 Total mass, holocellulose, lignin and ash for fresh bagasse lime-treated with air purging at 50°C.

Figures 4.64 and 4.65 show the holocellulose-to-lignin selectivities for the treatment with and without air for both the old stored bagasse and fresh bagasse. The values reported for the old stored bagasse are the same as those show in Figures 4.19 and 4.24. As mentioned, values for the selectivities are for the residual phase. For the bulk phase, more data near the beginning of the delignification process would need to be collected to measure the selectivity.

The value of the selectivity for fresh bagasse for the treatment without air at 50°C was 0.79±0.23 g holocellulose lost/g lignin removed (error = ± 1 standard error), whereas for the old bagasse under these same conditions the value was 1.28±0.37 g holocellulose lost/g lignin removed. The errors are too large to conclusively compare the results.

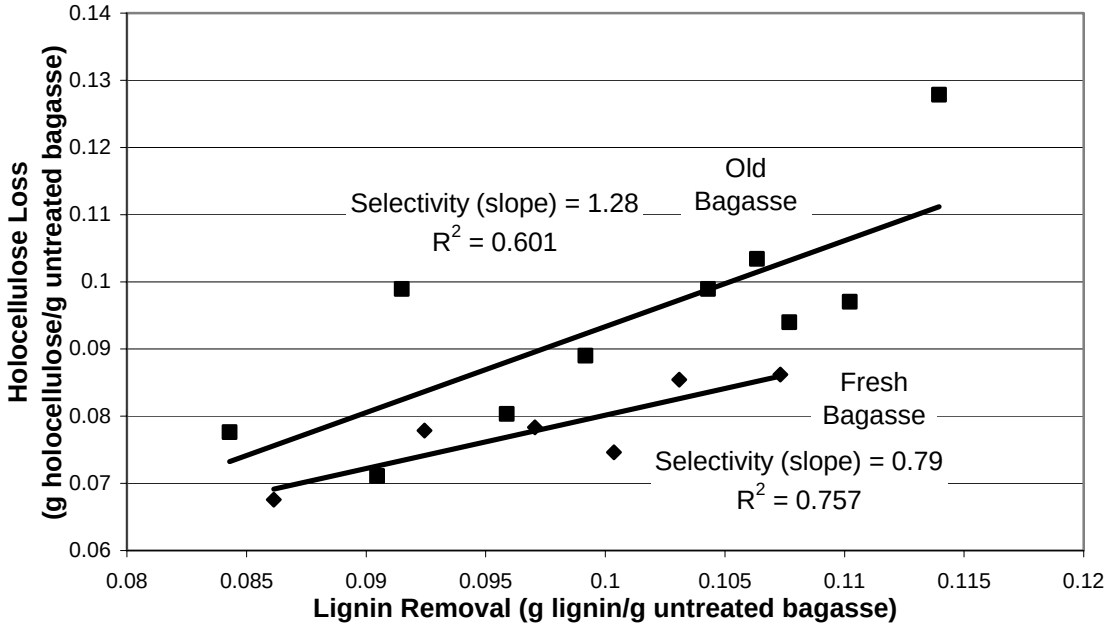


Figure 4.64 Residual phase holocellulose loss as a function of lignin removal for lime pretreatment of fresh and old bagasse without air purging at 50°C.

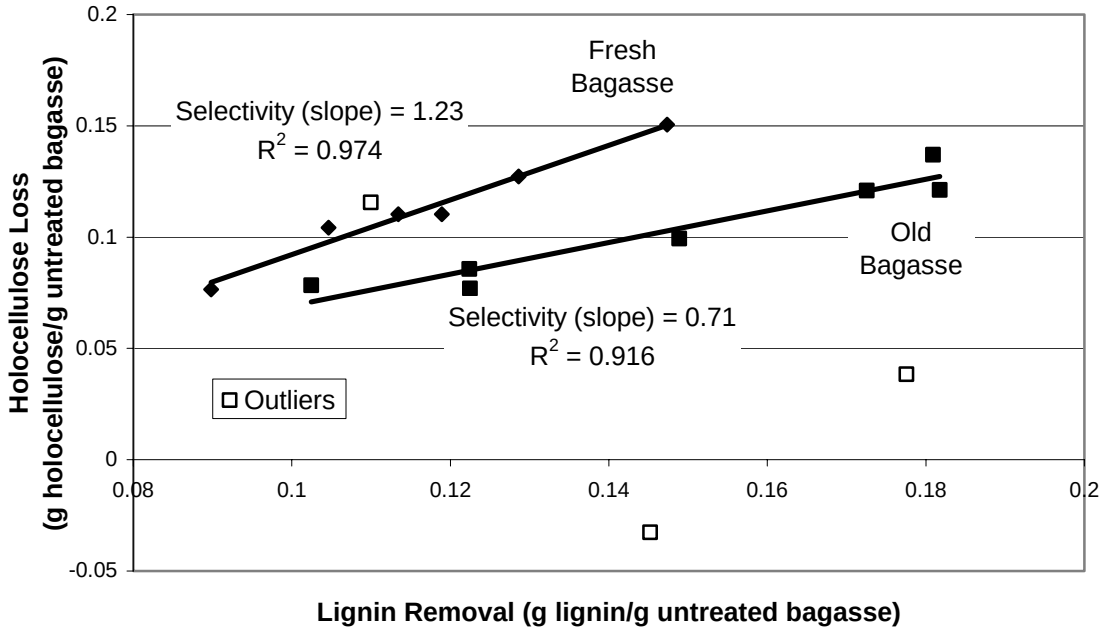


Figure 4.65 Residual phase holocellulose loss as a function of lignin removal for lime pretreatment of fresh and old bagasse with air purging at 50°C.

In the case of the treatment with air, the selectivity for the fresh bagasse was regressed to be 1.23±0.10 g holocellulose lost/g lignin removed (error = ±1 standard error) and that of the old bagasse was 0.71±0.01 g holocellulose lost/g lignin removed. The results suggest that the treatment with air was more selective towards lignin for the old bagasse than for the fresh bagasse for the residual phase of the delignification.

Figure 4.66 shows the lignin content (g lignin/100 g treated bagasse) as a function of time for both fresh bagasse and for the old stored bagasse. Because the initial lignin contents are different, the two types of bagasse cannot be compared. However, if the delignification is expressed as lignin conversion (g lignin removed/g lignin in untreated bagasse) as shown in Figure 4.67, it can be observed that delignification for the two types of bagasse for the treatment with air is only slightly higher for fresh bagasse. However, for the treatment in the absence of air, the difference is considerable. The old stored bagasse settles after the first week at about 30% conversion (0.3 g lignin removed/g lignin in untreated bagasse), whereas fresh bagasse

achieves about 40% conversion (0.4 g lignin removed/g lignin in untreated bagasse). This result suggests that the portion of lignin that is labile to lime alone, and that is removed mostly during the first week, is higher in the fresh bagasse than in the old stored bagasse. This labile lignin corresponds to the lignin that degrades in the bulk phase. The values for the old stored bagasse reported in Figure 4.66 and 4.67 are the same as those reported in Figure 4.30 and 4.37, respectively.

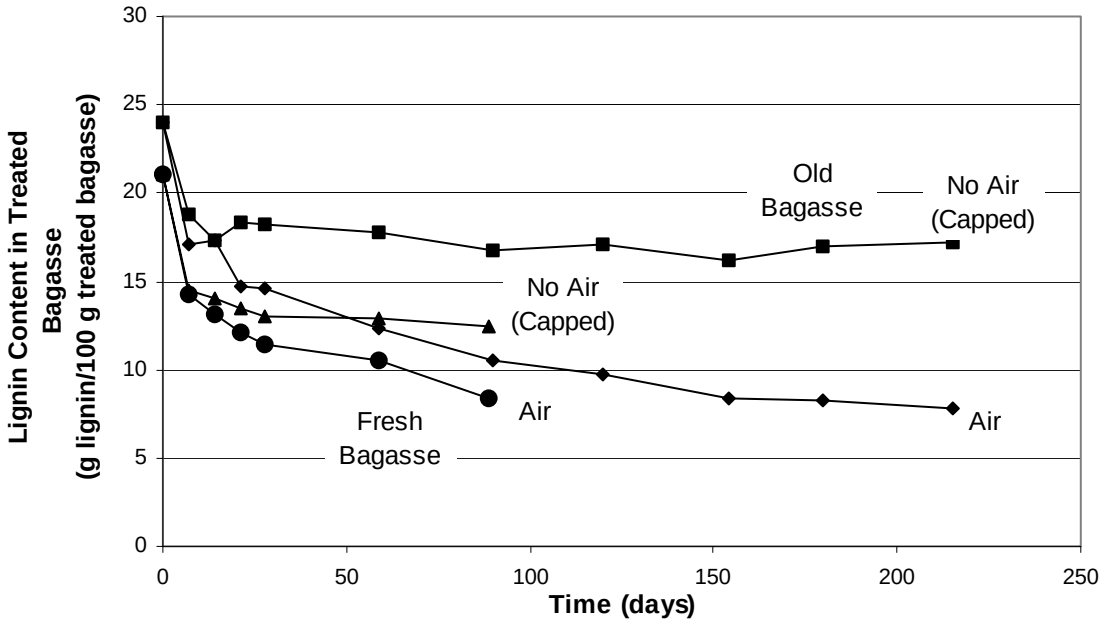


Figure 4.66 Comparison of lignin content as a function of time in lime-treated fresh and old bagasse (50^{o}C).

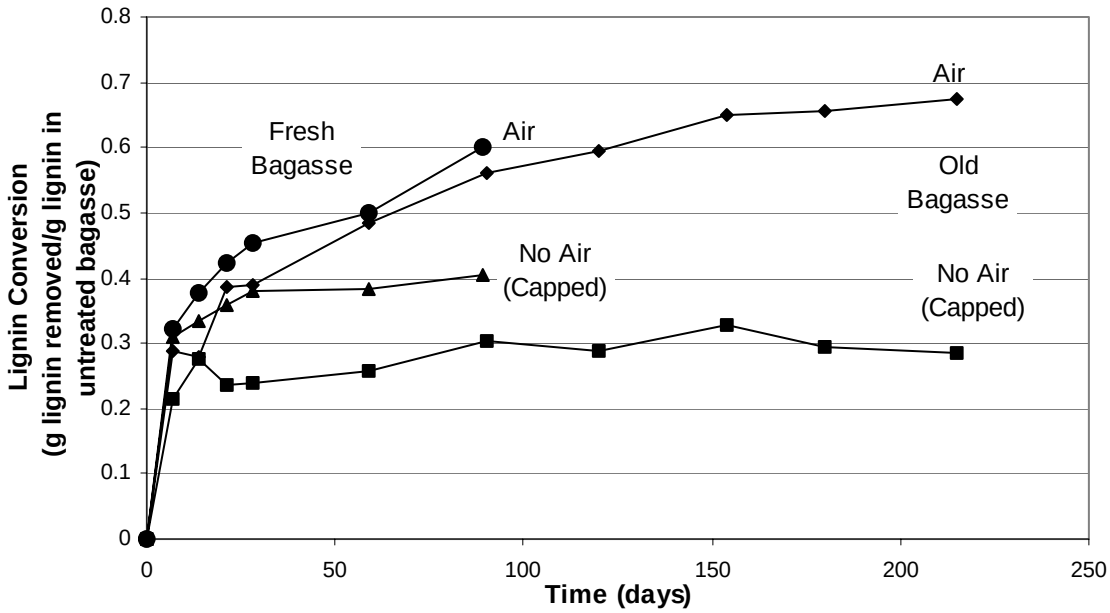


Figure 4.67 Comparison of lignin conversion of lime-treated fresh and old bagasse as a function of time at 50°C.

Figure 4.68 shows the fitting of the delignification model to the data for the treatment of fresh bagasse at 50°C. Table 4.4 compares the different model parameters between the fresh and old bagasse for the treatments with and without air. The values for a_b (fraction of lignin that degrades in the bulk phase) for the treatments with air are virtually the same. On the other hand, as has already been inferred from the lignin conversion plot (Figure 4.67), the value for a_b for the treatment without air is slightly higher for the fresh bagasse.

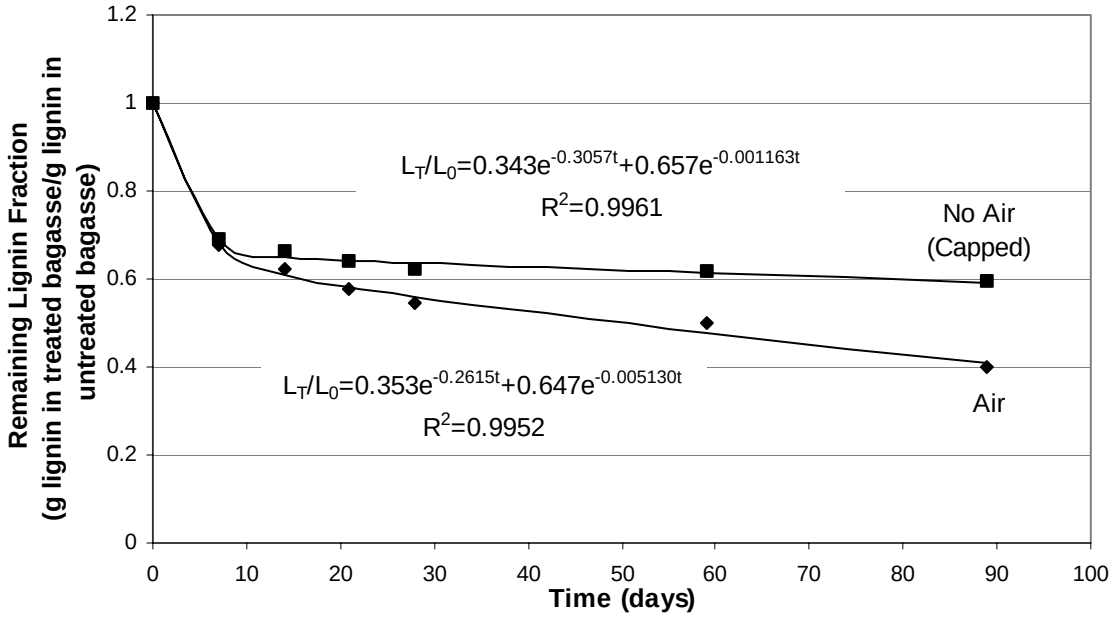


Figure 4.68 Delignification model for fresh bagasse at 50°C.

Table 4.4 Comparison of the delignification model parameters for the old and fresh bagasse.

		Air†	No Air (Capped)†
Old Bagasse*	a_b	0.329±0.046	0.253±0.029
	k_b	0.172±0.062	0.290±0.123
	a_r	0.666±0.032	0.748±0.016
	k_r	0.00386±0.00047	0.000367±0.000172
Fresh Bagasse*	a_b	0.353+0.028	0.343±0.017
	k_b	0.262+0.066	0.306±0.057
	a_r	0.647+0.022	0.657±0.012
	k_r	0.00513+0.000706	0.00116±0.000346

* Units: *a*'s (g lignin in specified phase/g lignin in untreated bagasse); *k*'s (1/day)
† Error = ± 1 standard error

Figure 4.69 shows that the lime consumptions for the fresh bagasse and old bagasse samples treated without air at 50°C are the same. In the case of the treatment with air, the lime consumption rate for the fresh bagasse in the residual phase is considerably lower than the lime consumption for the old bagasse (1.00±0.06 mg $Ca(OH)_2$/(g untreated bagasse · day) for the fresh bagasse and 1.61± 0.05 mg $Ca(OH)_2$/(g untreated bagasse · day) for the old bagasse. Error = ± 1 standard error). The reason for this improvement in the lime consumption can be attributed to the fact that the carbon dioxide was scrubbed out of the air with lime prior to delivery to the system. It is unlikely that the quality of the bagasse had an effect on the lime consumption for the treatment with air. This can be inferred because the degree of delignification was about the same for both types of bagasse in the treatment with air (actually slightly higher for the fresh bagasse, Figure 4.67) and the use of the lime depends, primarily, upon the degree of delignification achieved when using air (i.e., the higher the delignification, the higher the lime consumption).

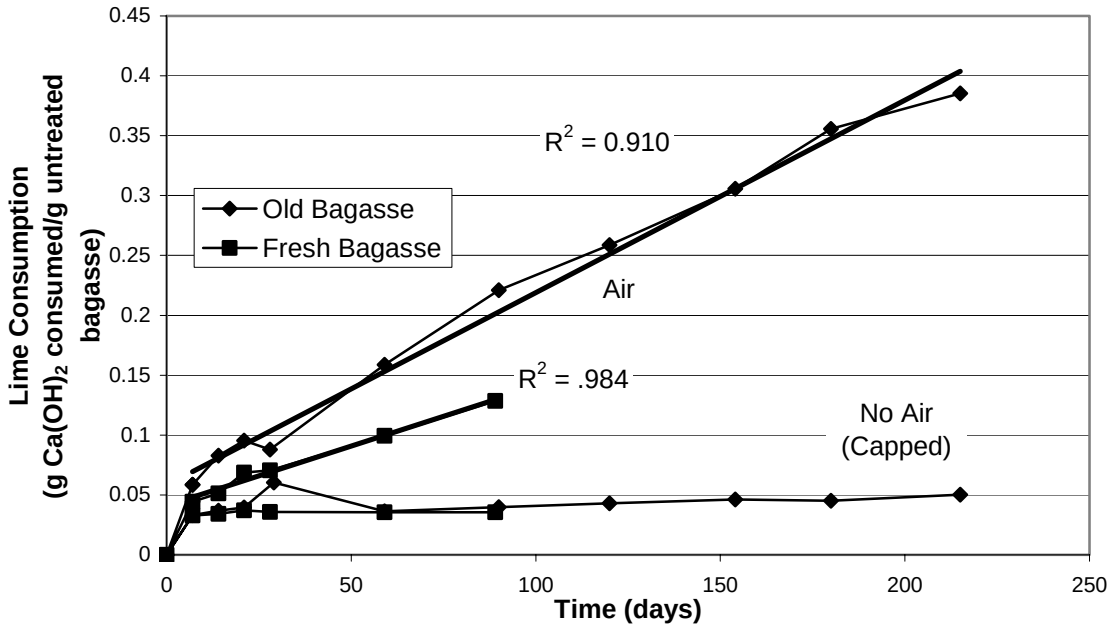


Figure 4.69 Comparison of lime consumption as a function of time in treatment of old and fresh bagasse at 50°C.

Figure 4.70 shows that the sugar yield for 3-day enzyme digestibility analysis is considerably higher for fresh bagasse, to the point that the bagasse treated without air attains about the same yield as the old bagasse treated with air during the first 2 to 3 months. This correlates well with the delignification data because during this time, fresh bagasse treated without air and old bagasse treated with air had about the same lignin content (Figure 4.66). However, it is possible that other factors, such as lower cellulose crystallinity, also improved the results for the fresh bagasse.

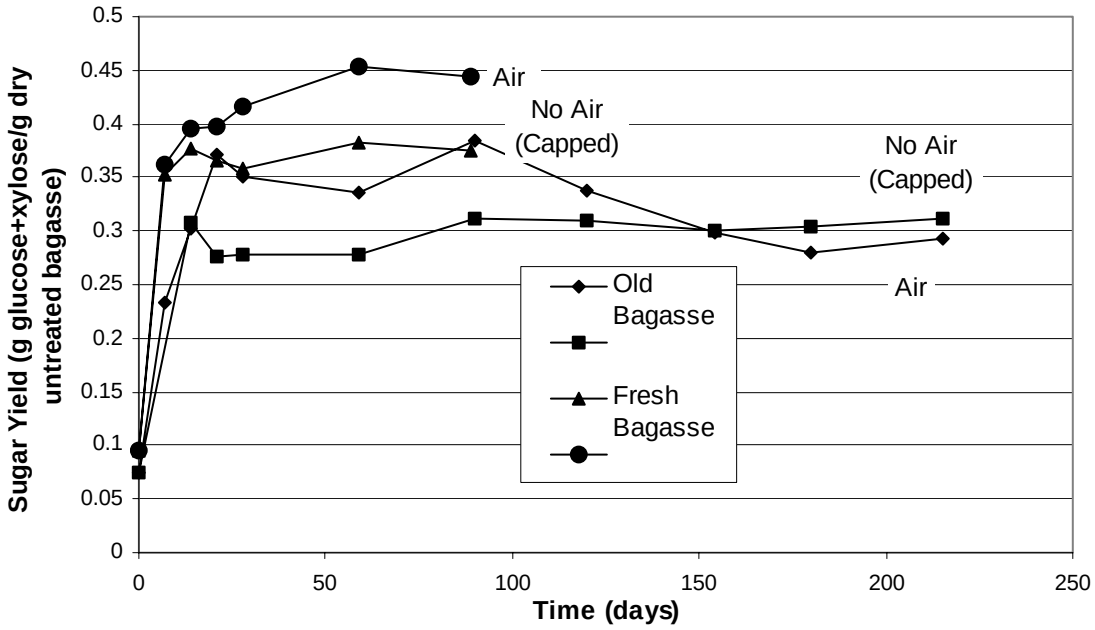


Figure 4.70 Comparison of 3-day enzyme digestibility yield for old and fresh bagasse lime-treated at 50°C (5 FPU/g treated bagasse, Iogen enzyme).

In general, fresh bagasse was different and was of better quality than the old stored bagasse because better results – lignin conversion and 3-day enzyme digestibility yields – were obtained with the same treatment conditions. Further, the material itself introduced little variability, so its behavior in the process was more predictable. These results agree with the literature (Ashok et al., 1986), which also suggests that old bagasse is harder to delignify and is darker in color than fresh bagasse.

Figure 4.70 shows that for fresh bagasse, the treatment with air and without air, attained the same 3-day digestibility yields after 1 week of treatment. As the treatment continued, there was no digestibility enhancement after 2 months under oxidative conditions and after 1 week for non-oxidative conditions.

IV.3.2.3.8 Comparison of Sodium Hydroxide to Lime in Long-Term Pretreatment

Sodium hydroxide (NaOH) is a common chemical used to delignify bagasse, especially in paper manufacturing (Granick, 1979; Fernández, 1995), however the common conditions are short time (10 to 90 min) and high temperatures (160 to 170^{o}C). Ibrahim and Pearce (1983) treated bagasse with NaOH for 24 hours at ambient temperature, but periods longer than this have not been reported in the literature up to date.

To compare the effect of NaOH to the effect of lime ($Ca(OH)_2$) on long-term delignification of bagasse, a parallel experiment was performed along with the lime pretreatment of fresh bagasse (Section IV.3.2.3.8). Three 250-mL Erlenmeyer bottles were loaded with 6 g (dry basis) of fresh bagasse (Table 4.3) and water (12 mL/g dry biomass). Enough NaOH in pellets (Fisher Scientific Co, Pittsburgh PA) was added to the bottles slowly and under vigorous mixing to attain a pH of about 11.5, which is the pH of a saturated aqueous solution of $Ca(OH)_2$. This ensured that the same pH could be observed both in the bottles with $Ca(OH)_2$ and the bottles with NaOH. Because NaOH is very soluble and it cannot be added in the same way as $Ca(OH)_2$ (i.e., in excess so that it dissolves as it is consumed, keeping always a saturated solution with constant pH), the pH in the bottles with NaOH had to be checked every one to two days and more sodium hydroxide was added, if it had decreased, in an effort to control the pH.

The pretreatment with NaOH, as with $Ca(OH)_2$ pretreatment of fresh bagasse, was performed at 50^{o}C, and only under oxidative conditions because the bottles had to be opened on a regular basis for pH control; thus, exclusion of air was not possible.

The analyses performed on these samples were the same as those performed on the lime-treated samples, except for lime consumption by titration (i.e., mass balance by washing, Klason lignin and 3-day enzyme digestibility as described in Appendix I).

Because only three bottles were tested, they were taken off line after 1 week, after 1 month, and after 3 months.

Figure 4.71 shows the value for holocellulose-to-lignin selectivity for the final phase (i.e., residual phase) of the delignification in the $Ca(OH)_2$ treatment and the approximate value for the selectivity in the NaOH treatment. The results suggest that, although for this 3-month period the overall holocellulose loss/lignin removed is higher for $Ca(OH)_2$, during the residual phase $Ca(OH)_2$ is more selective towards lignin than NaOH. This would confirm the postulate set forth in Section IV.2.3 that for long-term (more than 3 months) pretreatment of bagasse, $Ca(OH)_2$ might be preferred because it performs better during the residual phase. It protects the fibers due to the formation of calcium carbonate deposits in places where lignin has already degraded.

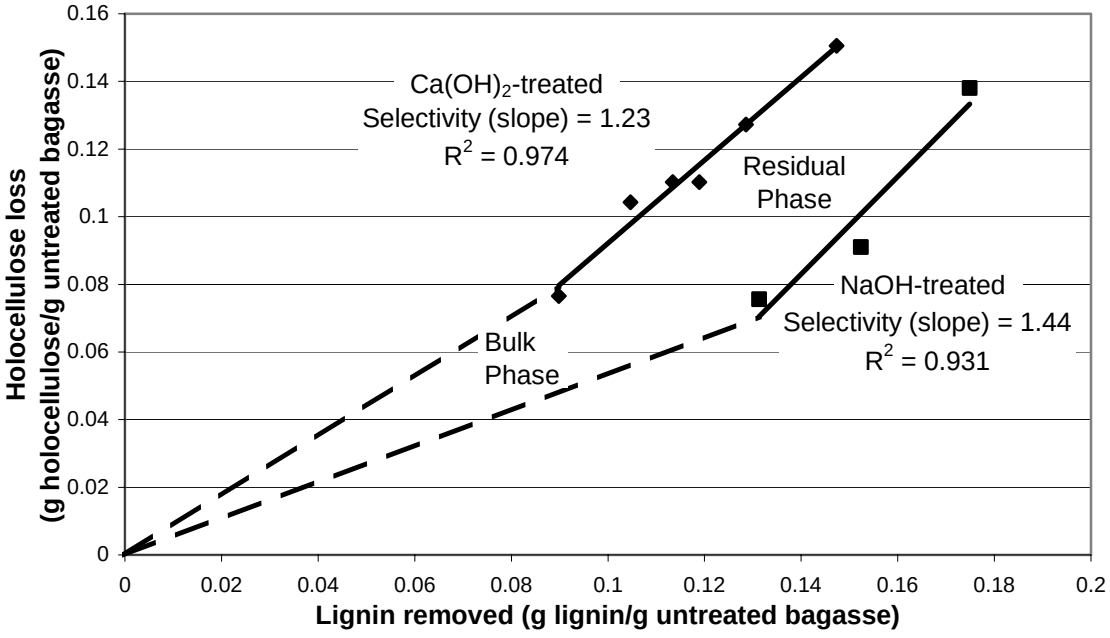


Figure 4.71 Residual phase holocellulose loss as a function of lignin removal for $Ca(OH)_2$ and NaOH pretreatment of fresh bagasse with air purging at 50°C.

As mentioned, in the residual phase, $Ca(OH)_2$ has advantages over NaOH in the delignification of bagasse. However, in the bulk phase, which occurs during the first week of treatment at 50°C, the situation is different as shown in Figure 4.71. Figure 4.72 also suggests that with NaOH, bagasse has a larger fraction of lignin that degrades in the bulk phase, where degradation of lignin is fast compared to carbohydrate loss; thus, a greater degree of delignification is achieved. In the residual phase, which under these conditions occurs after the first week, the rate of delignification is on average the same for both treatments (i.e., ~ 0.06 g lignin/(100 g treated bagasse · day)).

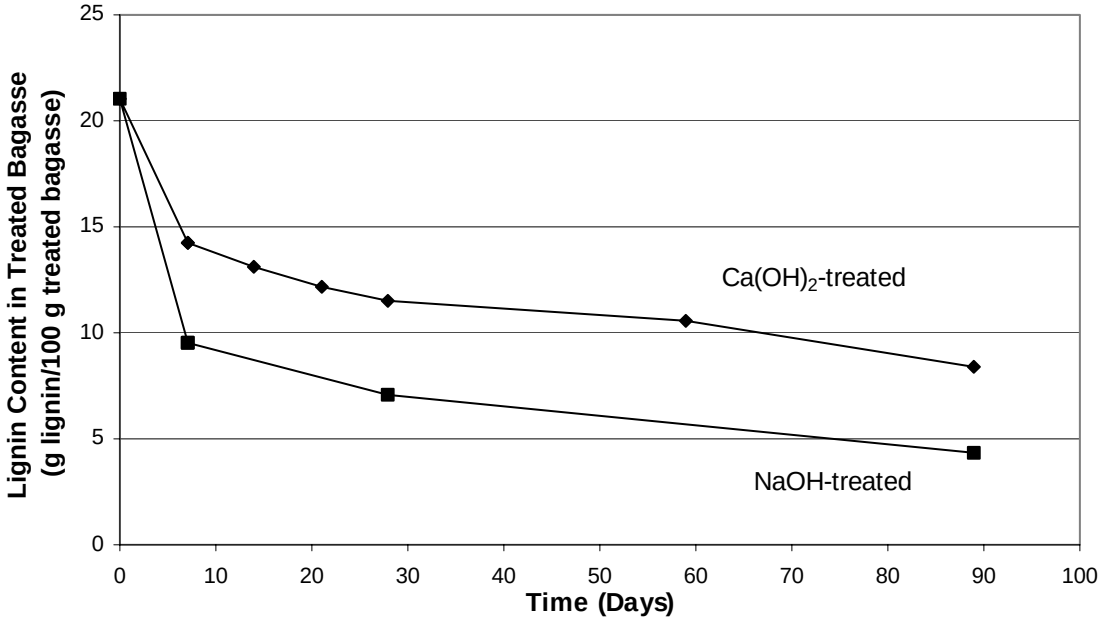


Figure 4.72 Comparison of lignin content as a function of time for $Ca(OH)_2$ and NaOH treatment of fresh bagasse at 50°C.

Figure 4.73 shows that because of the NaOH "headstart" during the first week, where the bulk phase dominates, lignin conversion is almost 80% (80 g lignin removed/100 g lignin in untreated bagasse) in only 3 months. This is even higher than the conversion attained in old bagasse treated with $Ca(OH)_2$ at 57°C for 5 months (i.e., ~72 g lignin removed/100 g lignin in untreated bagasse) shown in Figure 4.38.

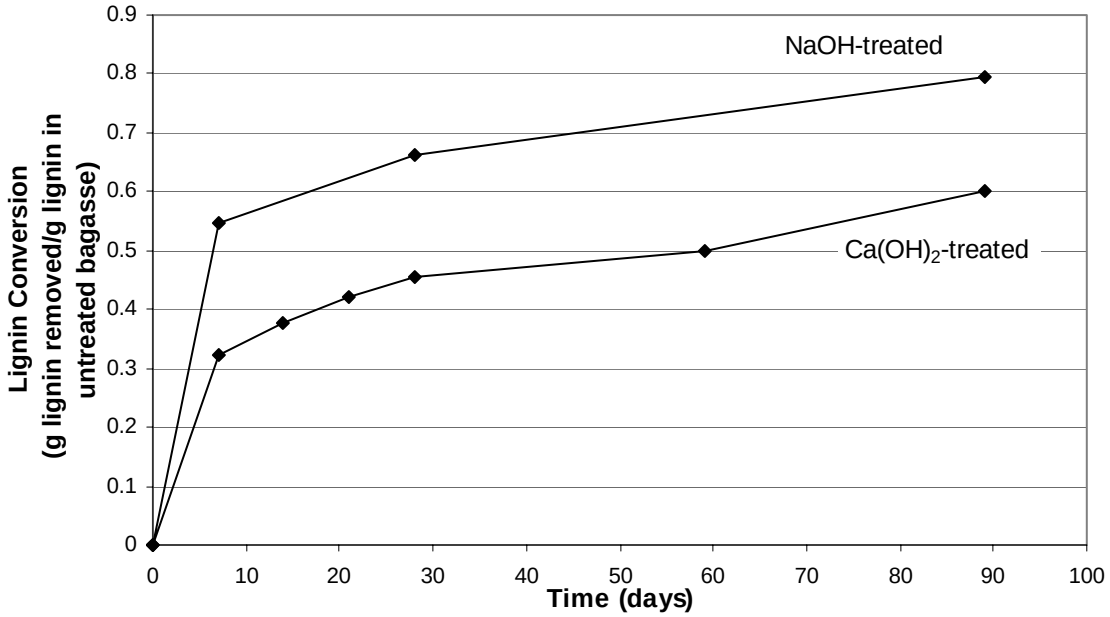


Figure 4.73 Comparison of lignin conversion for $Ca(OH)_2$ and NaOH treatment of fresh bagasse at 50°C.

Figure 4.74 shows that the 3-day enzyme digestibility yields are only slightly higher for the NaOH treatment in spite of the considerable difference attained in the degree of delignification. This agrees with the literature, which suggests that digestibility is not enhanced any further after a certain degree of delignification is achieved (Shimizu et al., 1984; Chang, 1999); therefore, because $Ca(OH)_2$ is cheaper, safer, and more convenient, it is the preferred source of alkali if the pretreatment is performed to enhance enzymatic or microbial digestibility. However, if high degrees of delignification are required (such as in pulping for paper manufacturing), the use of NaOH must be considered. Also, it is important to mention that after 3 months of pretreatment the resulting NaOH-treated bagasse looked highly bleached, displaying a very bright white color, whereas the $Ca(OH)_2$-treated bagasse had a brownish yellow color. In addition, after drying, the fibers bound together more strongly for the NaOH-treated than for the $Ca(OH)_2$-treated bagasse. As with $Ca(OH)_2$, digestibility was not enhanced after 2 months of treatment with NaOH under oxidative conditions.

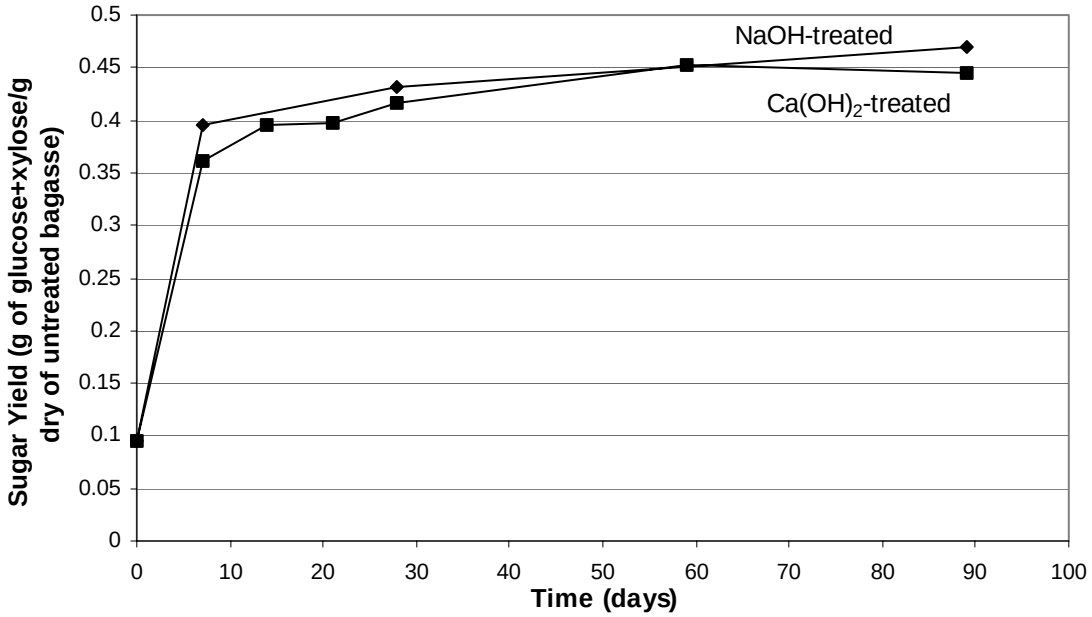


Figure 4.74 Comparison of 3-day digestibility for $Ca(OH)_2$ and NaOH pretreatment of fresh bagasse with air at 50°C (5 FPU/g treated bagasse, Iogen Enzyme).

IV.3.2.3.9 Issues About the Cellulase Enzyme

It was thought that the 3-day digestibility yields from all the treatments in previous sections were rather low compared to those obtained by Chang et al. (1998). They pretreated sugarcane bagasse with lime for only 24 hours at 50°C and obtained 3-day digestibility yields at 5 FPU/g dry bagasse on the order of about 0.4 g total sugar/g untreated bagasse. A closer look at their procedures revealed that their enzyme loading was based on g of untreated bagasse, adding the enzyme directly after the pretreatment without any washing or drying of the biomass. Consequently, they had to neutralize the lime with acetic acid, and enter a correction factor to account for calcium acetate inhibition. For these studies, on the other hand, the enzyme loading was based on g of treated bagasse. Because the biomass was washed and dried before it was analyzed, the calcium acetate correction was not necessary. To express the enzyme loading in these

studies on the same basis as it was reported by Chang et al. (1998), it is necessary to multiply it by the yield (g treated bagasse/g untreated bagasse). Because the approximate average yield was about 0.75 g treated bagasse/g untreated bagasse, the enzyme loading for these experiments, expressed on the same basis as reported by Chang et al. (1998), was approximately 3.8 FPU/g untreated bagasse, which would explain why the 3-day digestibility yields seemed to be smaller. It is concluded, therefore, that the 3-day enzyme digestibility yields from these studies cannot be compared to the values obtained by Chang et al. (1998).

Commercially available cellulase enzyme is actually a mixture of several different enzymes, each of which does a particular job. For example, endo-glucanase cuts the cellulose chain in the middle, exo-glucanase attacks cellulose from the end producing cellobiose, and β-glucosidase (also known as cellobiase) splits cellobiose into two glucose molecules (Mandels, 1982). It was also realized, that the conventional method for determining cellulase enzyme filter paper activity (i.e., NREL method No. 006 (NREL, 1992)) – so named because of the filter paper used as substrate – had several drawbacks (Coward-Kelly et al., 2003). Among them was the fact that this assay does not allow for comparison of activity in 3-day digestibility studies among enzyme batches that have varying amounts of cellobiase as part of its original enzyme mixture. This is because the conventional filter paper assay, NREL No. 006 (NREL, 1992), does not call for addition of excess cellobiase, as in 3-day enzyme digestibility analysis. If the enzyme mixture has little cellobiase as part of its original composition, its final product from the hydrolysis of the filter paper will mostly be cellobiose, but if the levels of cellobiase found in the batch are high, the final product will be mostly glucose. The assay uses the DNS spectrophotometric technique to quantify the reducing sugar yield. Because DNS gives higher results with glucose than with cellobiose, activity values cannot be compared if the enzymes have differing concentrations of cellobiase (Coward-Kelly et al., 2003).

The situation mentioned above was encountered with the enzyme from Iogen Corp. (Ottawa ON Canada), which had high concentrations of cellobiase in its original

mixture. This yielded a high activity as determined by the conventional filter paper assay. This, in turn, affected the 3-day digestibility study because its high activity meant that a smaller volume of enzyme was added given a fixed enzyme loading. To illustrate this, a comparison with another enzyme (Spezyme® CP, Genencor International, Inc., Palo Alto CA) was established. The activities as determined by the conventional filter paper assay (NREL method No. 006) were 67.4±1.0 FPU/mL for the enzyme from Iogen Corp. (Iogen) and 74.0±1.7 FPU/mL for the enzyme from Genencor International Inc. (Genencor) (error = ± 1 standard deviation, run in triplicate). Old stored bagasse (Table 4.1) was pretreated with lime at 50°C under non-oxidative conditions for 60 days. At the end of this time period, the material was neutralized with acetic acid and then was thoroughly washed and dried in the oven at 45°C for 2 days. The material was divided into six Erlenmeyer bottles (i.e., three bottles for each enzyme) and then 3-day digestibility analysis was run in triplicate. The enzyme loading, based on their activities from the conventional filter paper assay, was for both, 5 FPU/g treated bagasse. Figure 4.75 shows that the enzyme from Genencor produces a higher yield, even though the same nominal enzyme loading was used for both. The values obtained were 0.434±0.009 g glucose + xylose/g treated bagasse for the enzyme from Genencor and 0.375±0.007 g glucose + xylose/g treated bagasse for the enzyme from Iogen (error = ±1 standard deviation, run in triplicate). The error ranges do not overlap, even with three standard deviations.

The Spezyme® CP enzyme from Genencor had a very low cellobiase concentration in its original enzyme mixture; therefore, its activity was enhanced when the excess cellobiase was added in the 3-day enzyme digestibility analysis. In contrast, the enzyme from Iogen already had some cellobiase in its original enzyme mixture, which took part in the activity determination by the conventional filter paper assay. Its activity was not enhanced much when excess cellobiase was added in the 3-day digestibility analysis. Thus, this explains the lower yields obtained for the Iogen enzyme.

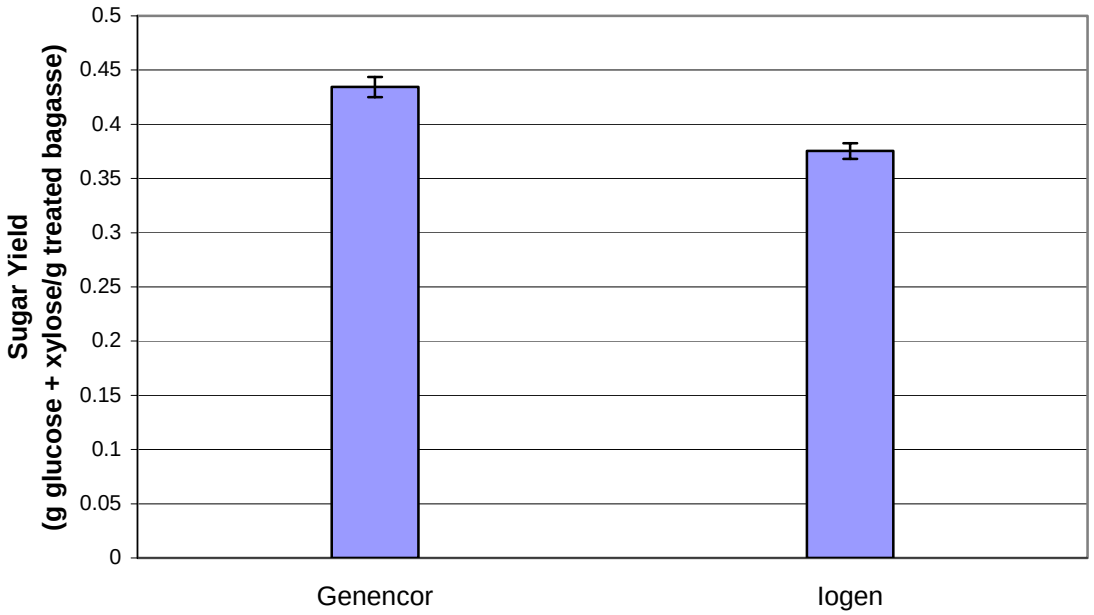


Figure 4.75 Comparison of sugar yields for enzymes Genencor and Iogen both at 5 FPU/g treated bagasse (error bars = ±1 standard deviation).

Such response from the Iogen enzyme was also observed by Almendarez (2000), who also used it in her studies. Coward-Kelly et al. (2003) suggest the addition of excess cellobiase to determine filter paper activity. The addition of excess cellobiase increases the measured activity of the enzyme, but it allows comparison between enzyme batches with different amounts of cellobiase in their original mixture (Coward-Kelly, 2004).

Figure 4.76 compares the two enzymes at a loading of 5 FPU/g treated bagasse on fresh and old bagasse lime-treated with air for two weeks at 57^{o}C. The fresh bagasse had 1.5 g acid-insoluble ash/100 g treated bagasse and 11.9 g lignin/100 g treated bagasse, whereas the old bagasse had 30.0 g acid-insoluble ash/100 g treated bagasse and 12.0 g lignin/100 g treated bagasse. The fresh bagasse performed better for both enzymes, and the Genencor enzyme, gave higher yields for both the old and fresh bagasse. In addition, Figure 4.76 shows a comparison to the 3-day digestibility/pretreatment time profile of old bagasse lime-treated at 57^{o}C (Figure 4.58).

Although there is variability in the profile shown in Figure 4.58, the 2-week value is higher than the value that would represent its repetition (i.e., old bagasse, Iogen, 30% acid-insoluble ash) shown in Figure 4.76. This difference can be attributed to the worsening quality of the old bagasse, which had almost twice as much acid-insoluble ash (30 g acid-insoluble ash/100 g of treated bagasse) as its corresponding point in the profile from Figure 4.58 (17.5 g acid-insoluble ash/100 g treated bagasse). The standard deviations in Figure 4.76 are from triplicate runs.

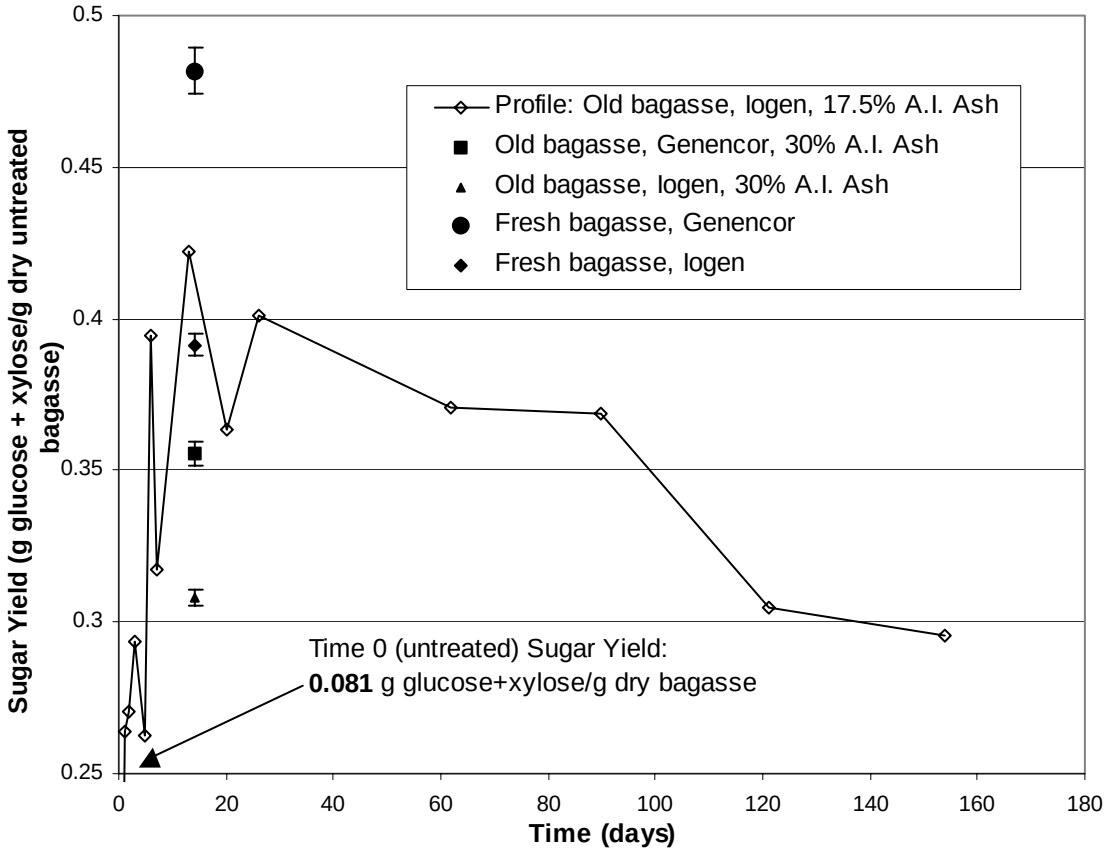


Figure 4.76 3-day digestibility yields from the two types of enzymes for lime treatment with air at 57°C (5 FPU/g dry treated bagasse) (error bars = ±1 standard deviation).

IV.3.3 Effect of High Water Vapor Pressure

IV.3.3.1 Equipment and Methodology

In previous sections, the temperatures for the experiments were chosen so that the water vapor pressure, and thus its partial pressure at normal atmospheric conditions, is low enough that it does not significantly displace oxygen. At lower temperatures, the preliminary studies indicated that there is little difference between the delignification process under pure oxygen and under air (see Figure 4.5). However, if higher temperatures were used, the water vapor pressure would increase, displacing oxygen. In this case, pure oxygen might perform better than air. Table 4.5 illustrates this situation.

To test this hypothesis, an experiment similar to those described in previous sections was implemented, except that the working temperature was 75^{o}C.

Table 4.5 Water partial pressure and the corresponding oxygen partial pressure in saturated air as a function of temperature at normal atmospheric conditions.

Temperature (^{o}C)	Water Partial Pressure (atm)	Oxygen Partial Pressure (atm)
50	0.122	0.184
60	0.197	0.169
70	0.308	0.145
80	0.468	0.112
90	0.692	0.065
95	0.834	0.035

(Perry and Green, 1984)

Several 150-mL test tubes were loaded with 6 g dry of soluble-substance-free old stored bagasse, 3 g of calcium hydroxide (0.5 g/g dry bagasse), and 54 mL of water (9 mL/g dry bagasse). The test tubes were kept under three different conditions, namely

oxygen purge, air purge, and nitrogen purge. This time, the conduit that delivers the air, oxygen, or nitrogen was introduced in the biomass to provide mixing. Figure 4.77 shows a schematic of the purging setup.

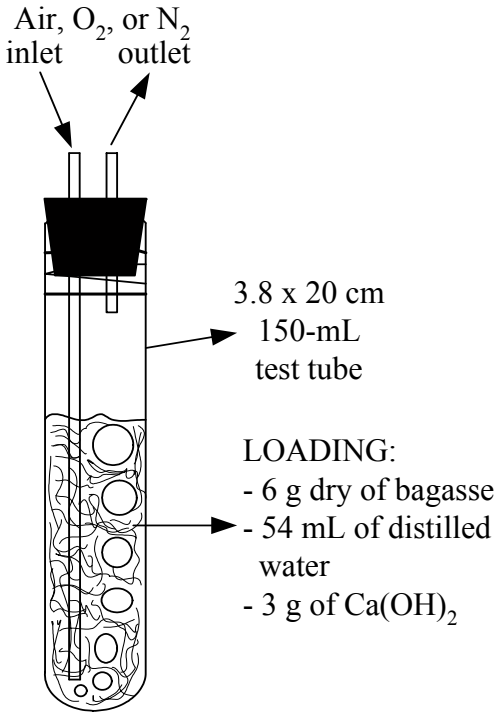


Figure 4.77 Schematic of the lime treatment of bagasse at 75°C.

The test tubes were placed in a convection oven at 75°C. The analyses performed were the same as with the pretreatments at lower temperatures described in Appendix I (i.e., mass balance by washing, lime consumption by titration, Klason lignin, and 3-day enzyme digestibility analysis). Due to space limitations in the oven, in this experiment, all the analyses were done to the sample in the same test tube because there were no duplicates of the same condition.

IV.3.3.2 Results and Discussion

Figures 4.78 through 4.80 show the amount of holocellulose, lignin and ash, and total mass or yield (g treated material/g of untreated material) as the sum of all three components, as function of time for the pretreatments at 75°C with nitrogen (N_2), air, and oxygen (O_2) purging. As with the pretreatment run at lower temperatures (Figures 4.6 through 4.15), there was a rapid decrease of lignin, and thus of total yield, during the first week for all three conditions (i.e., N_2, air and O_2 purging). After the first week of treatment with N_2 purging, there was only a minor decrease of lignin. However, with air and O_2, delignification continued after the first week, but it was considerably more pronounced for the treatment with O_2.

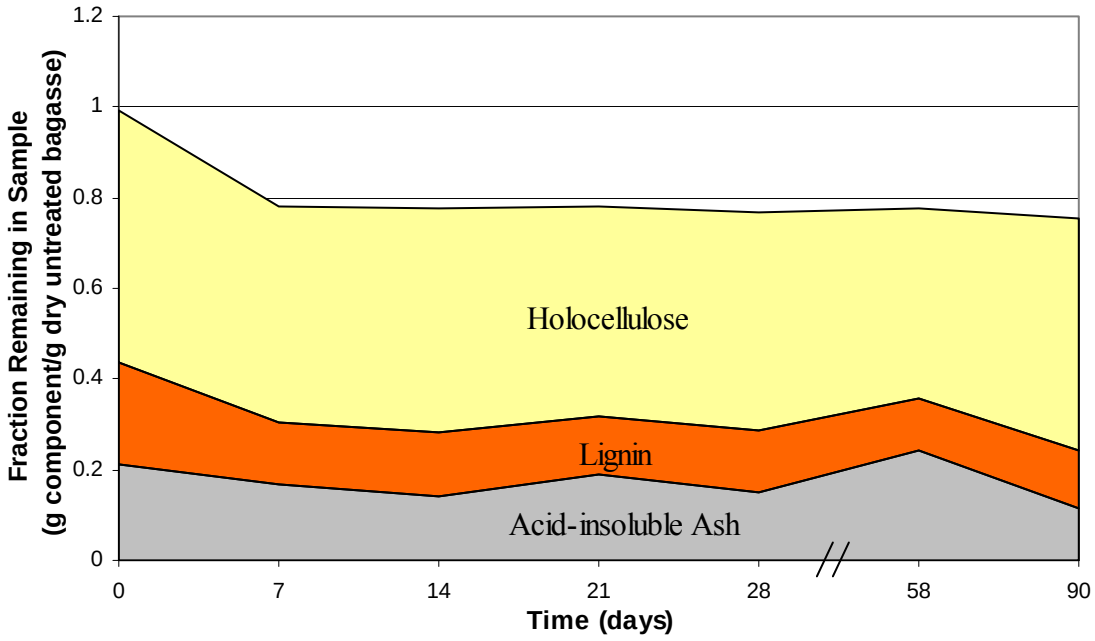


Figure 4.78 Total mass, holocellulose, lignin and ash for old bagasse lime-treated with nitrogen purging at 75°C.

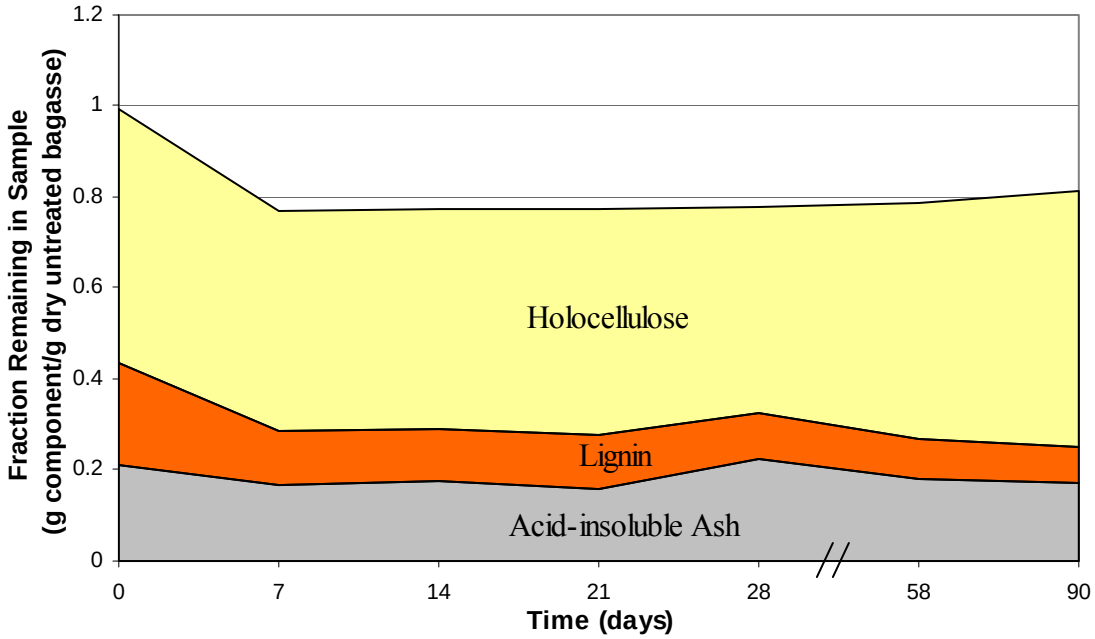


Figure 4.79 Total mass, holocellulose, lignin and ash for old bagasse lime-treated with air purging at 75°C.

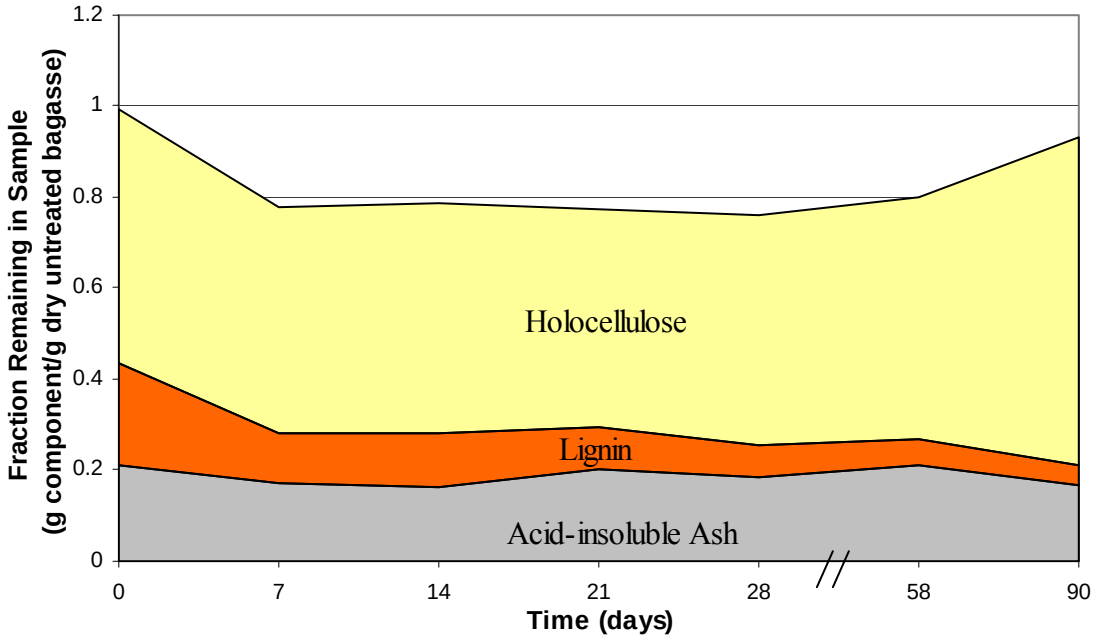


Figure 4.80 Total mass, holocellulose, lignin and ash for old bagasse lime-treated with oxygen purging at 75°C.

Figures 4.81 and 4.82 show that there was considerable difference in lignin content and lignin conversion as a function of time among the three conditions. The treatment with N_2 purging provided only minor delignification after the first week. The treatments with air and O_2 did not present any difference between them until after the first week, at which point O_2 considerably surpassed the treatment with air, attaining almost 80% conversion (80 g lignin removed/100 g present in untreated biomass) after 3 months, whereas air only achieved about 55% conversion.

Figure 4.83 shows that there were also considerable differences among N_2, air, and O_2 purging in lime consumption. Lime consumption was directly related to lignin conversion. It is important to note that for this test, all three gases were pre-scrubbed with a lime slurry; therefore, any CO_2 or other acidic gas present was removed from the gases prior to delivery to the system; the lime consumption, in this case, is the true lime consumption required by the pretreatment process alone.

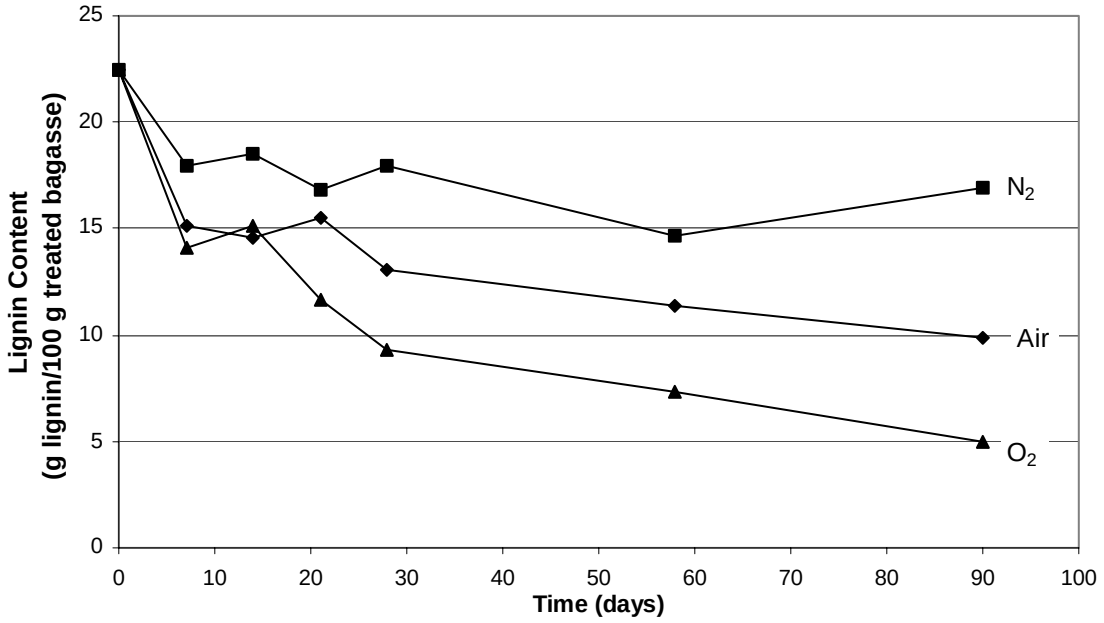


Figure 4.81 Lignin content as a function of time in lime-treated bagasse (75°C).

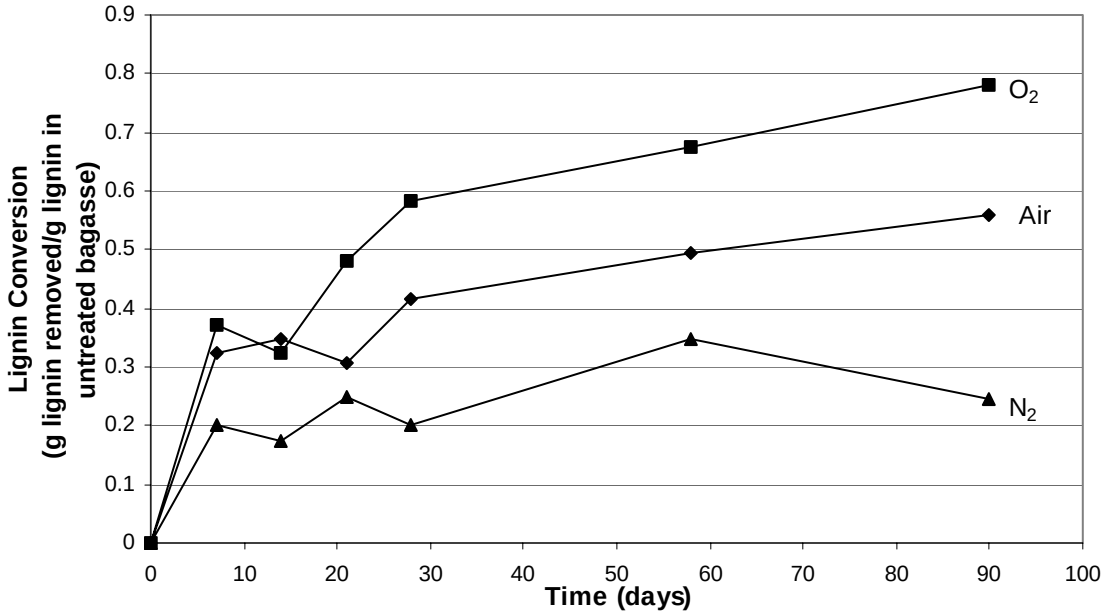


Figure 4.82 Lignin conversion of lime-treated bagasse as a function of time at 75°C.

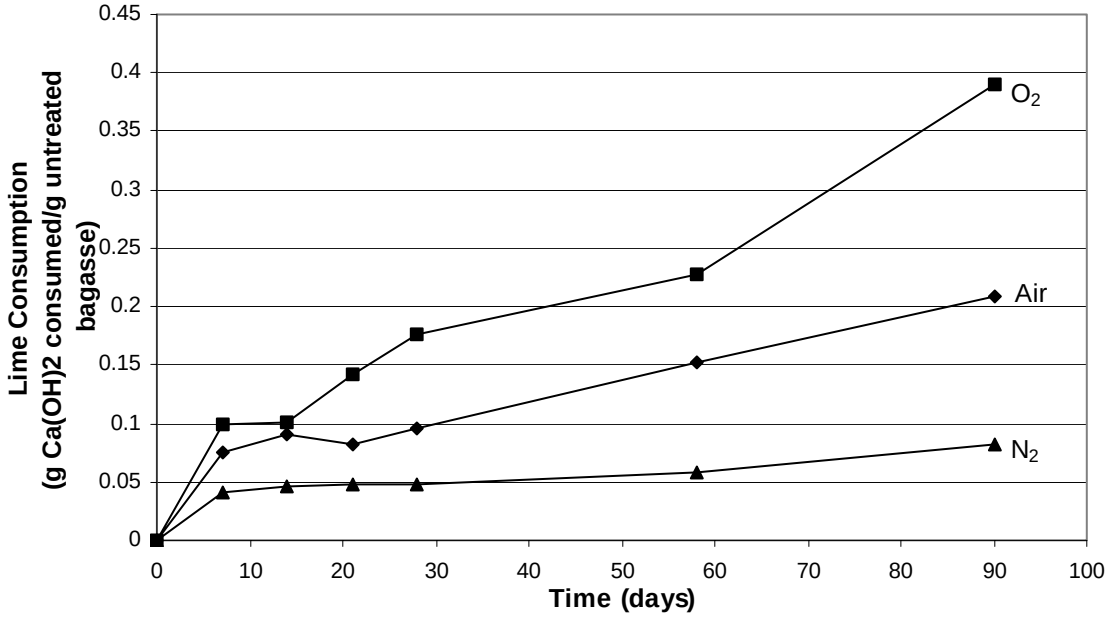


Figure 4.83 Lime consumed as a function of time in treatment of bagasse at 75°C.

Figure 4.84 shows that the 3-day digestibility yields did not display any significant increase after the first week and they were about the same for all three conditions. After the first week, the sugar yields were slightly lower for the treatment with N_2 purging, but there was no considerable difference between the treatments with air and O_2 purging. Also, it is interesting to notice that the 3-day digestibility yields were slightly lower than those obtained for the treatment with air at 50°C and 57°C (Figure 4.60), but because of the variability of the raw material, the comparison is uncertain.

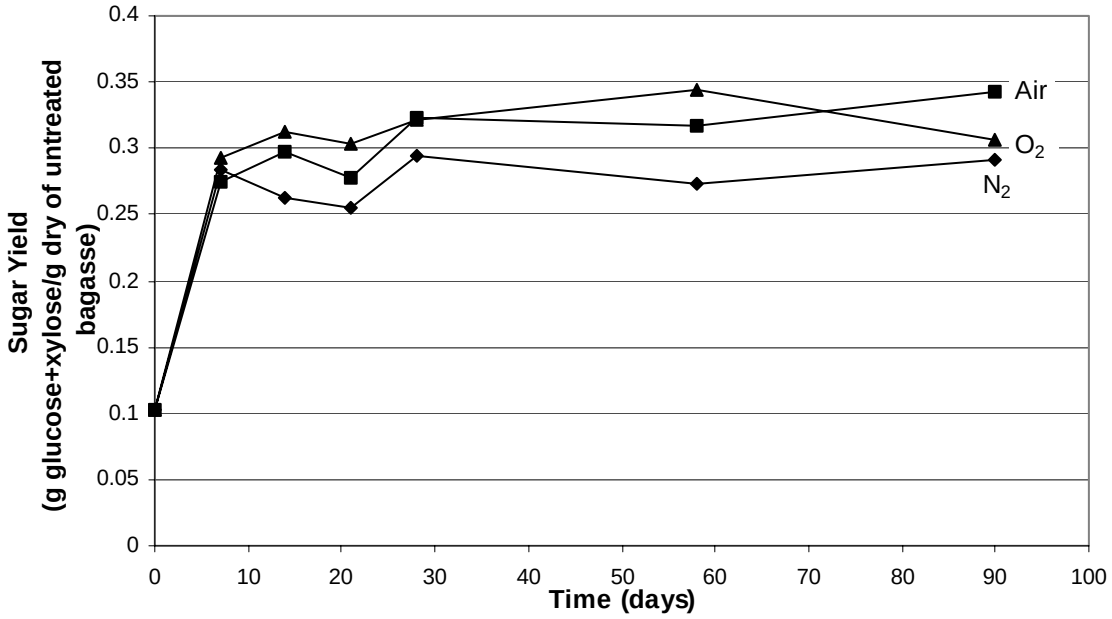


Figure 4.84 3-day enzyme digestibility of bagasse lime-treated at 75°C.

In conclusion, the results show that at high temperatures (such as 75°C) oxidative conditions with pure O_2 yield higher lignin degradation than with air. However, to enhance digestibility, long-term lime pretreatment with pure O_2 does not present any significant advantage over air. Because the temperature is higher, delignification is faster but holocellulose degradation is also faster; therefore, further studies should be

implemented to complete the profile and obtain more data points within the first week, where the 3-day digestibility yields in terms of untreated material might be higher.

IV.3.4 Bagasse Pulping for Paper Manufacturing

IV.3.4.1 Equipment and Methodology

To assess the effectiveness of bagasse pulping for paper manufacturing using long-term treatment with lime and air at low temperatures, two batches of fresh bagasse were treated under these conditions for several months. One batch of 0.6 kg wet and another of about 1.2 kg wet fresh bagasse, as obtained from W.R. Cowley Sugar House in Santa Rosa TX (i.e., no prior depithing or particle-size reduction), were pulped.

Batch #1 (0.6 kg wet fresh bagasse) was treated in a 6-L Erlenmeyer flask, and it was submerged in a water bath at 50^{o}C. The lime loading for this batch was 0.5 g of $Ca(OH)_2$/g dry of bagasse; thus, because the dry weight of the 0.6 kg wet bagasse was 294 g (~50% moisture), 160 g of industrial lime was added (0.92 g $Ca(OH)_2$/g of lime, Chemical Lime Co., New Braunfels TX). The water loading was 9 mL distilled water/g dry bagasse. Air, which was saturated with water by diffusing it through a water column also submerged in the 50^{o}C water bath, was bubbled into the flask to maintain oxidative conditions. There was no mixing implemented, except for the subtle stirring air bubbling caused. During the pretreatment, the Erlenmeyer flask broke and the liquid in the bottle was lost along with some of the lime; therefore, the actual lime loading was less than 0.5 g $Ca(OH)_2$/g dry bagasse. In addition, because the bubbling rate was considerable and no pre-scrubbing with lime was implemented, carbon dioxide in the air consumed some of the lime. To replenish the lost liquid, more distilled water was added at this point. The treatment lasted a total of 2 months. By then, the pH had decreased below 7; therefore, no acid was added for neutralization. The material was simply washed several times with distilled water in several 1-L centrifuge bottles and centrifuged at 4000 rpm to dewater the slurry. The washed material was dried in the

oven at 45°C, then broken apart by rubbing it against a 4-mesh screen, and separated by sieving into several fractions of various particle sizes. The fractions were sent to the Institute for Engineering Research, Forest Products Laboratory, University of Costa Rica (P.O. Box 36-2060, San José, Costa Rica C. A.) (IERFPL), for quality evaluation (i.e., morphometric study of the fibers, refining, handsheets formation and sheet characterization based on physical, chemical, mechanical and optical properties of pulp).

Batch #2 (1.2 wet kg of fresh bagasse, 50% moisture) was divided into six 200-g batches and each batch was placed in a 2-L Erlenmeyer flask and kept under constant air bubbling in an incubator. The air was scrubbed to rid it of CO_2 and water-saturated in a lime/water solution before it was delivered to the flasks. The treatment was run for 7 months and the lignin was decreased to about 7 to 8 g lignin/100 g treated bagasse from about 22 g lignin/100 g untreated bagasse as determined by the Klason lignin method (NREL methods No. 003 and 004 (NREL, 1992)). The temperature started at 50°C, but it was later increased first to 57°C after 100 days and then to 65°C after 155 days. At the beginning of the treatment, a lime loading of 0.3 g $Ca(OH)_2$/g dry bagasse was attained by adding 33 g industrial lime (0.92 g $Ca(OH)_2$/g lime, Chemical Lime Co., New Braunfels TX) to each Erlenmeyer flask. After 5 months of treatment, to ensure that the lime was in excess, an extra 0.1 g $Ca(OH)_2$/g dry of bagasse (i.e., 11 g industrial lime/Erlenmeyer flask) was added to complete a total loading of 0.4 g $Ca(OH)_2$/g dry bagasse. After the treatment was done, the bagasse was neutralized with glacial acetic acid and washed several times using a 5-gal bucket as the container and a 1/10-hp electric mixer to provide stirring (Arrow 850, Fisher Scientific Co., Pittsburgh PA). To dewater the pulp, a trigger-type polyester/cotton cloth was used to vacuum-filter the slurry. The wet pulp was dried in the oven at 45°C, then broken apart by rubbing it against a 10-mesh screen and finally sieved to separate the different particle sizes into fractions so that they could be sent to Integrated Paper Services Inc. (IPS) (101 W. Edison Ave., Suite 250 (54915), P.O. Box 446, Appleton WI 54912-0446, www.integratedpaperservice.com). IPS performed the analyses on pulp properties and characteristics to assess quality (i.e., Valley beater curve – including freeness,

handsheets, basis weight, caliper, bulk, density, tear, burst, tensile, and Gurley porosity – dirt count, ash at 525°C and 900°C, Klason lignin, brightness, color, opacity, MorFi fiber length, and digital microphotographs).

IV.3.4.2 Results and Discussion

After pretreatment, yields for both batches were close to 70% (70 g treated bagasse/100 g untreated bagasse). Tables 4.6 and 4.7 show the particle size distribution as obtained by sieving for Batches #1 and #2, respectively. Batch #1 was coarser.

The reports for the quality assessment of the pulps from Batches #1 and #2 are presented in full in Appendices N and O, respectively. For the refining process, which consists in beating the pulp to improve its properties, some of the fractions shown in Tables 4.6 and 4.7 were combined for each batch. In the case of Batch #1, the "coarse fiber", the "> 4 mesh", the "4 mesh – 10 mesh", and the "10 mesh – 16 mesh" fractions were blended together. For Batch #2, all the fractions < 16 mesh were combined.

Table 4.6 Particle size distribution for the pulp from Batch #1.

Fraction	Mass (g)
Handpicking	27.4
Coarse fiber	21.4
> 4 mesh	81.0
4 mesh – 10 mesh	34.1
10 mesh – 16 mesh	23.9
16 mesh – 30 mesh	40.1
30 mesh – 40 mesh	13.0
40 mesh – 50 mesh	15.4
< 50 mesh	39.8

Table 4.7 Particle size distribution for the pulp from Batch #2.

Fraction	Mass (g)
> 10 mesh	1
10 mesh – 16 mesh	6
16 mesh – 20 mesh	95
20 mesh – 30 mesh	114
30 mesh – 40 mesh	49
40 mesh – 50 mesh	37
< 50 mesh	95

The target quality for the pulping process was a pulp, which, after bleaching, would yield a good quality copy paper; therefore, comparisons with this type of paper were primarily done.

The average fiber length for the pulp from Batch #1 was about 1.8 mm (Table 1, Appendix N), which is longer than the fiber length for copy paper (~ 1 mm).

For Batch #2, the fiber lengths are, on average, smaller than those found in copy paper and the widths are larger (Table 1, Appendix O); therefore, these bagasse pulp fractions are not appropriate for manufacturing of copy-quality paper. Also, Table 1 in Appendix O shows that there is no significant difference in fiber length and width among the different particle sizes, which justifies the blending of all these fractions.

The fibers from Batch #1 are considerably longer than those from Batch #2, which suggests that long treatment times tend to break down the fiber, which is a detrimental effect in the process.

The Klason lignin for Batch #1 was reported to be 12.1 g lignin/100 g treated bagasse after 2 months of treatment and for Batch #2 was 8.8 g lignin/100 g treated bagasse after 5 months of treatment. For copy paper, the Klason lignin is in the order of

about 2 g lignin/100 g of treated bagasse. This result suggests that, given the present conditions, long-term lime pretreatment is not efficient in delignifying bagasse, which is necessary for good quality paper, because it cannot lower the lignin content to levels attainable with conventional pulping processes, which use NaOH, without compromising fiber integrity.

Table 4.8 shows that the strength properties for both Batches #1 and #2 are poor when compared with Kraft-type pulps, which are appropriate for copy paper manufacturing, thus confirming that the current lime+air pretreatment, is not adequate to obtain copy-quality paper. However, both pulps have strengths properties higher than those prescribed in the international standard for strawboards and they compare well with the pulps obtained from lime treatment at higher temperature for shorter times (Madan, 1981), which demonstrate that these bagasse pulps can be used in board applications or as corrugating medium.

One important operation that produces better yields and strength properties, and that is essential for producing copy paper from bagasse, is depithing, which was not implemented. Depithing can be dry, moist, or wet (Ashok et al., 1986). Dry depithing is normally done using a rotary drum screen after either artificially drying the bagasse or after long periods of time so that the moisture content may be about 35%. Moist depithing is conducted at the mill or nearby at about 50% moisture, which is the typical moisture content at which bagasse is discharged from the last roller mill (Valdes Delgado and De Armas Casanova, 2001). A depither, which breaks open the fiber bundles to dislodge the pith by mechanical rubbing and mild disintegrating action, is employed (Ashok et al., 1986). Wet depithing is done by adding water to the bagasse in a hydropulper (Valdes Delgado and De Armas Casanova, 2001). The slurry is then pumped through a depither machine to complete the defibrating operation and the pith passes through a perforated screen. For bagasse, moist and wet depithing are the two common methods (Ashok et al., 1986).

Table 4.8 Comparison of several pulp properties of Batch #1 and #2 with those of other types of pulp.

Pulping	Raw Material	Source	Conditions	Thickness (mm)	Density (kg/m^3)	Burst index ($kPa \cdot m^2/g$)	Burst Factor	Tensile index ($N \cdot m/g$)	Tear index ($mN \cdot m^2/g$)	Tear Factor	Breaking length (km)
Kraft-B	*Eucalyptus*	IERFPL	~1 h, > 100°C	---	619	3.3	34	59	9	92	---
Kraft-B	Hardwood mixture	IERFPL	~1 h, > 100°C	---	618	3.3	34	55	10.3	105	---
Kraft-B	*Pinus spp*	IERFPL	~1 h, > 100°C	98	641	5.46	56	85	9.38	96	---
Hydro-thermic	Banana	IERFPL		162	381	4.2	43	70	8.9	91	7.68
Lime (Batch #1)	Bagasse	IERFPL	2 months, 50°C	146	469	1.5	15	34	3.4	35	3.46
Lime (Batch #2)	Bagasse	IPS	5 months, 50, 57, 65°C	---	585	0.72	7.3	21	1.7	17	2.10
Soda	Depithed Bagasse	Hadli (1999)	~ 1 h, > 100°C	---	---	3.4 – 3.9	35 – 40	---	3.9 – 4.4	40 – 45	6.5 – 7.0
Lime	Bagasse	Singh (1959)	4 h, 162°C	---	---	3.0	30.9	---	---	---	4.6
Lime	Bagasse	Madan (1981)	4 h, 153°C	---	---	1.64	16.7	---	---	---	2.6
International Strawboard Standard		Madan (1981)		---	---	0.49	5.0	---	---	---	M.D. 1.2* C.D. 0.75

* M.D. ≡ Machine Direction, C.D. ≡ Cross-machine Direction

Pith particles are weak, have a high ash content, are spongy in texture (Figure 4.85), and they absorb more chemicals than fibers (Valdes Delgado and De Armas Casanova, 2001). Their removal is crucial to obtain good quality pulps. Nonetheless, the results agree well with the literature; for producing strawboards and other low-quality materials such as corrugating medium, depithing is not necessary (Ashok et al., 1986; Madan, 1981).

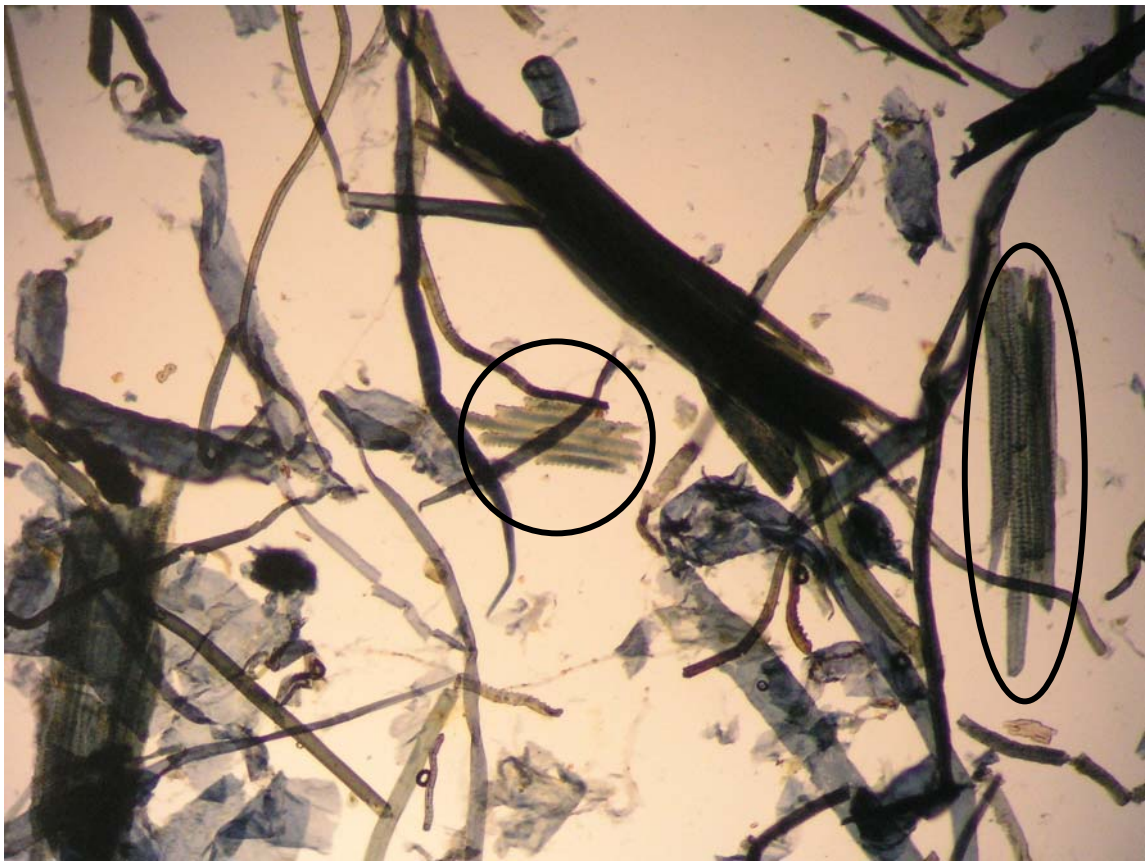


Figure 4.85 Digital micro-photograph of the bagasse pulp from Batch #2 showing some pith particles (circled).

Table 4.8 also shows that the strength properties are higher for the pulp from Batch #1 than from Batch #2 even though the Klason lignin content is lower in Batch #2.

As with the length and width results, it can be concluded that the harsher conditions used in Batch #2 (i.e., higher temperatures and longer time) deteriorated the fiber.

Also, it must be considered that because $Ca(OH)_2$ completely alters the fiber surface (Figure 4.2), it may not be a suitable pulping agent for good quality copy paper. NaOH, on the other hand, does not cause such surface alteration (Figure 4.2).

With the current process, as suggested by IPS, the resulting pulp can be used for corrugating medium or inside layers of a liner grade. The price of such types of materials is about 60% to 70% that of a bleached softwood Kraft pulp. For instance, for 26-lb/3000 ft^2 semi-chemical corrugating medium, the price ranged (January 2000 to April 2004) between $290 to $440/short ton. In the past 20 years, the price averaged about $350/short ton. On the other hand, the price of bleached softwood Kraft pulp ranged between $420 and $650/short ton (March 2000 to March 2004). The approximate average for the last 20 years was about $550/short ton (www.cpbis.gatech.edu).

IV.4 Conclusions

Long-term pretreatment of bagasse at temperatures lower than 60^oC presents a rapid decrease of the lignin content during the first week. Such sharp decrease occurs even in the absence of air (i.e., non-oxidative conditions). After the first week, under non-oxidative conditions, delignification is almost negligible. In contrast, under oxidative conditions, delignification occurs but at a slower rate. This behavior suggests the presence of two delignification phases known as bulk (rapid) phase, which dominates during the first week, and residual (slow) phase, which takes over after the first week. The existence of such phases is confirmed also by the lime consumption/pretreatment time profile and by the delignification model.

In general, during the residual phase there is about a 1:1 ratio of holocellulose loss to lignin removal, as the selectivities show (Section IV.3.2.3.2).

Lime consumption is directly related to lignin conversion; thus, for oxidative conditions, lime consumption continued to be significant after the first week, but in the case of the non-oxidative conditions, lime consumption practically ended after the first week.

Higher temperatures produce higher lignin conversions because the delignification model showed that a_b, the fraction of lignin that degrades in the bulk phase, increases with temperature. Also, a_b was slightly larger for delignification under oxidative conditions. Nonetheless, delignification occurred to the same extent for the treatment with and without air during the first week. This suggests that for oxidative conditions the bulk phase continues for a time slightly longer than 1 week. In general a_b was about 1/3, meaning that about 1/3 of the lignin degrades in the bulk phase.

The delignification model fit the data remarkably well, with all $R^2 > 0.87$. In comparison to the delignification of woody biomass, such as western hemlock wood with sodium hydroxide under non-oxidative conditions (Dolk et al., 1989), the activation energies and the natural logs of the Arrhenius constant for the delignification model were lower by a factor of about 4 and 3, respectively. This suggests that, as expected, bagasse is easier to delignify than hardwoods.

It is worth mentioning that the bagasse appearance changed significantly when treated under oxidative conditions. For instance, Figure 4.86 shows that after 6 months of lime treatment at 50^{o}C, the old bagasse treated without air (left) did not significantly changed its appearance compared to untreated bagasse (Figure 4.61). The fibers are still distinguishable and the color is still dark brown. On the other hand, the old bagasse treated with air (right), underwent clear morphological changes; it had a powdery texture and its color was light brown.

Figure 4.86 Photograph of old bagasse after 6 months of lime treatment at 50°C under non-oxidative (left) and oxidative (right) conditions.

The 3-day digestibility yields for an enzyme loading of 5 FPU/g dry treated bagasse were shown to be highest for the treatment at 57°C under oxidative conditions and after a treatment time of about 2 to 3 weeks (~0.4 g glucose+xylose/g dry untreated bagasse). The treatment time necessary to achieve the highest digestibility under oxidative conditions decreases with temperature. Thus, at 23°C, 120 – 150 days are necessary, whereas for 57°C, as mentioned, 2 – 3 weeks suffices.

Comparison of fresh and old stored bagasse showed that fresh bagasse was of better quality than old bagasse; it gave better lignin conversions and higher 3-day digestibility yields even when equal pretreatment conditions were used. Also, fresh bagasse was less variable; therefore, its behavior was more predictable.

For fresh bagasse lime-treated at 50°C, 3-day digestibility yields were the same after 1 week of treatment for oxidative and non-oxidative conditions. After 1 week, there was no digestibility enhancement for the treatment under non-oxidative conditions. In contrast, for the treatment under oxidative conditions, digestibility continued to improve until the 2nd month of treatment.

The results showed that NaOH in the presence of air is more effective than $Ca(OH)_2$ for short-term pretreatment. NaOH treatment has a larger bulk phase than $Ca(OH)_2$ treatment; however, for the residual phase, $Ca(OH)_2$ was more selective towards lignin. Although the degree of delignification was higher with NaOH treatment, attaining almost 80% lignin conversion (80 g lignin removed/100 lignin in untreated bagasse) in 3 months, 3-day digestibility yields were only slightly higher for NaOH; therefore, to enhance digestibility, $Ca(OH)_2$ is preferred because it is cheaper, safer, and more convenient. For bagasse pulping, however, where high degrees of delignification are important, NaOH must be considered. From these studies with air at 50°C, good results were obtained with NaOH, with lignin decreasing from 21 g lignin/100 g untreated bagasse to about 4 g lignin/100 g treated bagasse and an overall yield of 64% (64 g treated bagasse/100 g untreated bagasse) in 3 months. Also, the bagasse was highly bleached displaying a very bright white color.

3-day digestibility yields from cellulase enzyme batches with different amounts of cellobiase in their original mixture cannot be compared if their activity is determined by the conventional filter paper assay (NREL method No. 006, NREL, 1992). Instead, for comparison, the activity must be determined by adding an excess of cellobiase in the conventional filter paper assay, as suggested by Coward-Kelly et al. (2003). The cellulase enzyme used throughout these studies (Iogen Laboratories, Ottawa ON Canada) had a high cellobiase content. Based on the conventional filter paper activity, considerably higher 3-day digestibility yields were obtained when cellulase enzyme with little cellobiase in its original mixture (Spezyme® CP, Genencor International, Inc., Palo Alto CA) was used instead.

Preliminary studies showed that for temperatures below 60°C the use of pure oxygen to maintain oxidative conditions had no advantage over the use of air. However, studies showed that for higher temperatures, such as 75°C, the use of pure oxygen has delignification advantages. The use of air actually yielded lower lignin conversions than those obtained at 57°C. This effect is attributed to the increasing vapor pressure (i.e., water partial pressure) as the temperature increases, which displaces oxygen, as illustrated in Table 4.5. Although delignification is considerably enhanced by using pure oxygen at 75°C, 3-day enzyme digestibility yields are not significantly different for the treatments with pure oxygen and with air.

Bagasse pulping by long-term lime pretreatment was inadequate for obtaining pulps that, after bleaching, would yield good quality copy paper. The process was unable to decrease lignin content without compromising fiber integrity. Although the pulp treated for 5 months had a Klason lignin of about 8 g/100 g treated bagasse, it had poorer strength properties than the pulp treated for 2 months, which had about 12 g lignin/100 g treated bagasse. Nonetheless, the pulps were not rendered useless because their strength properties significantly surpassed the standard specifications for strawboard (Madan, 1981) and their characteristics were also appropriate for filler applications, such as corrugating medium or inside layers of a liner grade.

IV.5 Future Studies

Because the delignification process is fast in the first hours of the pretreatment, to complete the delignification profile, it is important to also obtain data points near the beginning of the curve, say at 3, 6, 12, 18 and 24 hours, 2, 3, 5, 6, and 7 days, especially for higher temperatures. These points will allow the assessment of the holocellulose-to-lignin selectivity for the bulk delignification phase and will yield more accurate values for the parameters in the delignification model.

Because lime in the scrubber is consumed by CO_2 present in the air, it is important to regulate the amount of air delivered to the system to save lime; therefore, studies to determine the actual amount of oxygen necessary in the pretreatment should be performed.

More studies with fresh bagasse, which is more predictable than old bagasse because it displays less variability, should be conducted. Studies should evaluate long-term lime pretreatment, short-term lime pretreatment, and methods to reduce cellulose crystallinity. Digestibility measurements should include not only 3-day cellulase-enzyme digestibility analysis, but also actual carboxylic acids yields from anaerobic fermentations, which simulate better the conditions of the MixAlco process.

The long-term studies done with NaOH showed good results both visually (i.e., a highly bleached pulp was obtained) and quantitatively (i.e., a yield of 64 g treated bagasse/100 g untreated bagasse and a lignin content of 4 g/100 g treated bagasse were attained). Pulping by long-term pretreatment for paper manufacturing should also be studied with NaOH alone and/or with a combination of NaOH and $Ca(OH)_2$ or $CaCO_3$ in different proportions, which will protect the fibers because of the calcium ions, as suggested in the literature (Trivedi and Murthy, 1982; Nagieb and El-Sayed, 2000; Robert et al., 1968; Aung and Boyle, 1973). The use of NaOH is important especially for pulping hardwoods, which are difficult to delignify. The effect of depithing bagasse prior to the pulping process should also be considered.

CHAPTER V

FINAL CONCLUSIONS – PUTTING IT ALL TOGETHER

Figures 5.1 and 5.2 show a potential configuration of the proposed process for producing sugar (as food), fuels, and chemicals using the appropriate set of conditions described in these studies. The extraction system is described in Chapter II, the juice preservation procedure is described in Chapter III, and the bagasse long-term lime pretreatment to enhance biological digestibility is described in Chapter IV.

V.1 Operation During Sugarcane Harvest Season

Figure 5.1 shows the process as it would occur during the harvest season. The sugar must be extracted from cane as soon as possible; therefore, the extraction equipment must be sized to process all the cane produced during the season. Fresh cane enters the system and is shredded using a conventional knife mill, which yields a high preparation index (i.e., high degree of cell rupture). The shredded cane enters the extraction system to separate the sugar from the bagasse in eight stages using an imbibition level of 260% on fiber (260 lb imbibing H_2O/100 lb dry fiber processed). The screw-press conveyors employ a cumulative power of 17 hp·h/ton dry fiber (14 kW·h/metric tonne dry fiber) for both squeezing and conveying. In addition, there is a final dewatering device, such as a conventional roller mill, which is used to attain a final bagasse moisture of about 45%. The power consumption for this device is about 20 hp·h/ton dry fiber (Hugot, 1986). The overall recovery for the extraction process is 98% (98 lb soluble solids recovered/100 lb soluble solids in cane fed to the system).

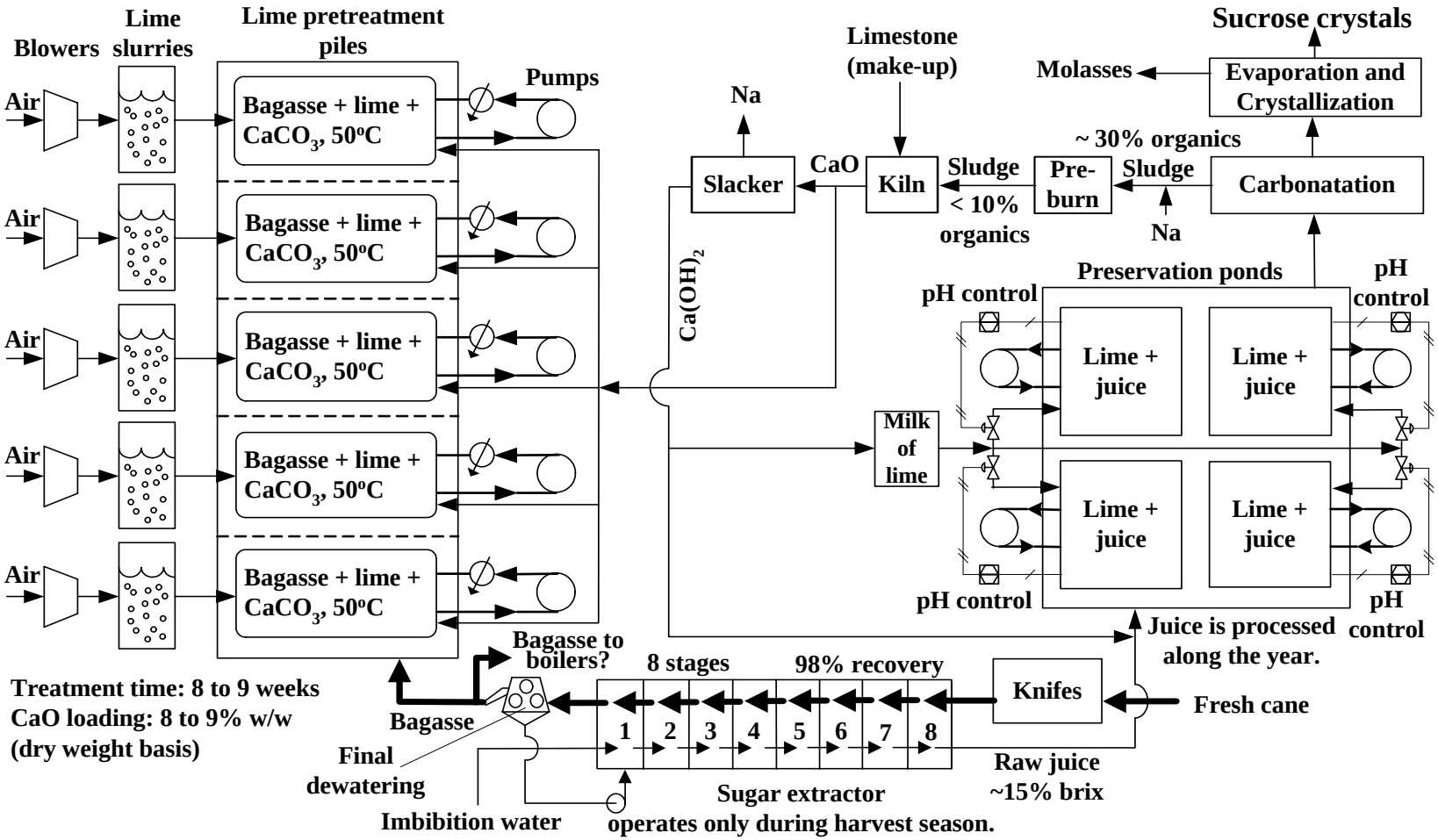


Figure 5.1 Layout of sugar/bagasse processing plant during harvest season.

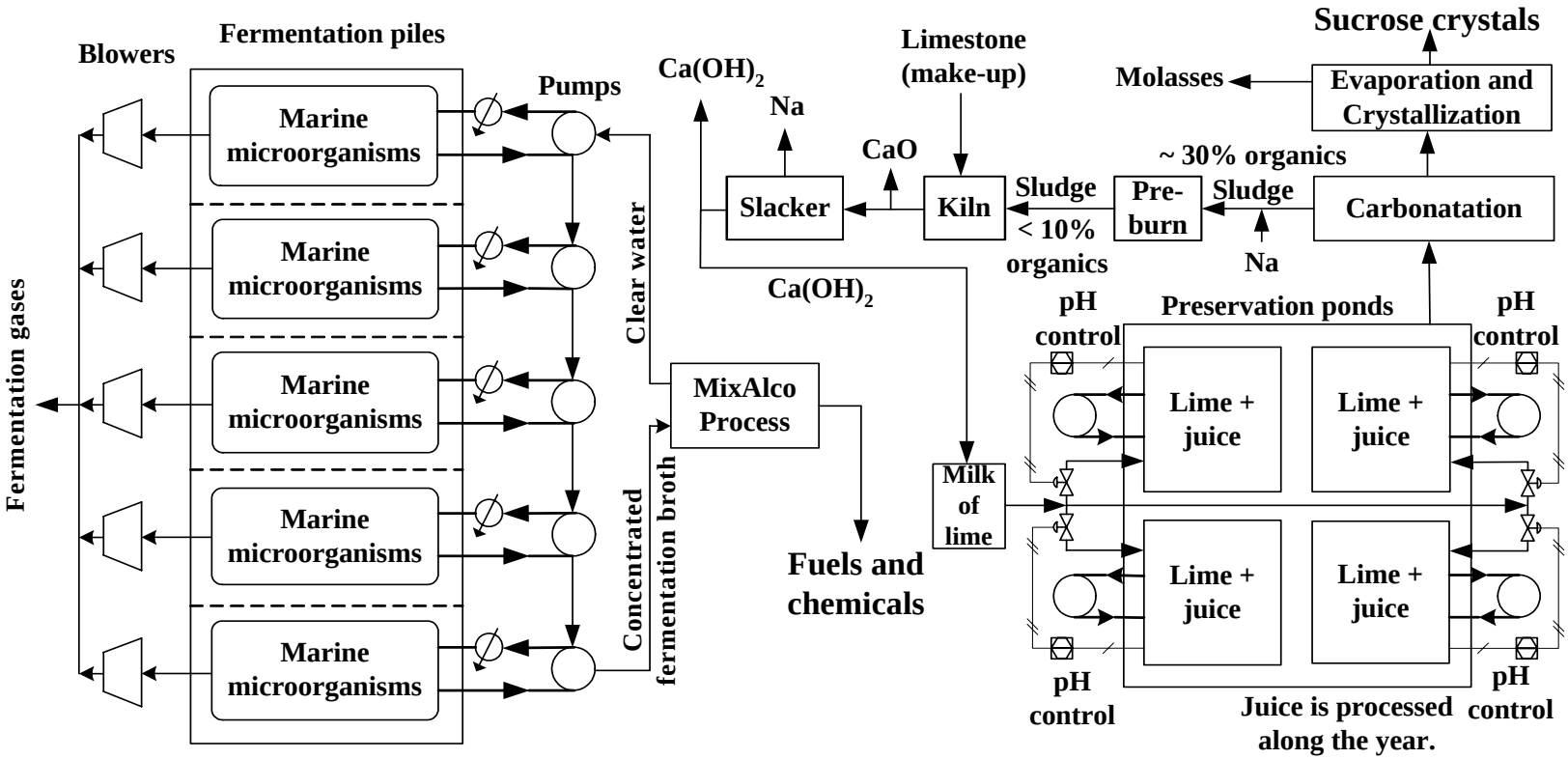


Figure 5.2 Layout of sugar/bagasse processing plant after harvest season.

Lime addition (higher pH) and/or higher temperatures, which inhibit microorganisms, must also be considered in the extraction process. However, if the cane residence time in the extractor is short enough, such conditions will not be necessary.

For preservation, the juice exiting the extraction system is mixed with $Ca(OH)_2$ and directed to ponds, which have been lined with a geo-membrane. Intermittent juice recirculation, by pumps or agitators, is implemented. The juice alkalinity is automatically controlled to maintain pH above 11, thus limiting the amount of lime used. Another possible option is to segment the juice in batches and add to each batch the amount of lime necessary for preservation until it is processed (Figure 3.21). In this way, necessary downstream equipment, such as carbonation and filtration (i.e., carbonatation) equipment, evaporators and boilers, crystallizers, etc., do not need to be oversized. The final product is raw or white sugar (sucrose) crystals.

The recovered carbonatation sludge is processed as shown in Figure 3.40. The sludge is mixed with a sodium-rich material, pelletized, and pre-burned in a reactor to decrease its organic contents below 10 lb/100 lb total sludge. Sodium acts as a high-temperature binder, giving strength to the pellets so that they do not disintegrate and clog the reactor (Kelly and Namazian, 1998). The low-organic-content sludge is then re-pelletized and calcined in a stationary kiln. Some limestone might also be added to make up for some of the lime lost in the process. The resulting CaO might be ground and used directly for bagasse pretreatment, or it may be slacked. During the slacking process, $Ca(OH)_2$ is formed, which is then added to the juice for preservation as it exits the extraction system. Most of the sodium must also be removed during the slacking process so that it does not end up in the juice causing sucrose losses during crystallization (Chen and Chou, 1993).

To enhance biological digestibility, the fiber (i.e., bagasse) exiting the extraction system is mixed with lime (0.08 – 0.09 lb CaO/lb dry bagasse or 0.1 – 0.12 lb $Ca(OH)_2$/lb dry bagasse) and calcium carbonate (either limestone or the carbonatation sludge itself) and formed into several piles on top of a gravel bed (details shown in Figure 4.1). Although either slacked lime ($Ca(OH)_2$) or quicklime (CaO) can be

employed, CaO is preferred to harness its heat of hydration. Blowers deliver carbon-dioxide free air to the system to induce oxidation. Each pile would be treated for about 8 weeks at 50 – 60^{o}C until its pH is low enough for microorganisms to subsist (~8 – 10). At this point the pile is inoculated with marine microorganisms to initiate fermentation. The blowers are reversed and coupled to exhaust pipes to extract fermentation gases (Figure 5.2).

V.2 Operation After Sugarcane Harvest Season Ends

Figure 5.2 shows the process as it would occur after the harvest season ends. The only oversized equipment, the extraction system, does not operate after the season; therefore, it is not shown in Figure 5.2.

The preserved juice continues to be processed along the year; thus, carbonatation, evaporation, and crystallization equipment operate all year round to produce sugar crystals. Also, the carbonatation sludge continues to be produced and it is converted to lime via the stationary lime kiln as described in Section V.1. However, except for the small amount needed to control juice pH in preservation ponds, the lime produced is not used immediately (unless integrated with some other process); therefore, it must be stored for next harvest season.

The bagasse piles formed at the beginning of the harvest season will enter the fermentation mode before the season ends. About 2 months after the harvest season ends, all the piles will have been treated for the required time (i.e., 8 weeks); therefore, all of them should be in the fermentation phase at this time. The marine microorganisms produce organic acids, which are readily converted to carboxylate salts because of the calcium carbonate present (Thanakoses, 2002). The carboxylate-salt-rich fermentation broth is then treated via the MixAlco process to make fuels and chemicals (Holtzapple et al., 1999).

V.3 The Biorefinery: The Grand Scheme

Figure 5.3 shows the flowchart of a proposed biorefinery, which fully and efficiently utilizes all the products and by-products from sugarcane and yields a wide variety of useful commodities. The different paths can be chosen according to the market. The highlighted units have been the subject of study in this work.

Sugarcane juice and bagasse are separated from cane during the harvest season via the extraction system. The juice is preserved so that it may be processed along the year, whereas the bagasse is treated with lime and air to enhance digestibility.

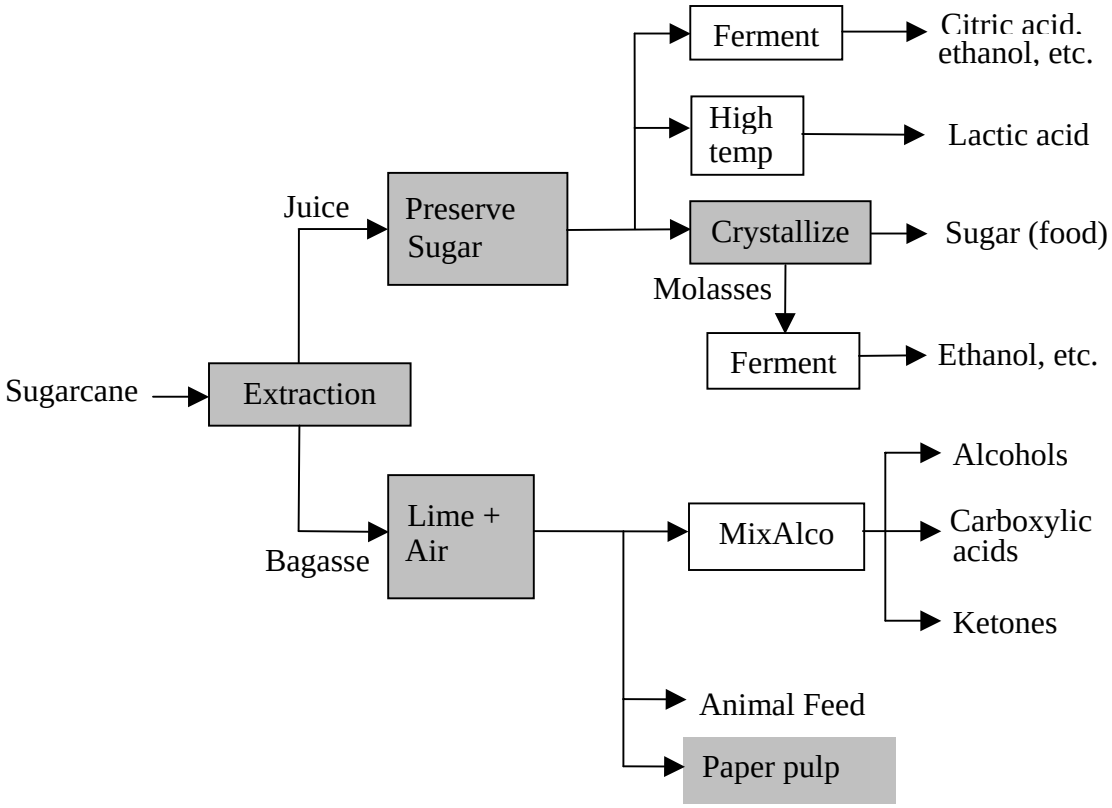


Figure 5.3 Flowchart of a biorefinery: the grand scheme.

The preserved juice may be clarified, concentrated, and crystallized to produce sugar for food. It may also be directly treated with high temperatures to produce lactic

acid, as it is known that sucrose, alkali (especially lime) and high temperatures produce high yields of lactic acid (O'Donnell and Richards, 1973; Kopriva, 1973). Fermentation may also be used to obtain chemicals or fuel (e.g., citric acid, ethanol, etc.) from cane juice or from molasses.

The lime-treated bagasse, which is now highly digestible, may be fermented to produce carboxylate salts, which may then be converted into fuels and chemicals (i.e., alcohols, carboxylic acids, and ketones) via the MixAlco process. Also, the highly digestible material may be used directly as animal feed. As the studies in Chapter IV show, the lime-pretreatment process can also be used as a pulping technology to produce paperboard pulp.

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APPENDIX A

DERIVATION OF EQUATIONS 2.2 AND 2.3

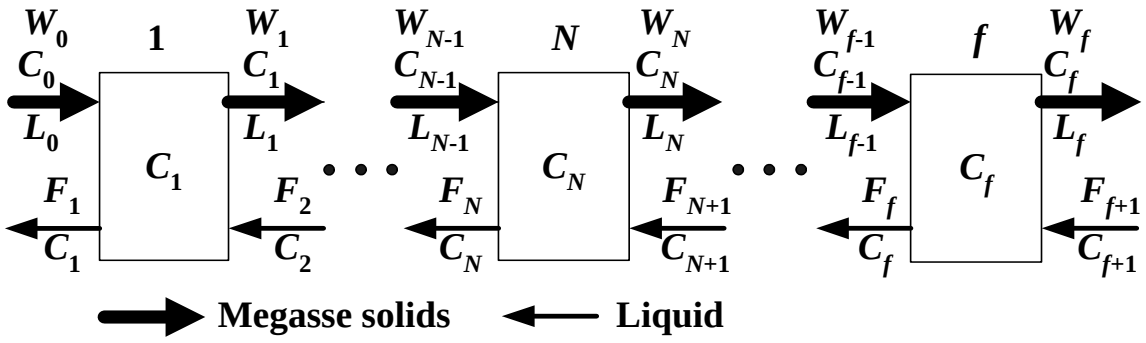

Figure A.1 Illustration of mass transfer details in gentle-squeeze screw-press conveyor extractor.

Consider Figure A.1, where the sugar extractor has f stages. The liquid and the megasse (i.e., fiber and liquid), which are moving countercurrently to each other, reach equilibrium soluble solids composition in each stage. For each stage, the soluble solids composition of the liquid in the exiting megasse is the same as that of the exiting liquid. The liquid flow rate for each stage is F_1, …, F_N, …, and F_f (lb/h) and the soluble solids mass fractions for each stage is C_1, …,C_N, …, and C_f .

The total wet throughput (lb/h) of the megasse leaving each stage is W_1, …, W_N, …, and W_f. This megasse has a liquid mass fraction L_1, …, L_N, …, and L_f , respectively. Fresh cane enters the system at a wet throughput of W_0, with a liquid mass fraction of L_0, which has a soluble solids concentration C_0. Imbibing water enters the system at a flow rate F_{f+1} (lb/h) at a soluble solids concentration C_{f+1}, which is commonly equal to 0. The raw juice obtained from the extraction, which continues downstream for clarification, concentration, and crystallization, leaves the system at a flow rate F_1 (lb/h) and at a specified soluble solid mass fraction C_1. The bagasse exiting the system has a liquid mass fraction L_f at a soluble solid mass fraction C_f , which are specified to meet a target overall recovery of soluble solids.

Given the system as described, for the *N*th stage, the material balance for the liquid is as follows:

$$W_{N-1}L_{N-1} + F_{N+1} = F_N + W_N L_N \tag{A.1}$$

Because the fiber that enters the system in the cane advances only in one direction, mass conservation shows that the material balance for the fiber in the megasse in the *N*th stage is,

$$W_{N-1}(1 - L_{N-1}) = W_N(1 - L_N) = S_0 \tag{A.2}$$

where

S_0 = Dry fiber mass flow rate as fed to the system, lb/h

For the soluble solids, the material balance in the *N*th stage follows:

$$W_{N-1}L_{N-1}C_{N-1} + F_{N+1}C_{N+1} = F_N C_N + W_N L_N C_N \tag{A.3}$$

Replacing Equation A.2 into Equation A.1,

$$\frac{L_{N-1}}{1 - L_{N-1}} S_0 + F_{N+1} = F_N + \frac{L_N}{1 - L_N} S_0 \tag{A.4}$$

Replacing Equation A.2 into Equation A.3,

$$\frac{L_{N-1}}{1 - L_{N-1}} S_0 C_{N-1} + F_{N+1}C_{N+1} = F_N C_N + \frac{L_N}{1 - L_N} S_0 C_N \tag{A.5}$$

Equation 2.3 is obtained by rearranging Equation A.4,

$$F_{N+1} = F_N + \frac{L_N}{(1-L_N)} S_0 - \frac{L_{N-1}}{(1-L_{N-1})} S_0 \tag{2.3}$$

Equation 2.2 is obtained by replacing Equation 2.3 into A.5 and rearranging,

$$C_{N+1} = \frac{\frac{L_N}{1-L_N} S_0 C_N + F_N C_N - \frac{L_{N-1}}{1-L_{N-1}} S_0 C_{N-1}}{\frac{L_N}{1-L_N} S_0 - \frac{L_{N-1}}{1-L_{N-1}} S_0 + F_N} \tag{2.2}$$

Given the specifications for the process, we must find F_{f+1} and F_1 from the overall material balance to be able to implement Equations 2.2 and 2.3 in an iterative calculation. Thus, the overall mass balance for the liquid is as follows:

$$W_0 L_0 + F_{F+1} = F_1 + W_f L_f \tag{A.6}$$

The overall mass balance for the fiber in the megasse follows:

$$S_0 = W_0 (1-L_0) = W_f (1-L_f) \tag{A.7}$$

Rearranging Equation A.7, the following equation is obtained:

$$W_f = \frac{S_0}{1-L_f} \tag{A.8}$$

The overall mass balance for the soluble solids follows:

$$W_0 L_0 C_0 + F_{f+1} C_{f+1} = F_1 C_1 + W_f L_f C_f \tag{A.9}$$

Replacing Equation A.8 in Equations A.6 and A.9,

$$W_0 L_0 + F_{f+1} = F_1 + \frac{S_0 L_f}{1 - L_f} \tag{A.10}$$

$$W_0 L_0 C_0 + F_{f+1} C_{f+1} = F_1 C_1 + \frac{L_f}{1 - L_f} S_0 C_f \tag{A.11}$$

Rearranging Equation A.11,

$$F_1 = \frac{W_0 L_0 C_0}{C_1} + \frac{F_{f+1} C_{f+1}}{C_1} - \frac{L_f}{1 - L_f} S_0 \frac{C_f}{C_1} \tag{A.12}$$

Replacing Equation A.12 into Equation A.10,

$$W_0 L_0 + F_{f+1} = \frac{W_0 L_0 C_0}{C_1} + \frac{F_{f+1} C_{f+1}}{C_1} - \frac{L_f}{1 - L_f} S_0 \frac{C_f}{C_1} + \frac{S_0 L_f}{1 - L_f} \tag{A.13}$$

Equation A.13 is then rearranged,

$$F_{f+1}\left(1 - \frac{C_{f+1}}{C_1}\right) = \frac{W_0 L_0 C_0}{C_1} - \frac{L_f}{1 - L_f} S_0 \frac{C_f}{C_1} + \frac{S_0 L_f}{1 - L_f} - W_0 L_0 \tag{A.14}$$

Multiplying through Equation A.14 by C_1 and rearranging,

$$F_{f+1} = \frac{W_0 L_0 C_0}{C_1 - C_{f+1}} - \frac{L_f}{1 - L_f} S_0 \frac{C_f}{C_1 - C_{f+1}} + \frac{S_0 L_f C_1}{(1 - L_f)(C_1 - C_{f+1})} - \frac{W_0 L_0 C_1}{C_1 - C_{f+1}} \quad \text{(A.15)}$$

APPENDIX B

SCREW-PRESS CONVEYOR DATA STATISTICAL ANALYSIS

SAS® statistical software (SAS Institute Inc., Cary NC) was used to perform the statistical analysis of the data. The methods used in the calculations for the values of the ANOVA tables, the regression statistics, the parameters and their standard errors for all the correlations are described by Milton and Arnold (1995). The detection of outliers was done using the influence diagnostics described by Belsley et al. (1980).

The criteria for investigating outliers were set by several parameters, as described in Belsley et al. (1980), which yield the influence diagnostics for the data. These parameters were calculated using SAS® for all the observations (*i*). The parameters were: 1) the diagonal elements of the hat matrix (h_i), 2) the studentized deleted residual (RSTUDENT), named as such because it is calculated by omitting the point in question from the correlation before calculating its studentized residual, 3) the determinantal ratio (COVRATIO), 4) the scaled change in fit (DFFITS), 5) the scaled change in the estimated regression coefficients that would occur if the *i*th row were deleted (DFBETAS), and 6) the Cook's D, which is very similar to DFFITS.

Belsley et al. (1980) recommended that values with $h_i > 2\,p/n$, where p is the number of parameters and n is the number of observations, are leverage points and are worthy of investigation. For RSTUDENT, values with |RSTUDENT| > 2 would indicate a potential outlier. In the case of COVRATIO, values with $|\text{COVRATIO-1}| \geq 3p/n$ are worthy of investigation. For DFFITS, the general cut off value, suggested by Belsley et al. (1980), above which influential observations can be realized is |DFFITS| > 2, and the size-adjusted cut off is $2\sqrt{p/n}$. For DFBETAS, also the general cut off above which the observation is considered influential is |DFBETAS| > 2 and the size-adjusted cut off is $2/\sqrt{n}$. Observations with a value for Cook's D > 0.2 would indicate that they are influential.

B.1 Throughput as a Function of Power

Table B.1 shows the ANOVA for the regression with all 29 observations for dry fiber throughput as a function of power (Figure 2.15). The regression is significant with P-value < 0.0001. However, the residuals (Figure B.1), show that the data are not scattered randomly but rather has a parabolic shape.

Table B.1 ANOVA of the regression of dry fiber throughput as a function of power (n = 29).

	df	SS	MS	F	P-value
Regression	1	1.51E+06	1.51E+06	2.13E+02	<0.0001
Residual	27	1.91E+05	7.08E+03		
Total	28	1.70E+06			

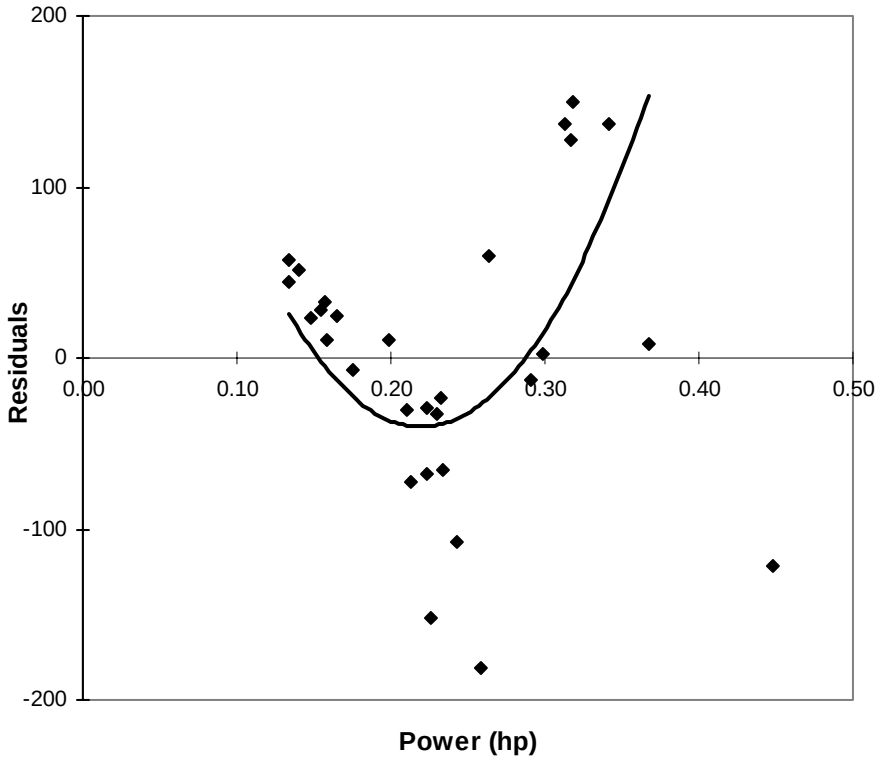

Figure B.1 Residual plot of the correlation of dry fiber throughput as a function of power (n = 29).

Table B.2 shows the ANOVA for the regression with 29 observations (i.e., including outliers) of the natural log of the dry fiber throughput as a function of power. The regression is significant, and the residuals scatter randomly (Figure B.2) confirming the exponential relation between dry fiber throughput and power.

Table B.2 ANOVA of the regression of the ln of the dry fiber throughput as a function of power (n = 29).

	df	SS	MS	F	P-value
Regression	1	11.1	1.11E+01	233.8	<0.0001
Residual	27	1.28	4.73E-02		
Total	28	12.3			

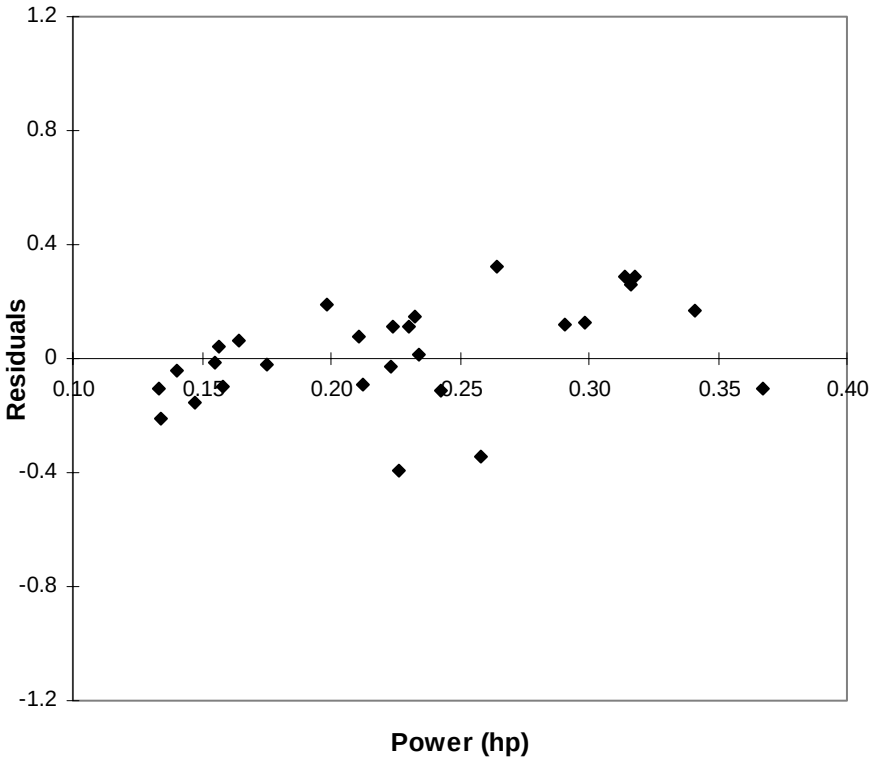

Figure B.2 Residual plot of the correlation of ln of dry fiber throughput as a function of power (n = 29).

Influence diagnostics detected Point 12 as an outlier, with an |RSTUDENT| value of 4.46 (well above its cut-off of 2), h_i value 0.30 (cut-off is 0.13), which means that this value is a leverage point. |COVRATIO-1| was 0.51 (cut-off is 0.21), |DFFITS| is 2.93 (general cut-off is 2) and its Cook's D is 2.54 (cut-off is 0.2), the DFBETAS are also higher than their general cut off of 2. Investigation of this point showed that there was considerable variation and therefore it yielded a considerably large standard deviation. This variation was attributed to the fact that a large amount of bagasse had just been added to the system; therefore, longer times were necessary to achieve steady state. When the measurements were taken, it seems that the system was not yet at steady state. In conclusion, the considerably high values for the influence diagnostics parameters, which were well above their cut-offs, and the experimental evidence found, justified the elimination of this data point.

After Point 12 was eliminated, the influence diagnostics was once again run on the data, and this time it found three potential outliers, namely Point 2, 18, and 23. These values slightly exceeded the cut-off for |RSTUDENT| (i.e., 2). Only the h_i value for Point 23 exceeded its cut-off of 0.14, which means that this point was a leverage point. Investigation of these points found no evidence that would justify their elimination.

Table B.3 shows the ANOVA for the regression with 28 observations (i.e., excluding the outlier) of the natural log of dry throughput as a function of power. As expected, the regression is significant, and the residuals scatter randomly (Figure B.3).

Table B.3 ANOVA of the regression of the ln of dry fiber throughput as function of power (n = 28)

	df	SS	MS	F	P-value
Regression	1	10.36	10.36	372.27	<0.0001
Residual	26	0.72	0.0278		
Total	27	11.09			

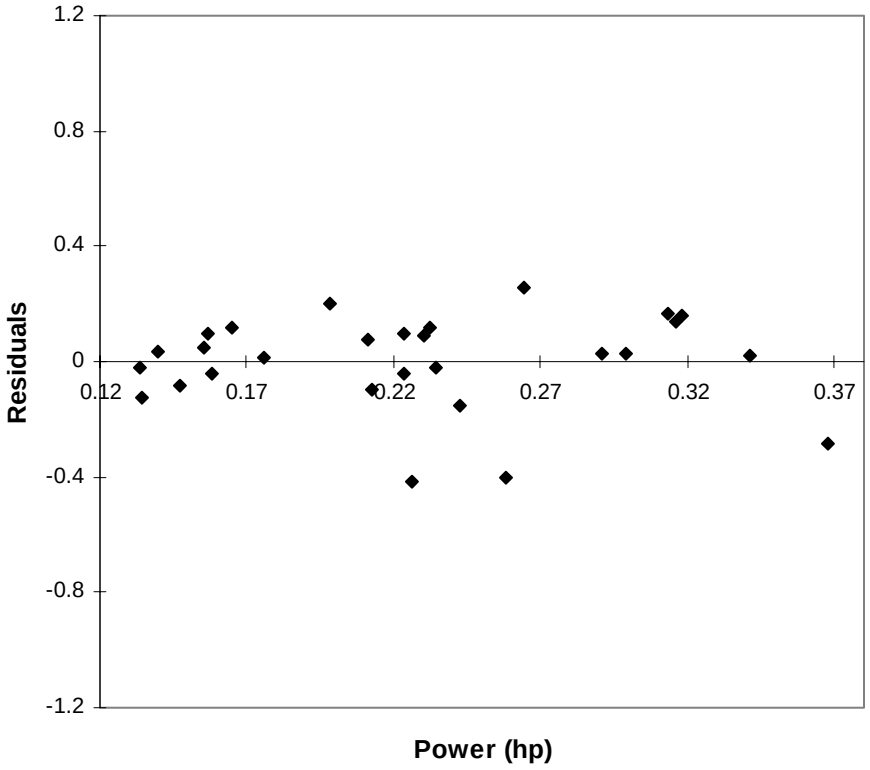

Figure B.3 Residual plot of the correlation of ln of dry fiber throughput as a function of power (n = 28).

The regression statistics and the standard errors for the regression parameters (slope and intercept) were found using SAS®. The results follow:

Table B.4 Regression statistics, parameters and standard errors for the regression of dry fiber throughput as a function of power (n = 28).

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.9668	Intercept	3.54	0.11	31.38	<0.0001
R^2	0.9347	Slope	9.20	0.48	19.29	<0.0001
Adjusted R^2	0.9322					
Standard Error	0.167					

B.2 Moisture Content as a Function of Power

Table B.5 shows the ANOVA for the regression of moisture content as a function of power (n = 29 observations) (Figure 2.16). Although the variation of the moisture content is not considerable, the ANOVA shows that the regression is significant (99.2% probability). Figure B.4 shows that the correlation residuals scatter randomly, however, to ensure that this, the regression significance of the residuals should also be tested. Table B.6 shows the ANOVA of the regression of the residuals. The P-value is 1; therefore, this suggests that the regression is not significant and that the residuals do scatter randomly.

Table B.5 ANOVA of the regression of moisture content as a function of power (n = 29).

	df	SS	MS	F	P-value
Regression	1	6.68	6.67	8.31	0.0076
Residual	27	21.7	8.03E-2		
Total	28	28.4			

Table B.6 ANOVA of the regression of the residuals of moisture content as a function of power (n = 29).

	df	SS	MS	F	P-value
Regression	1	3.55E-15	3.55E-15	4.42E-15	1
Residual	27	2.17E+01	8.03E-01		
Total	28	2.17E+01			

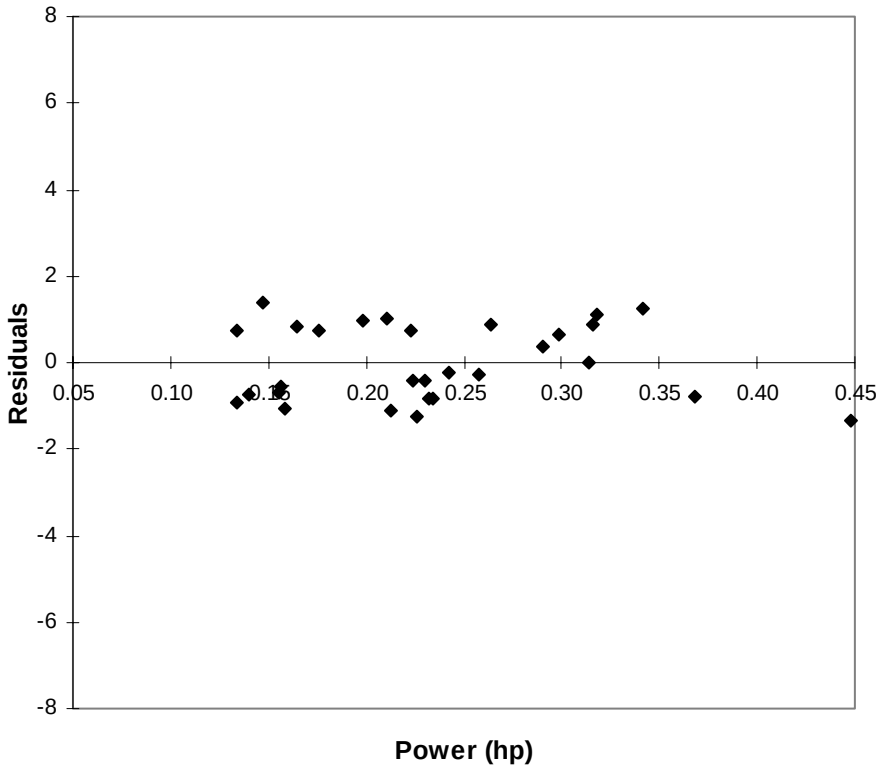

Figure B.4 Residual plot of the correlation of moisture content as a function of power (n = 29).

Although the data seems to scatter significantly (Figure 2.16), the influence diagnostics suggested that the highest |RSTUDENT| was 1.9, for Point 12. This is lower than cut-off of 2; however, the calculated Cook's D for this value was 0.7 (cut-off is 0.2), and the value for |DFITTS| and h_i also exceeded their cut-offs of 0.53 and 0.14, respectively, which meant that this data point had a lot of leverage and it was an influential point. Based on the experimental evidence about this point mentioned in Section B.2, its elimination was justified.

After excluding Point 12, no more outliers were detected by the influence diagnostics. Table B.7 shows the ANOVA for the regression with 28 observations (i.e., excluding the outlier).

Table B.7 ANOVA of the regression of moisture content as a function of power (n = 28).

	df	SS	MS	F	P-value
Regression	1	9.333	9.333	12.75	0.0014
Residual	26	19.037	0.732		
Total	27	28.370			

Table B.8 shows the regression statistics, the parameters and their respective standard errors for the regression of moisture content as a function of power (n = 28 observations) as calculated by SAS®. Although the fit is poor (i.e., R^2 is low), the parameters are significant (i.e., P-values are small). As expected, the regression is significant, and the residuals scatter randomly (Figure B.5).

Table B.8 Regression statistics, parameters and standard errors for the regression of moisture content as a function of power (n = 28).

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.5736	Intercept	88.3	0.58	152.51	<0.0001
R^2	0.3290	Slope	8.73	2.45	3.57	0.0014
Adjusted R^2	0.3032					
Standard Error	0.8557					

B.3 Throughput as a Function of Moisture Content.

Table B.9 shows the ANOVA for the regression of dry fiber throughput as a function of moisture content (n = 29 observations). In spite of the considerable scattering of the data (Figure 2.17) and the small variation of the moisture content, the regression is statistically significant (99.9% probability).

Figure B.6 depicts the residual plot for the regression. To ensure that the residuals have a normal distribution around 0, Table B.10 shows the significance of the regression of the residuals. The P-value is equal to 1, which means that the regression of the residuals is not significant, suggesting random scattering.

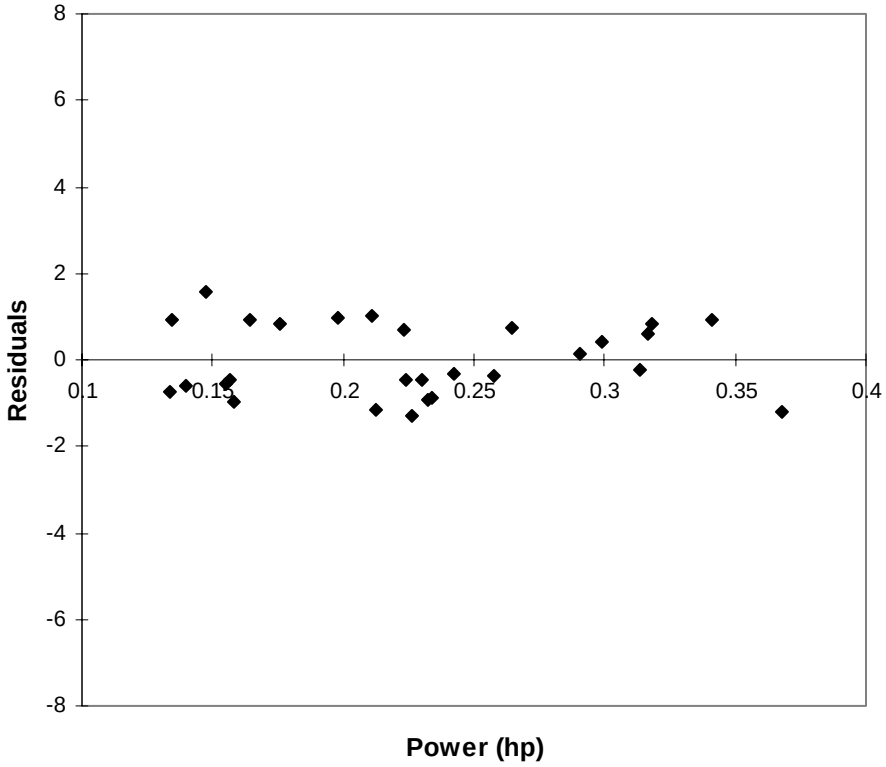

Figure B.5 Residual plot of the correlation of moisture content as a function of power (n = 28).

Table B.9 ANOVA of the regression of dry fiber throughput as a function of moisture content (n = 29).

	df	SS	MS	F	P-value
Regression	1	6.05E+05	6.05E+05	14.9	0.0006
Residual	27	1.10E+06	4.06E+04		
Total	28	1.70E+06			

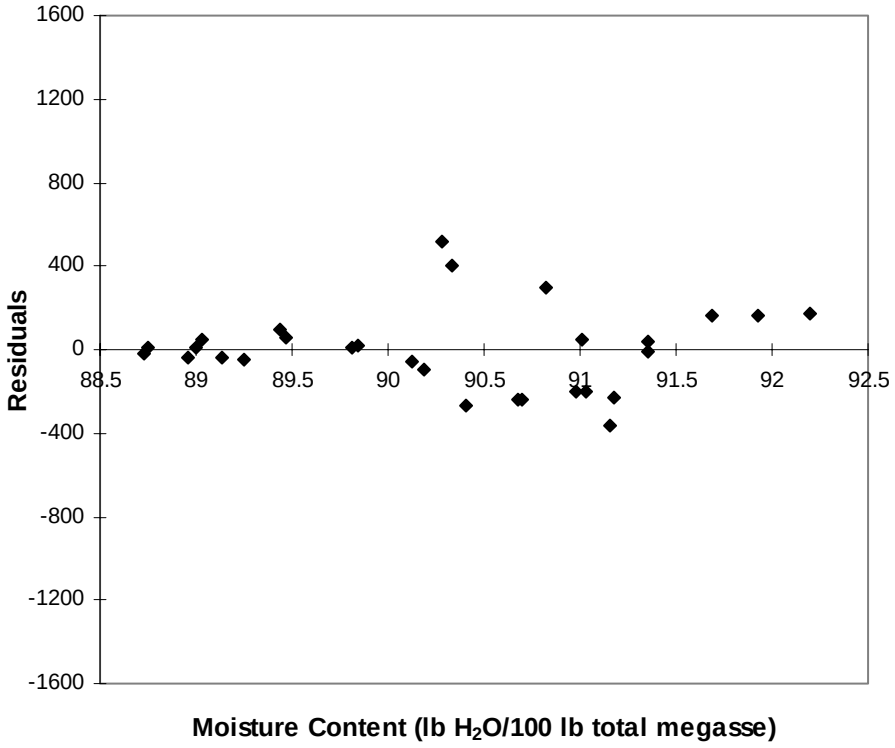

Figure B.6 Residual plot of the correlation of dry fiber throughput as a function of moisture content (n = 29).

Table B.10 ANOVA of the regression of the residuals for dry fiber throughput as a function of moisture content (n = 29).

	df	SS	MS	F	P-value
Regression	1	-2.33E-10	-2.33E-10	-5.73E-15	1
Residual	27	1.10E+06	4.06E+04		
Total	28	1.10E+06			

Influence diagnostics suggested the presence of two potential outlier, which display |RSTUDENT| values > 2; Point 12 and 23 have |RSTUDENT| values of 2.97 and 2.15, respectively. The value for |DFFITS| and |COVRATIO-1| for Point 12 also exceeds the cut-offs suggesting that it is an influential point. Based on the experimental evidence already mentioned, there is evidence that justifies the exclusion of Point 12.

Table B.11 shows the ANOVA for the regression of dry fiber throughput as a function of moisture content for 28 observations (i.e., excluding the outlier).

Table B.11 ANOVA of the regression of dry fiber throughput as a function of moisture content (n = 28).

	df	SS	MS	F	P-value
Regression	1	6.084E+05	6.084E+05	19.3	0.0002
Residual	26	8.182E+05	3.147E+04		
Total	27	1.427E+06			

Table B.12 shows the regression statistics, parameters and standard errors as calculated by SAS®. Although the fit is poor (R^2 is small), the parameters are significant (i.e., P-values are small). Figure B.7 shows the residual plot for the regression with 28 observations.

Table B.12 Regression statistics, parameters and standard errors for the regression of dry fiber throughput as a function of moisture content (n = 28).

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.6530	Intercept	-12880	3008	-4.28	0.0002
R^2	0.4264	Slope	146	33	4.40	0.0002
Adjusted R^2	0.4044					
Standard Error	177.4					

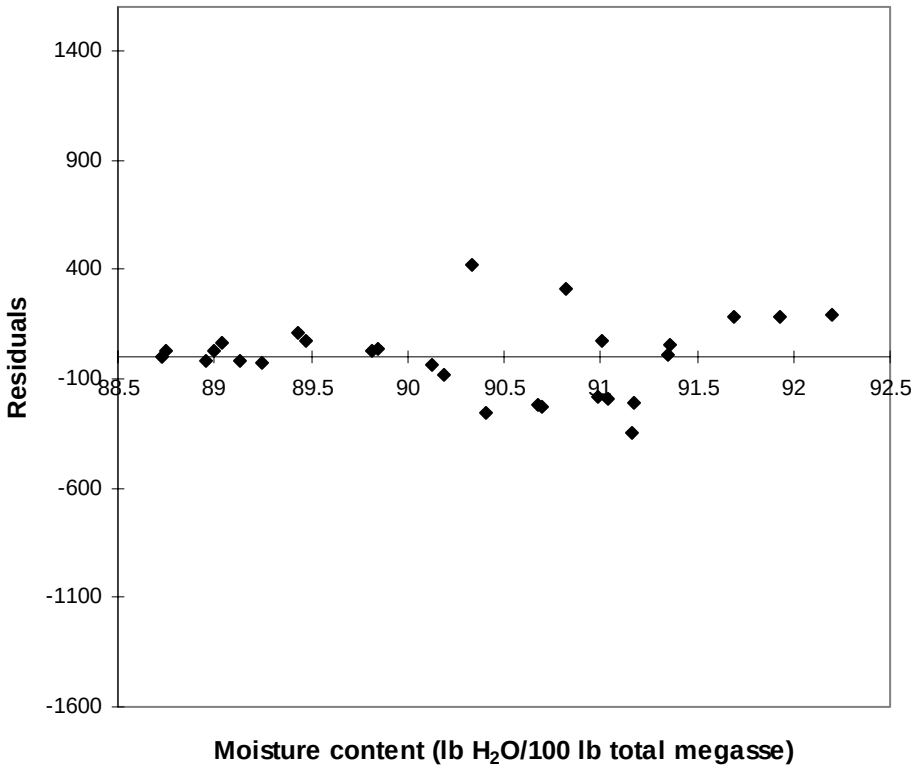

Figure B.7 Residual plot of the correlation of dry fiber throughput as a function of moisture content (n = 28).

APPENDIX C

SCREW-PRESS CONVEYOR EXTRACTION SIMULATION

MatLab™ PROGRAM

```
%This program simulates the sugar extractor.

clear all
% The following parameters must be specified. MatLab does not take 0 as index; therefore,
% the indexes will be offset by 1, so for example C{1} will actually be C{0}.

C{1}=.20;
C{2}=.15;
F{1}=0.0;
S=150;
L{1}=0.85;
Cfin = 0
Lf = 0.45;
percentextraction=98;

% End of specified parameters

Fintemp=-500;

amountsugin=S/(1-L{1})*L{1}*C{1};

leftbagasse=(1-(percentextraction/100))*amountsugin;

Cf=leftbagasse/S*(1-Lf)/Lf

ctest=Cf;

for j=2:90
     clear C;
   C{1}=.20;
   C{2}=.15;
   Fin=S/(1-L{1})*L{1}*C{1}/(C{2}-Cfin)-Lf/(1-Lf)*S*Cf/(C{2}-Cfin)+S*Lf/(1-Lf)/(1-Cfin/C{2})-
S/(1-L{1})*L{1}/(1-Cfin/C{2});

   F{2}=S*L{1}/(1-L{1})*C{1}/C{2}+Fin*Cfin/C{2}-Lf/(1-Lf)*S*Cf/C{2};


   amountsugin=S/(1-L{1})*L{1}*C{1}
   leftbag=S/(1-Lf)*Lf*C{2}

extractionpercent=(1-leftbag/amountsugin)*100

for i=2:90
```

```
   x=i+1;
   y=i-1;

  %Specify attained liquid fraction in each stage, that is, in each screw-press conveyor unit.
   L{i}=0.889;
  %End

   C{x}=(L{i}/(1-L{i})*S*C{i}+F{i}*C{i}-L{y}/(1-L{y})*S*C{y})/(L{i}/(1-L{i})*S-L{y}/(1-
L{y})*S+F{i});

   F{x}=F{i}+L{i}/(1-L{i})*S-L{y}/(1-L{y})*S;

   amountsugin=S/(1-L{1})*L{1}*C{1};
   leftbag=S/(1-Lf)*Lf*C{x};

   extractionpercent=(1-leftbag/amountsugin)*100


   if C{x}<= ctest
      Cf=C{x};
      break
   end



end
val=abs(Fintemp-Fin)
Fintemp=Fin
if val <=5.0
   break
end
end

C
F
Fin
Cf
amountsugin=S/(1-L{1})*L{1}*C{1}
leftbag=S/(1-Lf)*Lf*Cf

extractionpercent=(1-leftbag/amountsugin)*100

Numberofstages=x-1
```

APPENDIX D

CALIBRATION PROCEDURE FOR THE LOAD CELL

The calibration or scaling of the load cell transducer with the strain meter used for torque measurement was done using a known load. The procedure is as follows:

1) If not already displayed, press "MENU" until the unit shows: "Rd.S.O"
2) Apply the minimum known load (0%).
3) Press the key labeled as "►/TARE". The unit displays: "IN 1"
4) Press the "►/TARE" button once again. The unit shows the last value stored for "IN 1".
5) Press "►/TARE" again. The meter shows the actual reading of the signal being received from the load cell.
6) Press the "MENU" button. The meter stores the value for "IN 1" and displays "Rd 1".
7) Press "►/TARE" again". The meter shows the last entered value for "Rd 1".
8) The reading in the meter starts flashing. Pressing "▲/NT/GRS" to move to the desired digit (it flashes), and "►/TARE" to scroll to the desired value of the digit, change "Rd 1" as necessary to display the value of the minimum load applied.
9) Press the "MENU" button to store the value entered for "Rd 1". The unit automatically displays "IN 2"
10) Apply the maximum known load (100%)
11) Press "►/TARE". The meter displays the last valued stored for "IN 2"
12) Press "►/TARE" again to show the actual signal received from the load cell.
13) Press the "MENU" button to store this value for "IN 2". The unit displays "Rd 2"
14) Press "►/TARE" once again. The units displays the last entered value for "Rd 2".

15) Press "▲/NT/GRS" to move to the desired digit (it flashes), and "►/TARE" to scroll to the desired value of the digit to change the value of "Rd 2" to match the actual weight of the known load.
16) Press "MENU" to store this value. The meter displays "StRd" and then "Rd.CF".
17) To start measurements, press the "RESET" button twice or press "MENU" until the unit displays "RSt" (reset) flashing on the LCD. Once the meter displays a numeric reading, the unit is ready to use.

APPENDIX E

PROCEDURE FOR DATA COLLECTION IN THE SCREW-PRESS CONVEYOR STUDY

The 29 observations collected for this study, as discussed in Chapter II, were done using the following procedure:

1) Set the height of the outer perforated casing to set the desired level of flow restriction. This is done by adjusting the nuts of the threaded rods, which hold the outer casing in place.
2) Fill the tank with water (~100 gal).
3) Start the mixer by connecting it to the AC outlet.
4) Turn on strain meter to measure torque and tachometer to measure the rotational speed.
5) Start the motor using the speed controller, and set to the desired angular speed for the measurement as displayed in the tachometer. Because of the speed controller, the reading for the angular speed is sufficiently steady.
6) While the screw-press conveyor is turning, add bagasse to the tank. Previously, the bagasse should have been weighed and a sample should have been taken to determine its moisture content. This is important to estimate the initial moisture content of the megasse in the tank.
7) Because the added bagasse is considerably dried (~40% moisture), it tends to float. A shovel may be used to make it sink until it is completely soaked and thus attain homogeneous mixing faster.
8) Continue adding bagasse, keeping track of how much is being added, until the a considerable amount can be seen being processed by the screw-press conveyor.
9) Wait for 20 or more minutes so that the process achieves steady state.

10) In the mean time, weigh, using an appropriate scale, the empty sliding trays (two of them), which fit around the outer casing of the screw-press conveyor for material collection, and record these values.
11) Position the trays on their holder/rails to get them ready for the run.
12) When the reading on the strain meter is considerably stable (after about 15 to 30 min), it is a good indication that the system is at steady state. At this point, seek the help of other two persons and get them ready to collect the data. One person should hold a filming device to record the reading in the strain meter, the other should be ready to push in one of the trays to start collecting the material, and the third person should be in charge of the other tray and in charge of timing the run.
13) When ready, all three persons should be alert to start the data collection at the same time. The person holding the timer gives the signal. At time 0, the filming starts, both trays are pushed in and sample collection begins.
14) Collect enough material to fill the trays about half way. When this approximate target is reached, the timer is stopped and at the same time, the filming stops and the trays are pulled out.
15) Record the time (t).
16) Remove the trays + sample from the holders/rails, and weigh them in an appropriate scale. Record this value. The weight of the sample (W_{wet}) is then the difference between the tray + sample weight and the weight of the trays measured previously.
17) Wring as much liquid as possible from the soaked bagasse (*megasse*) collected and put the bagasse in a big Ziploc bag. Make sure that no material is lost during the transfer.
18) Take the collected bagasse to the laboratory for dry weight determination in the oven at 105^{o}C. Keep the samples in cooler until they are analyzed.
19) For dry weight determination, place the contents of the Ziploc bag, being careful not to lose any material in the transfer, into a large pre-weighed tray.

20) Place the tray and its contents in the oven at 105°C until constant weight is achieved. Record this value. The dry weight (W_{dry}) of the sample is the difference between the tray-and-contents weight and the weight of the empty tray.

21) Calculate parameters as follows:

$$T = \frac{W_{wet}}{t} \cdot 3600 \qquad \text{(E.1)}$$

where

T = Megasse (fiber + liquid) throughput, lb/h

W_{wet} = Sample weight collected in trays, lb

t = Time during which the sample was collected, s

$$S = \frac{W_{dry}}{t} \cdot 3600 \qquad \text{(E.2)}$$

where

S = Dry fiber throughput, lb/h

W_{dry} = Sample dry weight, lb

$$L = \left(1 - \frac{W_{dry}}{W_{wet}}\right) \cdot 100 \qquad \text{(E.3)}$$

where

L = Liquid fraction or moisture content, lb H_2O/100 lb total solids

Calculate the power (P) as shown in Equation 2.1. The torque is the average of the numbers for the force displayed in the strain meter, which were filmed during sample collection, multiplied by the lever arm.

To estimate the moisture content of the megasse in the tank or initial moisture content, it was necessary to determine the apparent density (ρ_{app}) of the bagasse in the conditions of this process. This procedure is as follows:

1) Dry about 100 g of bagasse (as obtain from mill) in the oven at 105°C for 24 hours.
2) At the end of this period, weight the sample and record this value (B_{dry})
3) Transfer this material to a large 2-L graduated cylinder or to a conventional pycnometer (density bottle) of appropriate sized and add 1500.0 mL of water. Add a small (i.e., negligible volume in comparison to the total volume) stirring bar and stir for several hours until all the bagasse is completely soaked and that the liquid level stops decreasing. Record this volume (V).
4) Calculate the apparent density of bagasse as follows:

$$\rho_{app} = \frac{B_{dry}}{1500 - V} \tag{E.4}$$

The experimental value found for ρ_{app} was 6.93 lb/gal. The moisture content of the megasse in the tank is then estimated as follows:

$$M_{Tank} = \frac{W_{added}\left(\frac{M_{added}}{100}\right)}{W_{added}\left(\frac{M_{added}}{100}\right) + W_{water}} \cdot 100 \tag{E.5}$$

where

M_{Tank} = Moisture content of megasse in tank, lb H_2O/100 lb total solids

W_{added} = Weight of bagasse added, lb

M_{added} = Moisture content of the added bagasse, lb H_2O/100 lb total solid

W_{water} = Weight of water in the tank, lb

The weight of the water in the tank (W_{water}) is estimated as follows:

$$W_{water} = \left[V_{read} - \left\{ \frac{W_{added}\left(\frac{M_{added}}{100}\right)}{\rho_{app}} \right\} \right] \rho_{water} \qquad \text{(E.6)}$$

where

V_{read} = Volume of the material as read from the graduation in tank, gal

ρ_{app} = Apparent density of the bagasse in the tank, lb/gal

ρ_{water} = Density of water, lb/gal

APPENDIX F

DATA FOR SCREW-PRESS CONVEYOR STUDIES

Table F.1 Parameters pertaining to mass balance of the material collected in the 29 runs of the screw-press conveyor studies.

n	T#1+ solids (lb)	T#2+ solids (lb)	Tray#1 (lb)	Tray#2 (lb)	W_{wet}* (lb)	time (s)	T* (lb/h)	Cont. (lb)	Cont+ W_{dry}* (lb)	L* (% w/w)	S* (dry lb/h)
1	41.0	44.4	31.4	31.2	22.8	40.45	2029.2	5.3	7.8	89.0	222.5
2	39.8	42.8	31.4	31.2	20.0	43.41	1658.6	2.7	4.9	89.0	182.4
3	39.0	46.6	31.4	31.2	23.0	59.56	1390.2	2.6	5.1	89.1	151.1
4	38.2	43.0	31.4	31.2	18.6	44.70	1498.0	2.6	4.6	89.2	161.1
5	38.2	40.2	31.2	31.2	16.0	45.66	1261.5	2.6	4.4	88.8	141.9
6	37.2	39.6	31.4	31.2	14.2	49.85	1025.5	2.6	4.2	88.7	115.5
7	38.6	38.8	31.4	31.4	14.6	48.10	1092.7	4.0	5.4	90.4	104.8
8	40.2	40.5	31.4	31.2	18.1	46.69	1395.6	4.0	5.6	91.2	123.4
9	42.4	43.6	31.2	31.2	23.6	44.93	1890.9	4.0	6.2	90.7	176.3
10	36.9	40.9	31.2	31.2	15.4	47.10	1177.1	4.0	5.7	89.0	129.9
11	43.8	44.4	31.2	31.2	25.8	48.99	1895.9	4.0	6.4	90.7	176.4
12	59.6	59.4	31.2	31.2	56.6	22.59	9019.9	4.0	9.5	90.3	876.5
13	49.0	51.8	31.2	31.2	38.4	44.73	3090.5	4.0	7.9	89.8	313.9
14	47.4	53.8	31.2	31.2	38.8	44.86	3113.7	4.0	8.1	89.4	329.0
15	48.3	50.4	31.4	31.2	36.1	46.69	2783.5	4.0	7.8	89.5	293.0
16	42.4	60.7	31.4	31.2	40.5	52.23	2791.5	4.0	8.0	90.1	275.7
17	48.5	51.4	31.4	31.2	37.3	45.82	2930.6	4.0	7.8	89.8	298.6
18	48.2	50.7	31.2	31.0	36.7	52.20	2531.0	4.0	7.6	90.2	248.3
19	46.0	52.1	31.2	31.2	35.7	43.87	2929.6	4.0	7.2	91.0	262.6
20	44.4	52.0	31.2	31.2	34.0	41.59	2943.0	4.0	7.0	91.2	259.7
21	48.8	50.2	31.2	31.2	36.6	46.11	2857.5	4.0	7.3	91.0	257.6
22	58.3	54.2	31.2	31.2	50.1	22.59	7984.1	4.0	8.6	90.8	733.1
23	51.0	50.7	31.2	31.2	39.3	17.87	7917.2	4.0	7.8	90.3	765.5
24	42.8	46.1	31.2	31.1	26.6	16.29	5878.5	3.9	6.2	91.4	508.3
25	48.3	46.4	31.2	31.1	32.4	18.18	6415.8	4.0	6.8	91.4	554.5
26	45.0	45.3	31.3	31.2	27.8	17.46	5732.0	4.0	6.5	91.0	515.5
27	49.7	51.2	31.3	31.1	38.5	15.76	8794.4	4.0	7.2	91.7	731.0
28	48.0	59.0	31.2	31.2	44.6	17.07	9406.0	4.0	7.6	91.9	759.2
29	56.6	57.1	31.2	31.2	51.3	17.68	10445.7	4.0	8.0	92.2	814.5

***** For calculation procedure and nomenclature refer to Appendix E

Table F.2 Data for the force (lbf) applied on lever arm from the videos for all 29 observations (n = 29).

n	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	8.0	8.8	8.7	8.1	8.6	8.7	9.6	9.0	9.4	10.1	11.2	11.3	11.5	13.3	15.1
2	10.0	9.8	9.3	9.2	8.5	9.8	9.2	8.6	8.0	7.8	9.0	10.4	10.3	10.7	10.3
3	4.7	4.5	4.7	5.0	5.1	5.8	7.0	7.9	7.4	7.2	7.0	6.8	6.5	6.6	7.1
4	4.1	3.9	4.0	3.6	3.5	3.4	3.5	3.6	3.9	4.1	4.2	4.8	4.9	4.7	4.5
5	4.4	4.8	5.3	5.5	5.2	5.4	7.0	6.5	5.9	6.7	6.4	6.5	6.1	6.2	7.0
6	3.1	2.9	3.0	2.9	2.5	2.4	2.6	2.5	2.4	2.3	2.1	2.2	2.4	2.3	2.6
7	2.4	2.6	2.5	2.4	2.5	2.4	2.3	2.7	2.6	2.9	3.1	3.0	3.3	3.4	3.1
8	2.8	2.6	2.5	2.4	2.2	2.4	2.3	2.5	2.4	2.6	2.7	2.9	3.1	2.9	3.1
9	3.3	3.4	3.9	3.7	3.5	3.6	3.9	4.0	3.9	3.6	3.3	3.4	3.5	4.0	4.7
10	3.8	3.7	4.0	4.3	4.9	4.8	4.6	4.4	4.6	4.5	4.3	3.9	3.7	3.9	3.8
11	3.3	3.2	3.1	3.2	3.0	2.9	2.8	2.9	2.8	2.7	2.8	3.0	2.8	2.9	2.7
12	14.8	14.9	14.5	14.6	15.1	15.2	14.8	15.4	16.1	16.7	17.1	17.2	19.1	22.2	21.5
13	12.6	13.0	12.2	11.3	10.4	10.3	10.0	8.9	9.4	10.2	10.5	10.9	11.5	12.6	13.0
14	8.0	8.4	8.7	8.3	8.1	8.2	7.9	8.0	8.3	8.7	8.5	8.7	8.9	8.7	9.2
15	9.5	9.7	9.6	9.5	10.2	10.0	9.9	10.1	10.4	10.1	9.6	9.9	10.1	9.6	9.3
16	5.6	5.9	6.2	6.3	7.3	7.7	8.1	7.9	8.0	7.8	8.2	8.0	7.9	7.7	8.3
17	6.3	6.2	6.3	6.4	6.6	6.9	7.1	7.9	6.3	5.8	6.2	5.6	5.3	5.9	5.7
18	7.9	8.1	8.5	8.4	8.7	9.1	9.3	8.5	8.7	8.3	8.8	8.0	8.1	8.3	7.8
19	3.4	3.3	3.7	3.5	3.6	3.9	4.2	4.6	4.3	4.2	4.1	4.0	4.1	4.0	3.9
20	3.8	4.1	4.0	4.4	4.5	4.3	4.9	5.6	5.5	5.9	6.5	5.9	5.6	5.5	5.6
21	6.1	5.4	4.8	4.5	4.7	4.5	4.3	4.0	4.1	3.9	4.3	4.1	4.2	4.0	4.8
22	13.4	14.2	14.1	13.9	13.7	14.0	13.8	15.3	15.6	14.9	13.7	12.7	12.1	12.4	13.3
23	24.6	24.2	23.6	23.1	20.4	19.1	19.9	22.0	21.1	20.9	20.5	20.0	18.1	16.1	15.2
24	7.9	7.6	7.7	7.6	7.5	7.6	7.4	7.5	7.3	7.6	7.3	6.8	6.7	6.5	6.4
25	10.9	10.0	9.4	9.5	7.8	8.2	7.9	8.0	8.3	8.0	8.1	8.5	8.8	9.0	9.1
26	6.9	7.4	7.3	8.0	8.2	8.3	8.5	8.9	8.7	8.8	9.2	8.9	8.7	8.5	8.3
27	7.9	7.5	7.8	8.2	8.7	8.2	7.8	7.7	7.5	7.2	6.4	6.7	6.4	6.5	6.2
28	7.0	6.7	6.9	6.6	6.9	6.6	6.8	6.5	6.6	6.4	6.8	6.7	6.8	7.2	7.1
29	7.4	7.3	8.0	7.8	8.2	7.9	8.1	8.0	7.7	7.5	7.4	7.3	6.7	6.0	6.7

Table F.2 Continued.

n	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
1	12.7	12.0	12.4	14.6	15	13.7	12.9	13.5	13.6	12.3	11.2	10.5	9.5	8.6	7.4
2	10.6	9.9	10.4	9.6	9.3	9.9	9.0	9.5	9.4	11.3	10.8	12.4	11.6	10.3	9.9
3	6.6	6.2	6.1	6.5	6.0	5.8	5.5	5.8	5.2	4.8	4.4	4.2	3.9	4.2	4.1
4	4.4	4.2	4.1	4.4	4.7	3.9	5.3	5.0	5.5	5.7	5.3	5.4	5.8	5.5	4.9
5	6.4	5.6	5.1	4.9	3.8	4.2	4.8	4.7	4.5	5.4	5.5	5.3	5.8	5.7	5.6
6	2.9	3.1	3.5	4.3	4.2	3.8	4.0	3.6	3.4	3.6	3.5	3.3	3.5	4.2	4.6
7	3.0	2.8	2.9	2.7	2.8	2.6	2.9	3.0	3.1	2.8	3.0	2.8	3.2	3.0	3.1
8	3.0	2.9	2.8	2.9	3.0	3.3	3.5	3.6	4.2	4.0	3.9	4.1	3.9	3.8	4.1
9	4.6	5.2	4.8	4.9	4.8	4.5	4.0	3.7	3.2	3.7	3.3	3.5	3.3	3.1	3.2
10	3.6	3.7	4.4	4.7	4.9	5.2	5.0	4.8	4.7	4.5	4.8	4.9	5.6	6.6	7.2
11	2.6	2.5	2.6	2.4	2.6	2.7	2.8	2.9	2.8	2.7	2.8	2.7	3.0	2.9	3.0
12	20.3	19.8	19.4	20.1	20.3	20.2	20.5	19.6	19.1	18.6	18.4	17.7	16.0	16.5	16.1
13	12.4	12.2	12.7	11.9	11.1	10.4	10.2	10.6	10.7	10.3	10.9	11.3	11.2	10.4	10.9
14	9.3	8.9	8.8	9.0	8.8	8.9	9.2	9.3	9.6	10.1	10.0	10.2	9.7	9.9	9.5
15	9.6	9.8	9.7	10.0	11.3	11.7	12.0	13.0	12.5	12.3	12.8	14.6	14.4	15.0	14.8
16	8.1	7.9	8.0	7.8	8.4	8.2	7.9	7.7	7.5	5.9	6.1	6.2	6.3	5.9	6.0
17	5.8	6.6	7.4	7.8	11.2	10.9	10.2	11.3	10.8	10.4	9.6	10.3	9.1	8.5	8.2
18	8.9	8.5	8.4	8.1	8.0	8.6	8.2	9.1	8.6	9.0	8.9	8.7	8.3	8.2	8.0
19	4.2	4.1	4.2	4.1	4.3	4.2	4.6	4.3	4.9	4.8	4.7	4.5	4.6	4.8	4.5
20	5.7	5.8	5.4	5.3	5.1	5.2	5.7	5.5	5.6	5.2	4.9	4.7	4.5	4.6	4.5
21	4.6	4.7	5.5	5.6	6.7	6.6	6.3	6.6	7.1	7.7	7.3	7.0	6.3	6.5	6.8
22	13.0	12.3	12.8	12.9	13.0	12.6	13.1	13	12.6	12.3	12.5	12.3	12.0	12.8	12.9
23	12.7	13.0	14.7	13.9	13.3	13.1	12.7	12.6	13.2	13	12.8	12.4	11.9	11.6	11.9
24	6.1	5.5	6.2	6.3	6.6	6.9	7.0	7.5	7.3	7.7	7.5	7.7	7.8	8.0	7.8
25	10.0	9.7	9.3	9.2	9.4	8.8	8.3	8.1	7.6	7.2	6.7	6.6	6.4	6.7	7.3
26	7.9	7.1	7.5	7.1	7.0	7.4	7.3	6.9	7.1	7.6	8.2	8.0	8.3	8.2	7.9
27	6.1	5.8	5.5	5.6	5.3	5.4	5.3	5.5	5.3	5.6	6	5.9	6.1	6.4	6.5
28	7.2	7.5	7.3	7.5	7.6	7.4	7.1	6.8	6.5	6.4	6.2	5.6	5.7	5.8	5.9
29	6.6	6.7	6.8	7.0	6.9	6.8	7.2	7.1	7.4	7.5	7.0	6.9	6.5	6.6	6.4

Table F.2 Continued.

n	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45
1	8.4	8.3	8.1	7.8	6.9	6.1	6.4	6.7	6.8	6.7	6.5	6.8	6.7	6.6	6.3
2	9.0	9.3	8.7	8.3	8.1	7.9	7.5	7.8	9.1	9.4	9.2	11.4	14.6	13.8	14.7
3	4.3	4.1	4.6	4.4	5.0	5.2	6.1	6.0	6.2	7.2	7.7	8.3	8.5	8.0	7.2
4	4.3	4.1	4.0	3.3	3.4	3.3	3.5	3.6	3.9	3.8	3.6	3.7	3.8	3.7	3.5
5	5.0	5.1	4.7	4.5	4.6	4.9	5.6	7.0	6.9	6.7	8.5	8.0	7.6	6.9	7.0
6	5.6	5.1	4.7	4.4	5.8	5.9	5.7	6.2	5.3	4.8	4.9	4.5	4.3	4.9	4.6
7	3.0	2.8	2.9	2.8	2.7	2.8	2.6	2.8	2.9	2.7	2.6	2.7	2.6	2.5	2.6
8	4.2	3.9	3.6	3.3	3.2	3.0	2.8	2.7	2.8	3.0	2.8	2.7	2.6	2.7	2.8
9	3.5	3.6	3.9	3.7	3.6	4.0	4.1	4.4	4.7	4.6	4.4	4.0	3.8	3.3	3.0
10	7.6	6.8	6.6	6.3	6.6	7.2	7.6	7.8	8.2	7.8	8.5	8.8	8.3	7.6	7.0
11	3.3	3.7	3.3	2.9	2.8	2.7	2.8	3.2	3.0	2.9	3.1	3.0	2.9	3.1	3.2
12	15.6	14.9	15.4	14.4	14.8	15.2	14.7	14.6	14.7	16.2	16.0	15.3	15.8	17.0	17.7
13	10.7	11.1	10.9	11.1	10.2	10.5	10.6	11.4	11.5	11.8	11.3	10.9	11.3	10.9	11.3
14	9.7	10.2	9.8	9.4	8.9	9.4	9.1	8.2	8.4	8.2	9.0	9.1	9.4	9.5	10.0
15	15.6	17.3	19.0	18.1	17.2	15.7	15.4	15.1	14.0	5.1	5.9	6.0	7.4	7.1	7.4
16	6.4	6.5	6.6	6.4	6.5	6.1	7.0	7.1	6.6	6.7	7.0	6.9	7.2	7.5	7.8
17	8.1	7.7	6.6	6.2	7.0	6.6	6.3	6.5	6.4	6.6	6.3	6.5	5.9	6.0	5.3
18	7.6	5.3	6.0	7.7	8.4	8.1	8.0	8.1	7.9	7.5	7.6	7.4	7.1	7.2	6.8
19	4.3	4.2	4.5	4.7	4.8	4.3	4.7	4.6	4.5	4.0	4.3	4.4	4.2	4.0	3.8
20	4.4	4.5	4.4	4.3	4.2	4.1	4.4	4.1	3.8	3.7	3.3	3.4	3.7	4.0	4.2
21	7.0	7.6	8.3	7.9	7.2	6.8	7.1	6.7	7.0	7.1	6.9	6.6	6.1	5.5	4.9
22	12.5	12.1	12.3	12.7	12.6	12.3	12.5	12.8	13.1	13.2	14.6	14.7	13.0	12.5	13.2
23	11.7	11.4	11.6	11.0	10.8	10.9	11.3	11.4	10.9	11.0	11.6	11.3	10.7		
24	8.0	7.6	8.0	7.9	7.6	7.5									
25	7.2	7.3	7.7	7.6	7.2	7.0	7.9	8.2	8.0						
26	8.5	8.8	9.1	9.3	8.8	8.4	7.8	7.2	7.3	7.0					
27	6.2	6.3	6.2												
28	5.8	5.7	5.6	5.7	6.1	6.4	6.3	6.2	6.5						
29	6.6	6.4	6.6	6.2	6.5	6.4									

Table F.2 Continued.

n	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60
1	6.2	6.6	6.8	7.2	7.3	7.5	7.4	7.8	8.4	7.9	8.3	8.2	8.5	9.2	8.5
2	15.8	16.3	16.2	17.5	17.8	18.4	18.9	16.8	14.6	14.5	12.6	11.6	11.4	10.6	7.5
3	6.8	7.4	9.0	8.6	9.3	8.3	8.4	7.6	7.5	7.6	7.5	7.3	6.9	7.0	6.6
4	3.3	3.7	3.5	3.6	3.9	4.0	4.2	4.3	4.1	4.3	4.1	4.2	4.7	5.3	5.4
5	6.7	6.2	5.5	4.5	4.2	3.1	3.0	2.5	3.2	3.3	3.6	3.3	3.9	4.3	4.2
6	4.7	4.5	4.7	4.6	4.9	4.7	4.2	3.7	3.5	3.0	2.8	2.3	2.5	2.3	2.4
7	2.7	2.5	2.8	2.7	2.9	3.2	3.1	3.0	3.4	4.1	3.7	3.5	3.1	2.8	2.5
8	2.9	3.0	3.3	4.5	3.7	4.0	3.5	3.2	3.0	2.9	2.7	2.6	2.7	2.6	3.0
9	3.2	4.0	3.6	3.8	3.7	3.6	4.1	3.8	3.6	3.5	3.3	3.0	2.8	2.9	2.8
10	6.4	6.8	7.5	8.3	8.4	8.8	9.2	8.6	8.7	8.6	9.0	8.1	8.0	7.5	7.6
11	3.4	3.7	3.6	3.3	3.4	3.5	3.7	3.6	3.5	3.2	3.5	3.3	3.1	2.9	3.2
12	17.9	18.3	20.9	30.9	26.8	24.5	24.4	25.5	24.4	25.2	24.7	25.9	24.6		
13	10.4	9.8	10.0	10.1	10.8	11.1	11.2	10.2	9.7	10.0	9.7	9.4	9.6	9.9	9.5
14	9.7	9.8	8.7	8.4	8.6	8.3	8.2	8.3	8.6	9.0	8.7	8.9	9.1	9.7	9.5
15	8.1	8.0	8.3	9.0	8.9	8.6	9.0	8.3	8.2	7.7	7.2	7.5	7.9	7.5	7.3
16	8.8	8.6	8.1	7.6	7.2	6.9	6.5	5.7	5.9	6.7	7.3	7.8	7.6	6.9	6.2
17	5.2	5.3	6.0	5.9	5.6	6.0	5.6	5.3	6.6	6.2	6.6	6.1	6.0	5.7	5.1
18	6.3	6.5	6.9	6.8	7.3	7.2	7.8	7.6	8.2	8.3	8.0	9.0	9.3	9.5	10.1
19	4.1	4.2	4.3	4.7	4.4	4.8	4.7	4.6	5.1	4.8	4.6	4.5	4.6	4.5	4.3
20	4.7	3.8	4.1	3.9	4.0	3.9	4.1	4.3	4.2	4.3	4.0	3.9	4.0	3.8	3.7
21	4.3	3.9	3.6	3.8	3.7	3.6	3.5	3.4	3.5	3.4	3.8	3.7	3.9	4.3	4.4
22	12.3	11.7	11.6	11.9	11.5	10.8									
23															
24															
25															
26															
27															
28															
29															

Table F.2 Continued.

n	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
1	8.4	8.2	8.5	8.0	8.1	8.0	8.5	7.9	7.5	7.3	7.9	8.6	8.9	9.5	9.8
2	9.2	11.1	9.9	10.1	8.8	8.3	7.8	7.7	7.0	6.3	6.6	7.2	7.1	6.4	7.0
3	6.7	6.5	6.8	6.6	7.4	7.3	8.2	7.7	7.4	7.0	6.9	6.7	6.3	6.4	6.5
4	5.1	5.4	5.2	5.0	4.9	5.0	5.7	5.3	5.1	5.4	4.9	4.8	4.7	4.4	4.3
5	4.6	4.8	4.4	3.9	3.8	3.5	3.3	3.5	3.3	3.1	2.7	2.6	2.7	2.4	2.8
6	2.5	2.6	2.8	2.7	2.9	3.0	3.2	3.0	3.1	3.3	3.1	3.0	3.7	3.8	3.6
7	2.7	2.6	2.5	2.3	2.7	2.8	2.9	3.0	2.8	2.7	2.4	2.2	2.3	2.4	2.5
8	2.8	2.9	2.6	2.4	2.3	2.4	2.5	2.6	2.9	2.7	2.9	3.2	3.3	3.2	3.1
9	2.5	2.4	2.6	2.7	2.6	2.5	2.6	2.5	2.6	2.7	2.9	2.8	3.0	3.2	3.5
10	6.8	6.9	6.7	6.5	5.5	5.2	5.0	4.5	3.2	4.7	4.2	4.8	4.5	4.9	4.7
11	3.3	3.4	3.3	3.6	4.6	4.9	4.8	4.9	5.1	4.5	4.2	3.8	4.6	4.3	4.5
12															
13	9.7	9.1	8.6	8.9	9.2	9.3	8.9	9.7	9.6	9.2	9.5	9.0	8.2	7.5	7.2
14	9.8	10.0	10.5	9.8	9.9	10.8	10.7	10.9	10.4	10.3	9.9	9.5	10.2	9.6	9.3
15	7.6	8.0	8.4	8.5	8.6	8.4	8.0	7.9	8.1	8.0	8.7	9.4	9.3	8.8	8.1
16	5.7	3.1	4.3	4.7	5.2	5.3	5.7	6.6	6.3	5.9	6.0	5.9	6.4	6.5	6.3
17	5.0	4.7	3.8	4.1	4.6	4.8	5.2	5.3	5.1	5.4	5.1	5.2	5.4	5.8	5.6
18	9.2	8.2	7.8	7.0	6.9	6.6	4.1	5.1	6.0	5.9	5.8	5.5	6.0	6.3	5.9
19	4.2	4.1	4.0	3.8	3.9	3.8	3.9	4.0	3.9	3.6	3.4	3.2	3.1	3.3	3.2
20	3.8	4.0	3.9	3.8	3.7	4.0	3.9	3.7	3.9	4.0	3.9	4.0	3.8	4.2	4.0
21	4.7	4.2	3.9	3.8	3.6	3.5	3.3	3.4	3.6	3.7	3.6	3.5	3.8	3.6	3.2
22															
23															
24															
25															
26															
27															
28															
29															

Table F.2 Continued.

n	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90
1	10.6	10.0	9.3	9.1	8.4	7.2	5.3	6.0	9.4	9.2	8.7	8.6	8.0	7.1	6.3
2	9.0	7.5	6.6	6.0	5.3	5.2	5.0	5.4	4.9	5.0	5.2	6.3	5.6	5.2	5.1
3	6.7	6.6	6.4	6.8	6.9	7.5	8.7	9.4	9.8	10.6	10.0	9.8	7.8	7.4	8.1
4	3.9	3.6	3.7	3.5	3.7	3.5	3.7	3.9	4.1	4.4	4.5	4.9	6.0	4.3	3.8
5	2.9	2.7	2.9	3.1	3.2	3.5	3.4	3.2	3.1	3.0	2.9	2.7	2.6	2.7	3.0
6	3.8	4.0	3.9	3.6	3.5	4.1	3.7	3.5	3.7	3.8	3.6	4.0	4.1	4.2	4.7
7	2.6	3.2	2.9	3.1	2.8	2.7	2.5	2.4	2.3	2.2	2.3	2.2	2.4		
8	3.2	3.1	2.8	2.9	2.8	2.9	2.8	2.9	2.8	2.9	3.2	3.0	3.1	2.9	3.1
9	3.4	3.6	4.1	3.9	3.7	3.8	3.5	3.7	3.6	3.7	3.6	3.9	3.8	4.0	4.1
10	4.6	4.3	4.7	5.7	6.8	6.7	6.1	6.3	7.2	6.5	6.1	6.8	6.4	6.1	5.4
11	5.5	5.3	5.0	4.6	4.2	3.9	3.5	3.8	3.4	3.6	3.3	3.4	3.6	3.3	3.2
12															
13	7.0	4.6	5.8	5.6	5.9	6.8	6.7	7.0	8.1	7.8	7.6	7.1	7.2	7.4	7.3
14	9.1	8.9	8.3	9.0	10.1	10.5	11.1	11.3	12.1	12.0	11.1	10.8	11.4	11.3	11.5
15	8.2	7.8	7.9	8.1	8.4	8.6	9.0	9.3	9.0	9.6	10.3	10.6	10.2	9.9	9.6
16	6.2	6.9	6.7	6.4	6.9	7.1	6.6	6.5	6.8	6.6	6.2	6.5	6.7	6.3	6.0
17	5.3	5.1	5.0	4.6	5.0	5.1	4.9	4.8	4.5	4.8	4.9	5.3	5.8	5.5	5.8
18	6.0	6.5	6.4	6.5	6.8	6.6	6.7	6.8	7.0	7.2	7.5	7.4	7.2	6.9	6.6
19	3.4	3.3	3.4	3.2	3.4	3.7	3.6	3.7	3.8	4.0	4.1	4.2	3.9	3.8	3.9
20	4.1	4.0	4.2	4.6	4.3	3.8	3.7	3.4	3.7	3.6	3.4	3.7			
21	3.1	3.0	3.1	3.0	3.2	3.1	3.3	3.2	3.3	3.2	3.5	3.4	3.7	3.6	3.7
22															
23															
24															
25															
26															
27															
28															
29															

Table F.2 Continued.

n	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105
1	7.3	6.9	7.0	6.7	7.4										
2	4.9	5.2	5.8	5.2	5.9	5.3	5.1	5.0							
3	7.6	6.9	6.3	6.1	5.5	5.4	4.1	4.2	4.5	5.4	5.6	6.7	6.9	9.8	8.7
4	3.5	3.6	3.4	3.8	4.3	5.0	5.4	5.1	4.6						
5	2.9	3.4	3.0	3.5	3.2	2.9	3.0	3.1	2.9	3.1	3.0	2.7	2.5	2.6	2.5
6	5.0	5.1	4.4	4.1	4.0	3.5	3.2	3.1	3.7	3.4	4.1	4.4	4.2	4.0	4.6
7															
8	2.9	3.1	3.0	3.3	3.4	3.2	3.7	3.4	3.5	3.4	3.0	2.8			
9	4.2	4.1	4.2	4.1	3.9	3.8	4.0	4.1							
10	5.3	5.1	5.2	5.8	5.7	5.3	4.9	5.0	4.8	4.3	3.9	4.0	3.9	4.1	4.8
11	3.1	3.2	3.3	3.5	3.6	3.8	3.9	4.1	3.4	3.7	3.6	3.2	3.1	3.3	
12															
13	8.0	7.9	7.6	7.8	7.3	7.0	6.5	6.6	6.4	6.5	6.3	6.7	6.5		
14	11.4	11.0	10.8	10.7	10.0	9.3	10.0	9.9	10.2	10.6	10.3	10.4	10.8	11.2	12.1
15	9.9	9.0	8.9	8.3	8.4	7.8	7.6	7.3	7.7	7.5	7.4	7.3	7.7	8.6	9.6
16	5.8	5.7	5.6	5.8	5.9	6.0	6.1	6.2	6.3	7.5	7.1	6.9	7.3	6.9	6.5
17	5.6	5.7	5.6	5.2	5.3	5.1	5.4	5.7	5.5	5.6	5.7	5.4	5.3	5.4	5.3
18	6.5	5.4	5.6	5.3	5.4	5.2	5.8	5.7	5.2	5.5	5.4	5.8	5.9	6.0	5.6
19	4.1	3.8													
20															
21	3.6	3.9	3.8	3.9	4.3	4.1	4.0	4.2	4.0	3.9	3.8	3.7	3.6	3.5	3.6
22															
23															
24															
25															
26															
27															
28															
29															

Table F.2 Continued.

n	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120
1															
2															
3	8.1	6.3	5.6	5.4	6	5.1	4.5	3.9	3.8	4.1	4.7	4.8	4.7	5.4	6.4
4															
5	2.4	2.6	3.0												
6	4.1	3.6	3.7	3.5	3.2	3.0	2.9	2.8	2.6	3.1					
7															
8															
9															
10	4.4	4.3	4.2	5.3	4.8	5.0									
11															
12															
13															
14															
15	9.1	8.6	7.9	8.1	7.8										
16	6.4	6.0	5.8	5.6	6.6	6.3	6.4	6.2	6.3	6.4	6.3	6.9	7.3	6.7	
17	5.4	5.3	5.2												
18	5.7	5.9	5.6	5.7	6.5	6.6	6.5	6.6	6.5	5.9	5.8	5.7	5.3	5.5	5.6
19															
20															
21															
22															
23															
24															
25															
26															
27															
28															
29															

Table F.2 Continued.

n	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135
1															
2															
3	6.7	6.8	7.4	7.6	8.0	7.8	8.0	7.4	6.5	6.6	6.4	6.8	7.6	7.5	7.3
4															
5															
6															
7															
8															
9															
10															
11															
12															
13															
14															
15															
16															
17															
18	6.0	6.1	7.2	7.6											
19															
20															
21															
22															
23															
24															
25															
26															
27															
28															
29															

Table F.2 Continued.

n	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152
1																	
2																	
3	7.0	6.7	6.6	6.9	6.2	6.0	5.9	6.5	5.5	5.2	4.8	5.1	4.7	4.9	4.5	4.9	4.6
4																	
5																	
6																	
7																	
8																	
9																	
10																	
11																	
12																	
13																	
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Table F.3 Parameters measured and calculated for power consumption determination.

n	$\overline{F}$ (lbf)	τ (lbf· ft)	σ_{force}* (lbf)	σ_τ* (lbf· ft)	ω (rpm)	P (hp)	σ_P* (hp)
1	8.8	27.9	2.2	6.9	40.1	0.213	0.053
2	9.3	29.5	3.4	10.7	40.2	0.226	0.082
3	6.5	20.5	1.4	4.6	39.7	0.155	0.034
4	4.3	13.7	0.7	2.2	60.1	0.157	0.026
5	4.3	13.8	1.5	4.8	60.3	0.158	0.055
6	3.7	11.6	0.9	2.9	60.2	0.134	0.033
7	2.8	8.8	0.3	1.1	80.2	0.134	0.016
8	3.0	9.7	0.5	1.5	80.2	0.147	0.023
9	3.6	11.5	0.6	1.9	80.2	0.176	0.029
10	5.8	18.3	1.6	4.9	40.3	0.140	0.038
11	3.4	10.8	0.7	2.1	80.2	0.165	0.032
12	18.6	58.9	3.9	12.5	40.0	0.448	0.095
13	9.5	30.1	1.9	6.1	40.2	0.230	0.047
14	9.6	30.4	1.0	3.2	40.1	0.232	0.025
15	9.7	30.7	2.7	8.5	40.1	0.234	0.065
16	6.7	21.2	0.9	2.9	60.1	0.242	0.033
17	6.2	19.6	1.5	4.9	60.1	0.224	0.056
18	7.1	22.5	1.3	4.0	60.1	0.258	0.045
19	4.1	13.0	0.5	1.5	80.1	0.198	0.022
20	4.4	13.8	0.7	2.3	80.1	0.211	0.034
21	4.6	14.6	1.4	4.5	80.1	0.223	0.069
22	13.0	41.0	1.0	3.1	40.1	0.314	0.023
23	15.1	47.7	4.5	14.2	40.5	0.368	0.109
24	7.3	23.0	0.6	2.0	60.2	0.264	0.023
25	8.2	26.1	1.1	3.4	60.2	0.299	0.039
26	8.0	25.4	0.7	2.3	60.2	0.291	0.026
27	6.5	20.7	1.0	3.1	80.3	0.316	0.047
28	6.6	20.8	0.6	1.8	80.3	0.318	0.028
29	7.1	22.4	0.6	1.8	80.2	0.341	0.028

* $\sigma \equiv$ Standard deviation

For calculation procedure and nomenclature refer to Chapter II

APPENDIX G

DATA FOR SUGARCANE JUICE PRESERVATION STUDIES

Most data for these studies have already been shown in Chapter III. The data that follow (Tables G.1 through G.4) are the numerical values for Figures 3.1 through 3.21 and Figures 3.32 through 3.34.

Table G.1 Sucrose concentrations and pH for preservation of 40 and 20-g-sucrose/L juice at the specified lime loading. (Figures 3.1 – 3.20)

0.5 g $Ca(OH)_2$/100 g sucrose

40 g/L			20 g/L		
Time (days)	pH	Conc. (g/L)	Time (days)	pH	Conc. (g/L)
0	8.46	41.5	0	8.31	19.5
7	3	0	7	3	0
15	3.4	0	15	3.3	0

1.5 g $Ca(OH)_2$/100 g sucrose

40 g/L			20 g/L		
Time (days)	pH	Conc. (g/L)	Time (days)	pH	Conc. (g/L)
0	10.48	38.9	0	10.14	22.7
7	3.5	0.5	7	3.5	0
15	3.6	0	15	4.24	0

3 g $Ca(OH)_2$/100 g sucrose

40 g/L			20 g/L		
Time (days)	pH	Conc. (g/L)	Time (days)	pH	Conc. (g/L)
0	11.23	40.5	0	11.22	22.0
7	4	0	7	4	18.3
15	3.9	0	15	3.63	0

Table G.1 Continued.

4 g $Ca(OH)_2$/100 g sucrose

40 g/L			20 g/L		
Time (days)	pH	Conc. (g/L)	Time (days)	pH	Conc. (g/L)
0	11.56	40.5	0	11.5	24.8
7	10.30	39.2	7	10.08	18.2
15	4.52	0	15	3.82	0.2
	average	39.9		average	21.5

5 g $Ca(OH)_2$/100 g sucrose

40 g/L			20 g/L		
Time (days)	pH	Conc. (g/L)	Time (days)	pH	Conc. (g/L)
0	11.75	40.6	0	11.7	18.8
7	10.72	38.6	7	10.3	18.9
15	5.28	39.2	15	4.4	0
	average	39.6		average	18.9

7 g $Ca(OH)_2$/100 g sucrose

40 g/L			20 g/L		
Time (days)	pH	Conc. (g/L)	Time (days)	pH	Conc. (g/L)
0	11.97	39.7	0	11.91	21.1
7	11.48	38.3	7	10.84	22.1
15	10.15	42.1	15	10.16	19.7
37	4.78	0	37	4.79	0
88	5.2	0	88	5.2	0
	average	40.0		average	21.0

10 g $Ca(OH)_2$/100 g sucrose

40 g/L			20 g/L		
Time (days)	pH	Conc. (g/L)	Time (days)	pH	Conc. (g/L)
0	12.17	36.8	0	12.13	18.6
7	11.93	36.6	7	11.62	19.5
15	11.55	42.6	15	11.08	18.9
37	11.01	43.8	37	10.54	20.2
88	10.59	44.8	88	3.5	0
169	3.5	0	169	3.5	0
	average	40.9		average	19.3

Table G.1 Continued.

15 g $Ca(OH)_2$/100 g sucrose

40 g/L			20 g/L		
Time (days)	pH	Conc. (g/L)	Time (days)	pH	Conc. (g/L)
0	12.37	37.5	0	12.31	18.3
7	12.18	36.2	7	12.02	18.5
15	12.06	42.7	15	11.79	19.3
37	11.82	42.2	37	11.48	19.1
88	11.46	42.4	88	10.86	19.1
169	10.86	37.8	169	11.00	19.3
248	10.43	43.4	248	10.58	19.6
368	3.5	0	368	3.5	0
	average	40.3		average	19.0

20 g $Ca(OH)_2$/100 g sucrose

40 g/L			20 g/L		
Time (days)	pH	Conc. (g/L)	Time (days)	pH	Conc. (g/L)
0	12.43	38.6	0	12.41	18.8
7	12.31	39.9	7	12.22	18.5
15	12.22	42.1	15	12	19.0
37	12.07	41.5	37	11.77	17.4
88	11.88	41.9	88	11.26	18.7
169	11.26	40.9	169	11.32	19.9
248	10.88	40.4	248	11.07	19.5
368	10.56	40.2	368	10.7	19.0
	average	40.7		average	18.8

30 g $Ca(OH)_2$/100 g sucrose

40 g/L			20 g/L		
Time (days)	pH	Conc. (g/L)	Time (days)	pH	Conc. (g/L)
0	12.49	37.2	0	12.46	19.3
7	12.44	36.8	7	12.31	18.1
15	12.38	42.5	15	12.22	16.9
37	12.28	42.5	37	12.02	18.1
88	12.32	38.1	88	12.07	18.9
169	12.07	39.5	169	11.59	19.2
248	11.87	39.5	248	11.31	15.5
368	11.25	40.8	368	10.98	18.8
	average	39.6		average	18.1

Table G.2 Necessary lime loading as a function of preservation time (Figure 3.21)

Time (days)	Lime Loading (g $Ca(OH)_2$/100 g sucrose)
0	0.5
2	1.5
6	3
11	4
14	5
16	7
112	10
281	15
368	20
368	30

Table G.3 Sucrose concentrations at several dates for the preservation of the different batches of juice (Figures 3.32 and 3.33).

$B_{filtered}$

Time (days)	Date	Conc. (g/L)
0	12/5/2001	122.1±0.1
339	11/9/2002	120.7±0.9
	average	121.4

$B_{screened}$

Time (days)	Date	Conc. (g/L)
0	3/7/2003	117.4±1.8
155	8/9/2003	120.2±0.4
	average	118.8

$B_{clarified}$

Time (days)	Date	Conc. (g/L)
0	12/9/2002	118.9±0.3
63	2/10/2003	117.8±4.6
	average	118.3

$B_{periodic}$

Time (days)	Date	Conc. (g/L)
0	5/11/2003	155.3±4.2
90	8/9/2003	159.3±0.1
	average	157.3

$P_{no\text{-}prep\ \#1}$

Time (days)	Date	Conc. (g/L)
0	12/8/2000	108.7±0.3
37	1/14/2001	107.3±8.1
54	1/31/2001	109.7±0.8
138	4/25/2001	115.9±2.9
	average	110.4

$P_{no\text{-}prep\ \#2}$

Time (days)	Date	Conc. (g/L)
0	5/11/2001	131.1±0.0
117	9/5/2001	134.7±6.0
166	10/24/2001	134.0±1.0
315	3/22/2002	138.1±2.9
	average	134.5

Table G.3 Continued.

$P_{clarified}$		
Time (days)	Date	Conc. (g/L)
0	3/8/2003	73.4±0.2
190	9/14/2003	73.6±3.2
	average	73.5

Table G.4 Sucrose concentrations as a function of time at 45°C and 30°C (Figure 3.34).

45°C		
Date	Time (day)	Conc (g/L)
7/25/2003	0	116.1
7/31/2003	6	114.8
8/8/2003	14	113.9
8/17/2003	23	105.8
8/23/2003	29	109.8
8/30/2003	36	108.3
9/7/2003	44	108.1
9/14/2003	51	94.6
9/20/2003	57	94.1
9/30/2003	67	92.1
10/5/2003	72	89.9
10/12/2003	79	89.9
10/18/2003	85	86.1
10/26/2003	93	82.5
11/2/2003	100	84.9
11/10/2003	108	83.2
11/15/2003	113	83.0
12/1/2003	129	80.8

30°C		
Date	Time (day)	Conc (g/L)
7/25/2003	0	114.1
8/23/2003	29	117.6
9/23/2003	60	118.2
10/24/2003	91	117.2
12/1/2003	129	114.0

APPENDIX H

HPLC SUGAR ANALYSIS

This procedure is similar to the method described by Chang (1999). High Pressure (or Performance) Liquid Chromatography (HPLC) was used to measure concentrations of all sugars in these studies (i.e., glucose, xylose, and sucrose). For glucose and xylose a resin/lead-based ion exchange column (Aminex® HPX-87P, Bio-Rad Laboratories, Hercules CA) equipped with deashing guards (1 cation H^+ and 1 Anion CO_3^-, 125-0118, Bio-Rad Laboratories) was used. The deashing guards are necessary to remove citrate from the samples, which tends to degrade the column. For sucrose measurements, a resin/calcium-based ion exchange column (Aminex® HPX-87C, Bio-Rad Laboratories), equipped with a guard column (Carbo-C, Bio-Rad Laboratories), was used because of the high calcium concentrations sometimes found in these samples.

Both columns were operated at the same conditions as follows:

Samples injection volume: 20 μL

Loop size: 20 μL

Autosampler tray temperature: 5°C

Mobile phase: 18.3-mΩ-cm reverse osmosis deionized (RODI) water, degassed by vaccum filtration through a 0.45-μm nylon membrane

Flow rate: 0.6 mL/min

Column temperature: 85°C

Detector: refractive index (RI)

The HPLC system used the following equipment:

Pump: ConstaMetric 3200 (LDC Analytical, Riviera Beach FL)

Autosampler: AS100 (Spectra-Physics Analytical, Freemont CA)

Column Heater: Jones Chromatography (Hengoed, Wales UK)

Pulse dampener: LP-21 (Scientific Systems/Laballiance, Inc., State College PA)

Detector: Perkin Elmer RI detector, Series 200 (Perkin Elmer Life and Analytical Sciencies, Boston MA)

Integrator: SP4270 (Spectra-Physics Analytical, Freemont CA)

RODI water system: NANOpure Ultrapure Water System (Barnstead/Thermolyne, Dubuque IO)

H.1 Sample preparation

1) Centrifuge samples at 4000 rpm for 5 min to separate liquid from coarse solids (i.e., bagasse or lime).
2) Dilute samples accordingly to obtain 3 – 6 mL of diluted sample with a sugar concentration of 1 – 5 g/L in 12-mL polypropylene copolymer (PPCO) centrifuge tubes equipped with appropriate caps (Nalgene® 3110-0120, Fisher Scientific Co., Pittsburgh PA).
3) Centrifuge diluted samples at 15,000 rpm for ~30 seconds.
4) Using a syringe, pressure-filter the centrifuged diluted samples through a 0.45-μm nylon membrane (Fisher Scientific Co.) into autosampler vials equipped with a sealing lid. The volume in the vial should be ~ 1 mL.
5) Make sure that all tubes and vials are properly labeled.

H.2 Sugar Standards preparation

1) Prepare 5.00-g/L sucrose stock solution by dissolving 0.500 g of 45°C-dried sucrose in a 100-mL volumetric flask with RODI water or 5.00-g/L glucose+xylose stock solution by dissolving 0.500 g 45°C-dry glucose plus 0.500 g 45°C-dried xylose in a 100-mL volumetric flask with RODI water.
2) Prepare four or five standards with concentrations between 0.00 g/L and 5.00 g/L (e.g., 0.500, 1.00, 2.00, 3.00 and 4.00 g/L) by diluting the sucrose or glucose+xylose stock solution accordingly with RODI water.

3) Place ~ 1 mL of each of these standards in autosampler vials and cap them with sealing lids. The 5.00-g/L stock solution is also considered one of the standards.
4) Freeze the stock solutions and/or the standards if the analysis will be done later. Be sure to mix the solutions thoroughly after thawing because freezing separates the sugars from the water.

H.3 Equipment Setup

1) Degas ~ 4 L of 18.3-mΩ-cm RODI water by vacuum filtering through a 0.45-μm nylon membrane into a glass jug. The column requires the water to be degassed to avoid bubble formation and to keep the baseline from drifting; therefore, it is recommended not to run HPLC for longer than 2 – 3 days, because the water loses its degassed condition after a period of time.
2) While the water is being degassed turn on the pump, the autosampler, the RI detector and the integrator for warm-up.
3) Load the autosampler user file as follows:
   a) Press the MENU key to display the main menu. Select FILES, followed by EDIT and then INJECTION to display the edit menu, using the arrow keys to move the cursor and the ENTER key to select the desired option.
   b) Adjust loop size to 20 μL and the number of injections per sample to the desired number using the "+" key to increase or "–" key to decrease the values.
   c) Adjust the cycle time to 20 min.
   d) Turn on the built-in tray cooler by pressing the "+" key to select the option ON. Adjust the refrigerator temperature to 20^{o}C using the "+" or "–" keys.
   e) Press the ENTER key several times to use the default values for other parameters.
   f) Load the file by selecting FILES then LOAD from the main menu and then pressing the ENTER key.

4) Check the tray temperature by pressing STATUS and then with the cursor down-arrow key ("▼") scroll down until the temperature is displayed.
5) Wait for several minutes and when the temperature reaches the set point (i.e., 20^{o}C) repeat Step 3a then pressing ENTER several times to scroll down, select tray temperature once again, and adjust it to 15^{o}C as described in Step 3d. Then repeat Steps 3e and 3f to load the file.
6) Repeat Step 5 to decrease the tray temperature to 10^{o}C, then to 8^{o}C and finally to 5^{o}C. This sequential decrease of tray temperature is important, because the cooler overloads if the temperature is decreased directly to 5^{o}C.
7) Once the water has been degassed, place the glass jug on the stirring plate, and start stirring as slowly as possible. Place the pump inlets, equipped with filtering fittings, inside the glass jug, and prime the pump with a syringe by sucking about 40 mL of water from the priming port.
8) Start the pump to flush air bubbles from the system, and increase the flow rate to about 2 mL/min. The liquid goes from the pump, through the pulse dampener, through the autosampler, through a long piece of tubing, which for now takes the place of the column, through the RI detector and out to the waste container.
9) Turn on the purge in the RI detector. This allows both the reference and sample cells to be purged with water.
10) After about 30 – 40 minutes of purging, decrease the flow rate to 0.2 mL/min and be prepare to connect the column.
11) Take out the column from the refrigerator (4 – 10^{o}C), where it is normally stored, and remove its end screw-plugs, which are used to keep it from drying during storage.
12) Connect the column as described in the Bio-Rad manual, *Guidelines for Use and Care of Aminex® Resin Based Columns.*
13) After the column has been connected and fitted into the column heater, turn on the heater and adjust the temperature to 85^{o}C. Allow the column to reach this temperature. It usually takes about 1 h.

14) After the column heater reaches 85^{o}C as indicated by a mercury thermometer inside the heater, gradually increase the flow rate (i.e., 0.01 mL/min every 30 – 40 sec) from 0.2 to 0.6 mL/min. Do not operate the column at flow rates higher than 0.2 mL/min at ambient temperature because this causes the column to collapse.

15) Adjust the integrator to start marking peaks (PM), to start or inactivate integration (II) depending on the residence times of the desired peaks and to end the recording (ER) after 20 min. This is done as follows:

a) Press the integrator DIALOG key and press ENTER until the TIME/FUNCTION/VALUE option is displayed.

b) Enter the following information pressing the ENTER key after each value has been keyed in:

TIME	FUNCTION	VALUE
TT = 0.0	TF = PM	TV = 1
TT = 0.01	TF = II	TV = 1
TT = 4.0	TF = II	TV = 0
TT = 17.0	TF = II	TV = 1
TT = 20.0	TF = ER	TV = 1

The integrator has thus been set to do the following: 1) at time 0 min, it will start marking the peaks (PM), 2) at time 0.01 min it will turn on the inactivate-integration (II) option, 3) at time 4.0 min it will turn off the II option, so any peaks that show up between time 0.01 and 4.0 min will not be integrated, 4) at time 17.0 min it will turn on the II option again, so the peaks with residence times between 4.0 and 17.0 min will be integrated, and those that show up after 17.0 min will not, 5) at 20 min it will end the recording and report the integration results. This setting is appropriate for both sucrose and glucose+xylose samples because the sucrose peak appears at about 8 min, but to check for reducing sugars, it is important to also observe the times of 12 and 13 min, which are about the residence times for glucose and fructose, respectively in the HPX-87C

column. On the other hand, for glucose and xylose their residence times are about 11 and 12 min, respectively, but it is also important to check for cellobiose at a residence time of about 9 min.

16) Turn off the purge in the RI detector to stop circulating liquid through the reference cell and run a baseline by pressing INJ A in the integrator. Check the baseline for noise or drift. If the baseline does not display noise and it is straight, then it is possible to start running samples, otherwise, check the integrity of the equipment, especially the RI detector, by referring to the appropriate manual. The baseline recording can be stopped by pressing ABORT A in the integrator.

H.4 Sugar Concentration Measurements in Samples

1) Place the sample and standard vials in 1, 2 or 3 bins depending on the number of vials and place them in the autosampler tray.
2) Edit and load a sample file in the autosampler as follows:
   a) Press the SAMPLE key to display the sample menu.
   b) Specify the sample set number.
   c) Select the number of injections per vial.
   d) Specify the first vial to run according to its position in the tray. There are 3 bins (i.e., A, B and C) with 35 sample spaces each; therefore, say the first sample is in Space 23 in Bin B, you enter B23 using the "+" and "–" keys.
   e) Specify the number of samples that will be run.
   f) Add the sample set to the queue by pressing the ENTER key. The autosampler runs the first sample from the position specified in Step 2d and then it will continue in ascending order from that position until it completes the specified number of samples (Step 2e).
3) Press the RUN button to start measurements.
4) Collect the chromatograms after all samples have been run. Using the standards, prepare a calibration curve, which relates area to sugar concentration. Observe

the retention times to recognize the peaks, and calculate the sample sugar concentration from the area given in the chromatograms and the calibration curve.

H.5 Equipment shut-down

1) After running the samples, decrease flow rate gradually to 0.2 mL/min.
2) Turn off the heater, and, without disconnecting, expose the column, which is encased in the heater, to ambient temperature so that it cools faster.
3) Once the column has cooled to ambient temperature (usually takes about 30 min), disconnect it from its inlet and outlet tubing.
4) Replace the column end screw-plugs and return the column to the refrigerator for storage.
5) Replace the piece of tubing, which takes the place of the column, and increase the flow rate to about 2 mL/min to flush the system for about 15 min.
6) Decrease the flow rate to 0.1 mL/min and press the STAND BY button on the pump.
7) Turn off the pump, RI detector, the autosampler and the integrator.

For required maintenance of the column, autosampler and RI detector, refer to the appropriate manual.

APPENDIX I

PROCEDURES FOR ANALYSIS OF SAMPLES FROM LONG-TERM LIME PRETREATMENT

I.1 Preparation of Sample Flasks for the Pretreatment Process

1) Place 400 g of 40-mesh untreated bagasse into several 1-L centrifuge bottles to start the washing process. (This amount should be enough to monitor the pretreatment process as a function of time for as long as necessary.).
2) Add about 800 mL of water to each centrifuge bottle and stir for 15 min.
3) Centrifuge at 3500 rpm or more for 15 min.
4) Decant as much water as possible into the sink.
5) Repeat Steps 2 through 4 until the water does not get any clearer.
6) Transfer the contents of the centrifuge bottles as much as possible to other containers.
7) Dry the washed biomass at 45^{o}C for 24 hours or longer if necessary.
8) Let the biomass regain equilibrium moisture content with the environment. This procedure might take several days.
9) Determine the moisture content of a sample biomass as described in NREL Standard Procedure No. 001 (X_1).
10) Load each flask with 3 g dry weight of bagasse, add 1.5 g of $Ca(OH)_2$, and 27 mL (9 mL/g dry bagasse) or 36 mL (12 mL/g dry bagasse) of distilled water. Record the exact amount of biomass (W_1) and lime ($W_{Ca(OH)2}$) added to each flask to the nearest 0.1 mg.
11) Place in shaking incubator at the appropriate temperature and start pretreatment procedure. The flasks are set up in duplicates, which will yield two subsets of samples (A and B) at the same conditions of time and oxygen presence.

Oxidative conditions are implemented by air purging, and oxygen is excluding by capping the bottles.

12) Take flasks off line as frequently and for as long as necessary to monitor the process.

I.2 Lime Consumption as a Function of Time

For this analysis, Subset A is used. The procedure follows:

1) After the flasks with the bagasse are taken out of the shaking air bath, transfer all the contents of Subset A to a beaker. Use as much water as necessary to aid in this procedure.
2) Set up a titration apparatus. Place the beaker with the sample on a magnetic stirrer and drop a magnetic bar into the beaker. Use a buret clamp to place a buret over the beaker. Fill the buret with a certified standard solution of hydrochloric acid (nominal concentration 1 N, Fisher Scientific Co., Pittsburgh PA) and record the starting volume (V_1).
3) Using a well-calibrated pH meter, titrate the solution in the beaker under constant stirring until the pH reaches 6.80 to 7.00. This procedure may take several hours because calcium carbonate formed in the fibers takes a long time to be released.
4) Record the final volume of HCl (V_2). Calculate the amount of $Ca(OH)_2$ left after pretreatment as follows:

$$W_{left} = \frac{1 \text{ mol } Ca(OH)_2}{2 \text{ mol } HCl} \times \frac{N_{HCl}(V_1 - V_2)}{1000} \times \text{MW } Ca(OH)_2 \qquad \text{(I.1)}$$

where

W_{left} = Total amount of $Ca(OH)_2$ left after pretreatment, g
N_{HCl} = Normality of the certified standard HCl solution, mol/L
V_1 = Starting volume of HCl in titration, mL
V_2 = Final volume of HCl in titration, mL

MW = Molecular weight of $Ca(OH)_2$ (74.092 g/mol)

5) During the titration there might be some variations introduced (e.g., the $Ca(OH)_2$ is not 100% pure, there might be some $Ca(OH)_2$ consumed during the titration due to exposure to carbon dioxide in the air, or from the distilled water used, etc.). To account for this, the value for $Ca(OH)_2$ left (W_{left}) must be multiplied by a correction factor (C_f) to obtain the corrected amount of $Ca(OH)_2$ left (W_{corr}). This values correlates better to the amount of $Ca(OH)_2$ added before pretreatment ($W_{Ca(OH)2}$). For this purpose, the titration procedures are performed on untreated bagasse by preparing a flask as described in Step 10 of Section I.1, and immediately proceeding to Steps 1 through 4 of this section. This sample serves as blank for the titration procedure. The corrected amount of $Ca(OH)_2$ left is calculated as follows:

$$C_f = \frac{W^0_{Ca(OH)2}}{W^0_{left}}$$

$$W_{corr} = W_{left} \cdot C_f \qquad \text{(I.2)}$$

where

C_f = Correction factor, g $Ca(OH)_2$ before titration/g $Ca(OH)_2$ after titration

$W^0_{Ca(OH)2}$ = $Ca(OH)_2$ added to untreated bagasse before titration, g

W^0_{left} = $Ca(OH)_2$ left after titration of untreated bagasse (Steps 1 through 4), g

W_{corr} = Corrected amount of $Ca(OH)_2$ left, g

6) The exact amount of $Ca(OH)_2$ added before pretreatment was recorded when the bottles were prepared for the experiment ($W_{Ca(OH)2}$ from Step 10 in Section I.1). From Step 5, the corrected amount of $Ca(OH)_2$ left was calculated (W_{corr}). The consumption of $Ca(OH)_2$ is calculated as follows:

$$Ca(OH)_2 \text{ consumed (g/g untreated bagasse)} = \frac{W_{Ca(OH)2} - W_{corr}}{W_1 \times (1 - X_1)} \qquad (I.3)$$

7) Transfer the titrated slurry to a 1-L centrifuge bottle, and wash and dry the bagasse as described in Steps 2 through 8 in Section I.1.

I.3 Determination of Weight Loss Due to Pretreatment

Subset B (Step 11 in Section I.1) is used for this analysis.

1) Take an empty container and four or five 11-cm Whatman 934/AH glass fiber filter paper (particle retention = 1.5 μm) (Fisher Scientific Co., Pittsburgh PA), which have been placed in a container. Dry both the empty container and the filter papers in 45°C oven for 24 h or longer. Place the 45°C-dried container and filter papers in a desiccator and let them cool. Accurately record their weights to the nearest 0.1 mg.
2) When the flasks are taken out from the air bath, transfer all the contents to a 1-L centrifuge bottle. Be careful not to lose any material in the process. Use as much water as necessary to aid in this procedure.
3) Add enough water to fill up the centrifuge bottle. Start mixing with a magnetic stirrer using a magnetic bar of appropriate size.
4) While mixing, add glacial acetic acid to bring the pH down to about 5 to 6 to solubilize any unreacted lime.
5) Continue stirring for 15 min.
6) Centrifuge the water/bagasse mixture at 3500 rpm or more for 15 min.

7) During the centrifuge period, set up a vacuum filtration apparatus using a Buchner funnel and one of the pre-dried/pre-weighed filter papers.
8) After centrifuging, carefully decant the water into the Buchner funnel with vacuum filtration. Decant as much water as possible being careful not to lose much solids. Observe the filtrate color.
9) Repeat Steps 3, 5, 6, and 8 until the filtrate becomes clear. If it takes too long to filter, replace the old filter with one of the other previously dried and weighed filter papers.
10) After completing the washing, transfer all the bagasse to the weighed empty container from Step 1. Be careful to transfer all the solids to the container. Use as much water as needed to aid in this task.
11) Dry the biomass and the filter papers at 45^{o}C for 24 h or longer.
12) Cool the biomass and filters in a desiccator until they reach room temperature. Weigh them and accurately record the values. After subtracting the weight of the containers and filter paper, the net weight of the bagasse is obtained (W_2).
13) Immediately after, using about 0.3 – 0.5 g of this 45^{o}C-dried washed biomass, determine the moisture content as described in the NREL Standard Procedure No. 001 (NREL, 1992) (X_2). Store the rest of the biomass for 3-day enzyme digestibility and lignin analysis.
14) The total yield is calculated using the following formula:

$$Y = \frac{W_2 \times (1 - X_2)}{W_1 \times (1 - X_1)} \tag{I.4}$$

where

Y = Total yield, g treated bagasse/g untreated bagasse

W_1 = Weight of the washed raw biomass before pretreatment in each flask, g

X_1 = Moisture content of the washed raw biomass at room

conditions (W_1), g H_2O/g total weight

W_2 = Weight of the 45°C-dried bagasse in container and filter papers, g

X_2 = Moisture content of the 45°C-dried biomass (W_2), g H_2O/g total 45°C-dried weight.

At this point, the remaining materials from lime consumption determination and mass balance are mixed together to be analyzed for lignin content and 3-day cellulase-enzyme digestibility.

I.4 Lignin Analysis of the Treated Biomass

The total Klason lignin content (g lignin/100 g dry bagasse) is determined using NREL Standard Procedures No. 003 and 004 (NREL, 1992).

From this same procedure, the acid-insoluble ash content (g acid-insoluble ash/100 g dry bagasse) in the bagasse can also be determined by weighing beforehand the filtering crucible used, which is taken as the tare for the "acid-insoluble ash + crucible" value. If we assume that bagasse is composed only of lignin, ash, and holocellulose, the holocellulose fraction (g holocellulose/100 g dry bagasse) can be obtained by subtracting acid-insoluble ash and lignin fractions from 100.

I.5 Determination of 3-day Enzyme Digestibility Yields

The method for these digestibility studies is similar to the analysis developed by Chang (1999). For this procedure, the enzyme activity as determined by the NREL method No. 006 (NREL, 1992) is needed.

1) Determine the moisture content of the sample to be analyzed as described in NREL Standard Procedure No. 001 (NREL, 1992) (X_i, g H_2O/g ambient

bagasse). This sample is from the remaining material from lime consumption determination and the mass balance procedure, which was also employed for Klason lignin determination.

2) 500 mL of a 1-M citric acid (citrate buffer) solution (pH 4.3), should have been prepared beforehand by dissolving 105 g of citric acid monohydrate in 500 mL of distilled water and then adjusting the pH with sodium hydroxide to 4.3. This solution when diluted to 0.05 M, should have a pH of 4.8. Also a 0.01-g/mL sodium azide solution should be prepared.
3) Based on the moisture content from Step 1, weigh approximately 2.5 g dry bagasse or less, and record the ambient weight (not the dry weight) to the nearest 0.1 mg (W_i).
4) Carefully place this weighed material into a 125-mL Erlenmeyer bottle equipped with a sealing cap. Be careful not to lose any of the sample during transfer.
5) The distilled-water loading is 16.8 mL/g dry bagasse. Compute the actual amount needed according to the dry weight of the bagasse present in the bottle (Step 3) and subtract 12 mL, which will be used later to clean the pH probe. Add the computed amount of water (minus the 12 mL) to the bottle.
6) Add 1 mL of citrate buffer/g dry bagasse and 0.6 mL of sodium azide/g dry bagasse, which will keep the pH constant and inhibit microbial growth, respectively.
7) Add glacial acetic acid or sodium hydroxide to each flask to adjust the pH to 4.8. While adjusting adding the acid or the base, continuously monitor the pH while shaking the bottle gently for mixing.
8) Use the 12 mL of distilled water from Step 5 to clean the probe.
9) Place the Erlenmeyer bottle in a 100 – 150 rpm shaking air bath at 50^{o}C.
10) While the temperature reaches 50^{o}C, set up boiling water, which will be used to denature the enzyme and quench the reaction.
11) When the temperature reaches 50^{o}C, add the appropriate amount of cellulase enzyme needed to have 5 FPU/g dry bagasse (based on W_i recorded in Step 3),

and add an excess of cellobiase enzyme (for an activity of 250 CBU/g enzyme, 0.114 mL/g dry bagasse should be sufficient). Proceed to next step immediately.

12) While shaking gently to ensure homogeneity, withdraw 4.0 mL of sample using a 5-mL pipette with a cut-off tip. Deposit this sample (liquid + solids) in a small screw-capped test tube and place it in the boiling bath. This is taken as time 0 h for the enzyme hydrolysis reaction.
13) Swiftly after Step 12, while the 4-mL sample is in the boiling water, return the capped Erlenmeyer bottle to the 50^{o}C-shaking air bath to continue the enzyme hydrolysis.
14) Boil the 4-mL sample for 15 min to denature the enzyme, and then immediately cool the sample in ice water.
15) Transfer the contents of the screw-capped test tube to a centrifuge tube, and centrifuge the sample for 5 min at 4000 rpm.
16) After centrifuging, transfer the liquid from the centrifuge tube into another appropriate sampling tube being careful not to transfer any solids. Keep this liquid sample in the freezer until HPLC analysis for xylose and glucose concentrations can be done. Ensure that the tubes are clearly labeled as 0 h samples.
17) Repeat Steps 12, and 14 through 16 again at 72 h, except that now Step 12 is taken as time 72 h for the hydrolysis reaction, and the labeling is now 72 h instead.
18) After withdrawing the 72-h 4-mL sample, before you dispose of the material in the Erlenmeyer bottle, measure its volume. The original volume (V) of the starting material is then calculated as follows:

$$\text{Initial volume} = \text{final volume} + \text{sample volume (i.e., 4 mL)} \times 2 \qquad \text{(I.5)}$$

19) Use HPLC equipped with an refractive index detector and a Bio-Rad HPX-87P (Bio-Rad Laboratories, Hercules CA) column to perform analysis on the concentrations of glucose and xylose for each sample.
20) The sugar yield in terms of the original untreated material, is computed as follows:

$$S = \frac{C_{72}V - C_0V}{W_i(1 - X_i)} \cdot Y \tag{I.6}$$

where

S	=	Glucose or xylose yield, g/g untreated bagasse
C_{72}	=	Concentration of glucose or xylose from HPLC at 72 h, g/L
C_0	=	Concentration of glucose or xylose from HPLC at 0 h, g/L
V	=	Volume recorded in Step 18, L
W_i	=	Initial bagasse weight from Step 3, g
X_i	=	Moisture content from Step 1, g H_2O/g ambient bagasse
Y	=	Total yield, g treated bagasse/g untreated bagasse

The total sugar yield is the sum of the glucose and xylose yields. This procedure certainly assumes that the water-soluble substances from the pretreatment, which are removed in the washing procedure, are not digestible by cellulase enzyme.

APPENDIX J

PRETREATMENT SELECTIVITY STATISTICAL ANALYSIS

The statistical regression and analysis for the pretreatment selectivity data was done using SAS® statistical software (SAS Institute Inc., Cary NC). Because the data were highly scattered, influence diagnostics, as described in Appendix B, was employed to detect potential outliers and leverage points worthy of investigation. These points, if enough evidence of their invalidity was found, were excluded.

In the pretreatment studies, the main source of error was the variability of the raw material. As it can be realized from the high ash content in Table 4.1, the bagasse used in these studies had a lot of sand and dirt in it, which tended to settle; thus, even though effort was made to keep the sampling uniform, such heterogeneities could not be avoided.

The variability of the material itself was exacerbated by the material balance (Appendix I), which had several drawbacks such as the fact that the liquid never got completely clear, thus not providing a clear indication that the washing was done. If biomass washing continued for too long, the solid particles became increasingly smaller, to the point that there might have been some material loss during filtration. Nonetheless, as it was later realized, the mass balance procedure worked remarkably well when fresh bagasse, rather than old stored bagasse, was used.

For the selectivity of the samples without air at 23^{o}C (Figure 4.16), the studentized deleted residuals (RSTUDENT) identified three potential outliers, namely the values for Weeks 1, 2 and 4. They showed |RSTUDENT| values of 2.10, 1.70 and -2.31, respectively, which would not necessarily indicate they were extreme outliers. Their Cook's D was greater than 0.4, indicating that they were influential values. Although their values of h_i and |COVRATIO| were below the cut off, their values for their |DFFITS|, |DFBETAS| were not. Figure 4.16 shows that the observations for Weeks 1 and 2 together influence the data tremendously, as it is realized also by their high values of their Cook's D. This influence affects the diagnostics, causing it to

consider observation for Week 4 as an outlier. Investigation of the observation for Week 1 showed that there was a mistake made during the mass balance. The percent dry weight for the sample is shown as 75.6% (75.6 g dry solids/100 g solids at ambient conditions), but this value should be in order of 96 – 98%. A dry-weight value as low as this one is impossible for a material that has been in a convection oven at 45^{o}C for two days; therefore, there is enough evidence to exclude it.

After excluding the value for Week 1, the observation for Week 2 becomes an extreme outlier, with a |RSTUDENT| value of 6.05, whereas the observation for Week 4, has a lower |RSTUDENT| of 2.05 and is not considered an extreme outlier. The error for the observation for Week 2, can be attributed to the lignin determination, where the acid-insoluble ash content was higher than expected (i.e., 18.8 g/100 g dry bagasse, but it should be in the order of 13–15 g/100 g dry bagasse). After excluding this extreme outlier, no more outliers were detected by the influence diagnostics. Table J.1 shows the ANOVA for the regression and Table J.2 shows the summary of the regression statistics as well as the value for the selectivity (slope) and its standard error. The small P-value suggests that the regression is significant.

Table J.1 ANOVA of the regression of the holocellulose-to-lignin selectivity for treatment without air, 23^{o}C.

	df	SS	MS	F	P-value
Regression	1	0.0030	0.0030	99.04	<0.0001
Residual	7	0.0002	2.997E-05		
Total	8	0.0032			

Table J.2 Regression statistics, parameters and standard errors for the regression of holocellulose-to-lignin selectivity for treatment without air, 23^{o}C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.9664	Intercept	-0.035	0.013	-2.6594	0.0325
R^2	0.9340	Slope	1.405	0.141	9.9516	<0.0001
Adjusted R^2	0.9246					
Standard Error	0.0055					

For the treatment at 30°C without air (Figure 4.17), one potential outlier is detected. The observation for Week 1, presents a |RSTUDENT| > 2, and its values for |DFFITS| and |DFBETAS| also greater than 2. Investigation of this point, however, yields no evidence that would indicate that this value should be excluded. This response on the influence from the observation at Week 1 may be because at the end of the first week, the phase of fast lignin removal is not completely over. Table J.3 is the ANOVA for the regression, which has a very small P-value indicating that the regression is significant. Table J.4 shows the regression statistics and the selectivity parameter with its standard error.

Table J.3 ANOVA of the regression of the holocellulose-to-lignin selectivity for treatment without air, 30°C.

	Df	SS	MS	F	P-value
Regression	1	0.0085	0.0085	87.67	<0.0001
Residual	8	0.0008	9.66E-05		
Total	9	0.0092			

Table J.4 Regression statistics, parameters and standard errors for the regression of holocellulose-to-lignin selectivity for treatment without air, 30°C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.9573	Intercept	-0.066	0.012	-5.572	0.0005
R^2	0.9164	Slope	1.413	0.151	9.363	<0.0001
Adjusted R^2	0.9059					
Standard Error	0.0098					

For the treatment at 40°C without air (Figure 4.18), a slight potential outlier is detected for the observation at Week 1, with $h_i > 0.4$, which is the size-adjusted cut off for this value. The |RSTUDENT| for all the observations is < 2. Investigation of the values for the observation at Week 1 showed no evidence that would justify its exclusion; however, this value is not influential because its Cook's D and |DFFITS| do not exceed the cut-offs of 0.2 and 0.9, respectively. As with the treatment at 30°C, this

observation response to the influence diagnostics may be attributed to the fact that at the end of Week 1, the fast-lignin-removal phase (known as bulk phase) might not have yet ended.

Table J.5 ANOVA of the regression of the holocellulose-to-lignin selectivity for treatment without air, 40°C.

	Df	SS	MS	F	P-value
Regression	1	0.0034	0.0034	17.41	0.0031
Residual	8	0.0016	0.0002		
Total	9	0.0049			

Table J.6 Regression statistics, parameters and standard errors for the regression of holocellulose-to-lignin selectivity for treatment without air, 40°C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.8278	Intercept	-0.056	0.023	-2.466	0.039
R^2	0.6852	Slope	1.236	0.296	4.173	0.003
Adjusted R^2	0.6458					
Standard Error	0.0139					

For the selectivity of the treatment without air at 50°C (Figure 4.19), the influence diagnostics detected three potential outliers, namely, the observation for Week 1 with a h_i slightly exceeding the cut-off of 0.4 and the observations for Week 4 and 8, which had a |RSTUDENT| of 2.20 and 2.36, respectively. Investigation of these values shows no evidence of invalidity; therefore, there is not enough evidence to exclude them. Table J.7 shows ANOVA for the holocellulose-to-lignin selectivity and Table J.8 shows the regression statistics, the selectivity and its standard error. The P-value for the regression is small enough to show that the regression is significant.

Table J.7 ANOVA of the regression of the holocellulose-to-lignin selectivity for treatment without air, 50°C.

	df	SS	MS	F	P-value
Regression	1	0.0014	0.0014	12.05	0.0084
Residual	8	0.0009	0.0001		
Total	9	0.0023			

Table J.8 Regression statistics, parameters and standard errors for the regression of holocellulose-to-lignin selectivity for treatment without air, 50°C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.7753	Intercept	-0.035	0.037	-0.932	0.378
R^2	0.6011	Slope	1.280	0.369	3.472	0.008
Adjusted R^2	0.5512					
Standard Error	0.0107					

In the case of the treatment at 57°C without air (Figure 4.20), all the |RSTUDENT| values were below the cut-off of 2, however, the observations for Day 1 was considered a leverage point because it displayed an h_i value of 0.37, which exceeded the cut-off of 0.33. This value and the observation for Day 2 were considered influential points, because their values for Cook's D, |DFFITS| and |DFBETAS| exceeded the cut-off values, especially the observation for Day 1. Inspection of these points showed that the variability comes from the lignin determination, particularly due to material heterogeneity, where the ideally-constant acid-insoluble ash content parameter expressed in terms of the original untreated material, shows significant fluctuations. For instance, for Day 1 this parameter was 0.13 g acid-insoluble ash/g untreated bagasse, whereas for Day 3 was 0.09 g acid insoluble ash/g untreated bagasse. The fact that the |RSTUDENT| values were below their cut-off, and that the inspection did not yield any conclusive evidence, especially because observations for Day 1 and Day 3 were opposite influential points (i.e., they pull the data towards themselves but opposite to each other), suggests that these values cannot be excluded. Table J.9 shows the ANOVA for the regression, which suggests that the regression is significant as it resulted in a P-value < 0.0001.

Table J.10 shows the regression statistics and the selectivity (slope) with its standard error.

Table J.9 ANOVA of the regression of the holocellulose-to-lignin selectivity for treatment without air, 57°C

	Df	SS	MS	F	P-value
Regression	1	0.0095	0.0095	43.88	<0.0001
Residual	11	0.0024	0.0002		
Total	12	0.0119			

Table J.10 Regression statistics, parameters and standard errors for the regression of holocellulose-to-lignin selectivity for treatment without air, 57°C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.8942	Intercept	-0.060	0.020	-2.97	0.0128
R^2	0.7996	Slope	1.333	0.201	6.62	<0.0001
Adjusted R^2	0.7814					
Standard Error	0.0147					

No outliers or leverage points were detected by the influence diagnostics for the treatment at 23°C with air (Figure 4.21). The |RSTUDENT| and h_i values are all below their cut-offs. The observation for Week 1 and Month 7 had a |COVRATIO-1| value higher than the cut-off of 0.55, and the observation for Month 8 showed a value for the |DFBETAS| of the slope slightly higher than the cut-off of 0.60. This result suggested that they were influential points, but further investigation showed no evidence of abnormality. Table J.11 shows the ANOVA for the regression. Although no outliers were detected, comparatively, the regression is not as good as with the other treatments, with only 95% confidence of its significance. This is also observed in the low value for R^2 shown in Table J.12, which shows the regression statistics and the parameters with their standard errors. In addition, from Figure 4.21, it can be observed that the resulting regression parameters would yield a holocellulose-to-lignin selectivity for the fast-lignin-removal phase (i.e., bulk phase), which is higher than the holocellulose-to-lignin

selectivity for the final (i.e., residual phase). This is not physically possible because the bulk phase is more selective towards lignin than the residual phase; therefore, these results are doubtful.

Table J.11 ANOVA of the regression of the holocellulose-to-lignin selectivity for treatment with air, 23°C.

	df	SS	MS	F	P-value
Regression	1	0.0015	0.0015	5.54	0.0431
Residual	9	0.0025	0.0003		
Total	10	0.0040			

Table J.12 Regression statistics, parameters and standard errors for the regression of holocellulose-to-lignin selectivity for treatment with air, 23°C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.6172	Intercept	0.041	0.019	2.16	0.059
R^2	0.3809	Slope	0.415	0.176	2.35	0.043
Adjusted R^2	0.3121					
Standard Error	0.0166					

For the treatment at 30°C with air (Figure 4.22), the regression diagnostics showed that the |RSTUDENT| values for all the data are below their cut-off of 2. Only the value for the observation at Week 1 was detected as an influential and leverage point with its values for h_i, Cook's D, |DFFITS| and |DFBETAS| for both the intercept and the slope all exceeding their cut-off values. Investigation of this point shows no evidence of invalidity; thus, their exclusion cannot be justified. A negative value is observed (Figure 4.22), which is physically impossible. However, this point cannot be excluded because the error in this case could have been introduced by raw material variability, namely, the values for the parameters of the bagasse at time 0. Because the values for the bagasse at time 0 are subtracted from all points, this variability is introduced equally to all the data. This causes a shift in the curve but does not affect the slope, which is the parameter of importance. This negative value, although not physically viable, is a valid point to find

the selectivity parameter (slope). The variability of the raw material can be realized from the acid-insoluble ash content expressed in terms of untreated material (i.e., g acid-insoluble ash present/g original untreated material). This value should remain fairly constant along the pretreatment; however, in this case the value for the raw material is about 0.16 g insoluble-ash/g original untreated material, when it should be about 0.11 as it is observed for the rest of the data. Table J 13 shows the ANOVA for the regression which suggests that, because of the small P-value, the regression is significant. Table J.14 shows the regression statistics, the selectivity and its standard error.

Table J 13 ANOVA of the regression of the holocellulose-to-lignin selectivity for treatment with air, 30°C.

	df	SS	MS	F	P-value
Regression	1	0.0107	0.0107	47.29	0.0001
Residual	8	0.0018	0.0002		
Total	9	0.0126			

Table J.14 Regression statistics, parameters and standard errors for the regression of holocellulose-to-lignin selectivity for treatment with air, 30°C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.9248	Intercept	-0.062	0.017	-3.70	0.0060
R^2	0.8553	Slope	1.129	0.164	6.88	0.0001
Adjusted R^2	0.8372					
Standard Error	0.0151					

For the treatment at 40°C with air (Figure 4.23), the observation for Month 7 was detected as an extreme outlier with a |RSTUDENT| value of 6.9 (cut-off is 2). This value is also very influential with a Cook's D of 1.0 (cut-off is 0.2) and |DFFITS| of 3.7 (size-adjusted cut-off is 0.9). Also, this value considerably exceeds the cut-offs for |COVRATIO| and |DFBETAS|. Investigation of this point reveals that the source of error may have resulted from using the same sample to do lime-consumption determination and the mass balance because the sample for Set B was lost. This caused

variability during the mass balance determination. The yield then seems to increase from 0.61 g treated bagasse/g untreated bagasse at Month 6 to 0.76 g treated bagasse/g untreated bagasse in Month 7. This is physically impossible as it is demonstrated by the negative value that results as holocellulose loss. The exceedingly high values for the parameters of the influence diagnostics, and the fact that the extreme outlying characteristics of this point can be realized by simple inspection of the data (Figure 4.23), justifies its exclusion from the correlation.

Without the influence of Month 7 in the data, the influence diagnostics detected the observation for Week 1 as a slight potential outlier, with its values for |RSTUDENT|, Cook's D, |DFFITS| and |DFBETAS| exceeding their cut-offs. It is interesting to notice that this response towards the observation for Week 1 has been observed in most selectivity analyses for the treatments at other temperatures. The reason for this response can be attributed, as mentioned, to the fact that at the beginning of the pretreatment for bagasse, delignification occurs fast without significant loss of holocellulose, and at Week 1, this phase might not have yet completely ended. There is not enough evidence, however, to exclude the observation for Week 1 from the correlation. Table J.15 shows the ANOVA for the regression, which suggests that the regression is significant. Table J.16 shows the regression statistics and the selectivity with its standard error.

Table J.15 ANOVA of the regression of the holocellulose-to-lignin selectivity for treatment with air, 40^{o}C.

	df	SS	MS	F	P-value
Regression	1	0.0083	0.0083	42.72	0.0003
Residual	7	0.0014	0.0002		
Total	8	0.0097			

Table J.16 Regression statistics, parameters and standard errors for the regression of holocellulose-to-lignin selectivity for treatment with air, 40°C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.9269	Intercept	-0.043	0.017	-2.53	0.0393
R^2	0.8592	Slope	0.955	0.146	6.54	0.0003
Adjusted R^2	0.8391					
Standard Error	0.0140					

For the treatment at 50°C with air (Figure 4.24), the influence diagnostics suggest the presence of an outlier. The observation for Month 3 has a |RSTUDENT| value of 3.40, and it is an influential point because its value for |DFFITS| exceeds the cut-off of 0.9. The variability seems to have been introduced in the mass balance calculation. The yield seems to increase from 0.72 g treated bagasse/g untreated bagasse at Month 2, to 0.87 g treated bagasse/g untreated bagasse at Month 3. This response is physically impossible as it is demonstrated by the resulting negative value for the holocellulose loss. Also, with this outlier, the regression was shown not to be significant, with a P-value of 0.68, which would mean that the slope could be 0 and that there is no loss of holocellulose as lignin is removed. As attractive as it might seem, this result is impossible; therefore, there is sufficient evidence to exclude this point from the correlation.

After excluding the observation for Month 3, the observation for Month 7 became an extreme outlier and a very influential point with all the parameters of the influence diagnostics considerably exceeding their cut-off values and the regression was still not significant, with a P-value of 0.53. Inspection of this point shows that the error lies in the mass balance, presenting a considerably higher yield than what was expected (i.e., 0.76 g treated bagasse/g untreated bagasse, in comparison to 0.67 g of treated bagasse/g of untreated bagasse for the previous month). The influence diagnostics and the inspection of the data suggest that this point is an outlier; thus, it was also excluded from the correlation.

Without the influence on the data of the outliers in Month 7 and Month 3, the influence diagnostics detects the observation for Week 2 as an extreme outlier and a very

influential point, with all the parameters considerably exceeding their cut-off values. Inspection of the data, reveals that the yield was considerably lower than expected; therefore, there is enough evidence to exclude this point.

After excluding the observation for Week 2, no more outliers were detected by the influence diagnostics. All the values for |RSTUDENT| were below its cut-off (i.e., 2), and, with the exception of the observation for Week 1, the other parameters were also below their cut-off. The observation for Week 1 was an influential point, with its values for Cook's D, |DFFITS| and |DFBETAS| exceeding their cut-off values. Nonetheless, no evidence was found that would justify its exclusion. Table J.17 shows the ANOVA for the regression, which suggests that it is significant because of the small P-value. Table J.18 shows the regression statistics and the parameter for the selectivity with their standard error. The P-value for the intercept is large, suggesting that its regression is not significant; however, the intercept is not of concern, but only the selectivity (i.e., the slope). The reason why the intercept is not significant could be due to the variability from the point at time 0, which shifts the curve but does not affect the slope.

Table J.17 ANOVA of the regression of the holocellulose-to-lignin selectivity for treatment with air, 50°C.

	df	SS	MS	F	P-value
Regression	1	0.0031	0.0031	54.33	0.0007
Residual	5	0.0003	5.765E-05		
Total	6	0.0034			

Table J.18 Regression statistics, parameters and standard errors for the regression of holocellulose-to-lignin selectivity for treatment with air, 50°C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.9569	Intercept	-0.002	0.015	-0.13	0.9006
R^2	0.9157	Slope	0.711	0.096	7.37	0.0007
Adjusted R^2	0.8989					
Standard Error	0.0076					

For the treatment at 57^{o}C with air (Figure 4.25), the influence diagnostics detected one extreme outlier, namely the observation at Month 5. This value displayed a |RSTUDENT| of 6.27, it is a leverage point because its value for h_i exceeded considerable the cut-off of 0.31, and it is also very influential because its value for |DFFITS| and |DFBETAS| exceeded the general cut-off of 2 and its Cook's D value is 1.14, which is well above the cut-off of 0.2. Inspection of this point, showed that the source of error was the material balance, which suggested that the yield increased from 0.66 g treated bagasse/g untreated bagasse in Month 4 to 0.78 g treated bagasse/g untreated bagasse. This condition is not physically possible; thus, it results in a negative value for the holocellulose loss. There is, then, strong evidence to exclude this observation from the correlation.

After excluding the observation for Month 5, the influence diagnostics detects the observation for Week 3 and Month 3 as potential outliers, with |RSTUDENT| values of 4.04 and 2.16, respectively. They both are influential points because their values for Cook's D and |DFFITS| exceeded their cut-offs of 0.2 and 0.82, respectively. Inspection of these points suggests that the source of error is the mass balance. Yields that are lower than expected were produced for Week 3 (i.e., the yield for Week 4 is 0.72 g treated bagasse/g untreated bagasse, whereas the yield for Week 3 is 0.62, thus indicating that the yield increased, which is physically impossible). In addition, yields higher than expected were obtained for Month 3 (i.e., the yield for Month 3 is 0.69 g treated bagasse/g untreated bagasse, while that of Month 2 is 0.67). When the influence diagnostics was run excluding one point, and then run again after returning it and excluding the other, the |RSTUDENT| for these two values became larger, and they became more influential as their values for |DFFITS|, |DFBETAS| and Cook's D also became larger. This condition suggests that they must be excluded together.

After excluding the observations for Week 3 and Month 3, the |RSTUDENT| for the observation for Day 3 was slightly larger than the cut-off of 2, but inspection of the data showed no evidence that would support its elimination. Table J.19 is the ANOVA

for the regression, which is shown to be significant. Table J.20 shows the regression statistics and the selectivity (slope) with its standard error.

Table J.19 ANOVA of the regression of the holocellulose-to-lignin selectivity for treatment with air, 57°C.

	df	SS	MS	F	P-value
Regression	1	0.0146	0.0146	138.76	<0.0001
Residual	8	0.0008	0.0001		
Total	9	0.0154			

Table J.20 Regression statistics, parameters and standard errors for the regression of holocellulose-to-lignin selectivity for treatment with air, 57°C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.9724	Intercept	-0.027	0.010	-2.83	0.0222
R^2	0.9455	Slope	0.920	0.078	11.78	<0.0001
Adjusted R^2	0.9387					
Standard Error	0.0102					

Figure J.1 shows the residual plot for the selectivity correlations for all the treatments at all the different temperatures. Visual inspection of the graph suggests that there is, in fact, random scattering of the residuals.

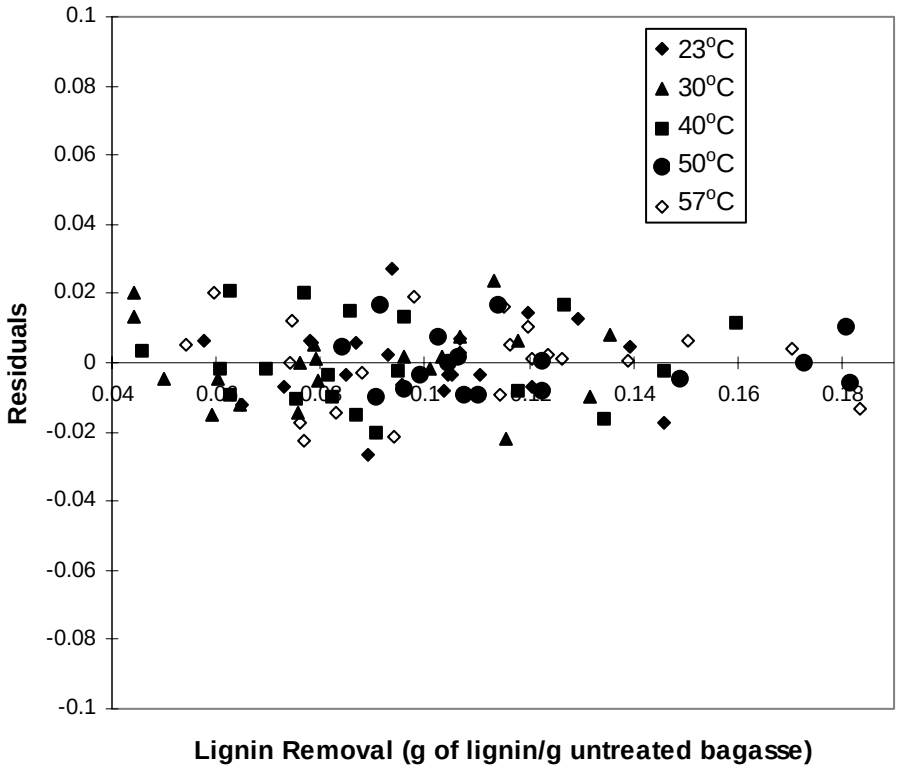

Figure J.1 Residual plot for the data of the selectivity correlations for all the treatments at all the different temperatures.

In the case of the treatment without air at 50°C for fresh bagasse (Figure 4.64), the value for Week 4 was detected as a potential outlier. It had a |RSTUDENT| value of 2.74 (cut-off is 2), a Cook's D value of 0.34 (cut-off is 2) and its values for |DFFITS| and |DFBETAS| also exceeded their cut offs, which means it is an influential point. Also, as in the other cases, the observation for Week 1 was also an influential point with Cook's D, |DFFITS| and |DFBETAS| exceeding their cut-offs. Further investigation of these points shows that there is no evidence that would support their exclusion. The regression is significant (Table J.21). Table J.22 shows the regression statistics and the selectivity (slope) with its standard error. The intercept was found not to be significant (probably due to the potential outlier), however this is not important because we are only interested in the slope.

Table J.21 ANOVA of the regression of the holocellulose-to-lignin selectivity for treatment without air for fresh bagasse, 50°C.

	df	SS	MS	F	P-value
Regression	1	0.0002	0.0002	12.48	0.0242
Residual	4	5.871E-05	1.468E-05		
Total	5	0.0002			

Table J.22 Regression statistics, parameters and standard errors for the regression of holocellulose-to-lignin selectivity for treatment without air for fresh bagasse, 50°C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.8702	Intercept	0.0007	0.0220	0.03	0.9757
R^2	0.7573	Slope	0.794	0.225	3.53	0.0242
Adjusted R^2	0.6966					
Standard Error	0.0038					

For the treatment with air at 50°C for fresh bagasse (Figure 4.65), the observation for Week 2 was detected as a potential slight outlier, with a |RSTUDENT| value of 2.51. It was also considered an influential point because its Cook's D, and |DFFITS| exceeded their cut-offs of 0.2 and 1.15, respectively. Also, once again, the value for Week 1 was also deemed as an influential point because its values for Cook's D, |DFFITS| and |DFBETAS| were above the cut-offs. Investigation of these points, however, found no evidence that would justify their exclusion. The ANOVA for the regression is shown in Table J.23. The regression statistics, and the selectivity and its standard error are shown in Table J.24.

Table J.23 ANOVA of the regression of the holocellulose-to-lignin selectivity for treatment with air for fresh bagasse, 50°C.

	df	SS	MS	F	P-value
Regression	1	0.0030	0.0030	149.09	0.0003
Residual	4	7.919E-05	1.98E-05		
Total	5	0.0030			

Table J.24 Regression statistics, parameters and standard errors for the regression of holocellulose-to-lignin selectivity for treatment with air for fresh bagasse, 50°C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.9868	Intercept	-0.030	0.012	-2.56	0.0627
R^2	0.9739	Slope	1.226	0.100	12.21	0.0003
Adjusted R^2	0.9673					
Standard Error	0.0044					

APPENDIX K

PRETREATMENT LIME CONSUMPTION STATISTICAL ANALYSIS

For the lime consumption studies, (Figures 4.39 through 4.42 for old bagasse and Figure 4.69 for fresh bagasse) the data behaved better than for the holocellulose-to-lignin selectivity; therefore, no outliers, whose exclusion might be justified, were found. The following statistical information was found using SAS® statistical software (SAS Institute Inc., Cary NC). Tables K.1 through K.8 show the ANOVA and the regression statistics and parameters with their standard errors for the correlations of lime consumption as a function of time for the treatments with air at the different temperatures for old stored bagasse (Figures 4.39 through 4.43). Figure K.1 shows the residual plot for all regressions at the different temperatures for old stored bagasse. Table K.9 and Table K.10 show the ANOVA and the regression statistics and parameters with their standard errors for the correlation of lime consumption as a function of time for the treatment with air at 50^{o}C for fresh bagasse (Figure 4.69).

Table K.1 ANOVA of the regression of the lime consumption as function of time for treatment with air, 30^{o}C.

	df	SS	MS	F	P-value
Regression	1	0.0095	0.0095	234.68	<0.0001
Residual	7	0.0003	4.059E-05		
Total	8	0.0098			

Table K.2 Regression statistics, parameters and standard errors for the regression of lime consumption as function of time for treatment with air, 30^{o}C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.9854	Intercept	4.022E-02	3.68E-03	10.94	<0.0001
R^2	0.9710	Slope	4.726E-04	3.09E-05	15.32	<0.0001
Adjusted R^2	0.9669					
Standard Error	0.0064					

Table K.3 ANOVA of the regression of the lime consumption as function of time for treatment with air, 40°C.

	df	SS	MS	F	P-value
Regression	1	0.0540	0.0540	140.47	<0.0001
Residual	7	0.0027	0.0004		
Total	8	0.0567			

Table K.4 Regression statistics, parameters and standard errors for the regression of lime consumption as function of time for treatment with air, 40°C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.9760	Intercept	0.0258	0.0114	2.27	0.0575
R^2	0.9525	Slope	1.093E-03	9.22E-05	11.85	<0.0001
Adjusted R^2	0.9458					
Standard Error	0.0196					

Table K.5 ANOVA of the regression of the lime consumption as function of time for treatment with air, 50°C.

	df	SS	MS	F	P-value
Regression	1	0.1314	0.1314	876.77	<0.0001
Residual	8	0.0012	0.0001		
Total	9	0.1326			

Table K.6 Regression statistics, parameters and standard errors for the regression of lime consumption as function of time for treatment with air, 50°C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.9955	Intercept	0.0584	0.0062	9.44	<0.0001
R^2	0.9910	Slope	1.606E-03	5.42E-05	29.61	<0.0001
Adjusted R^2	0.9898					
Standard Error	0.0122					

Table K.7 ANOVA of the regression of the lime consumption as function of time for treatment with air, 57°C.

	df	SS	MS	F	P-value
Regression	1	0.0721	0.0721	1165.37	<0.0001
Residual	6	0.0004	6.187E-05		
Total	7	0.0725			

Table K.8 Regression statistics, parameters and standard errors for the regression of lime consumption as function of time for treatment with air, 57°C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.9974	Intercept	0.0655	0.0043	15.14	<0.0001
R^2	0.9949	Slope	1.839E-03	5.39E-05	34.14	<0.0001
Adjusted R^2	0.9940					
Standard Error	0.0079					

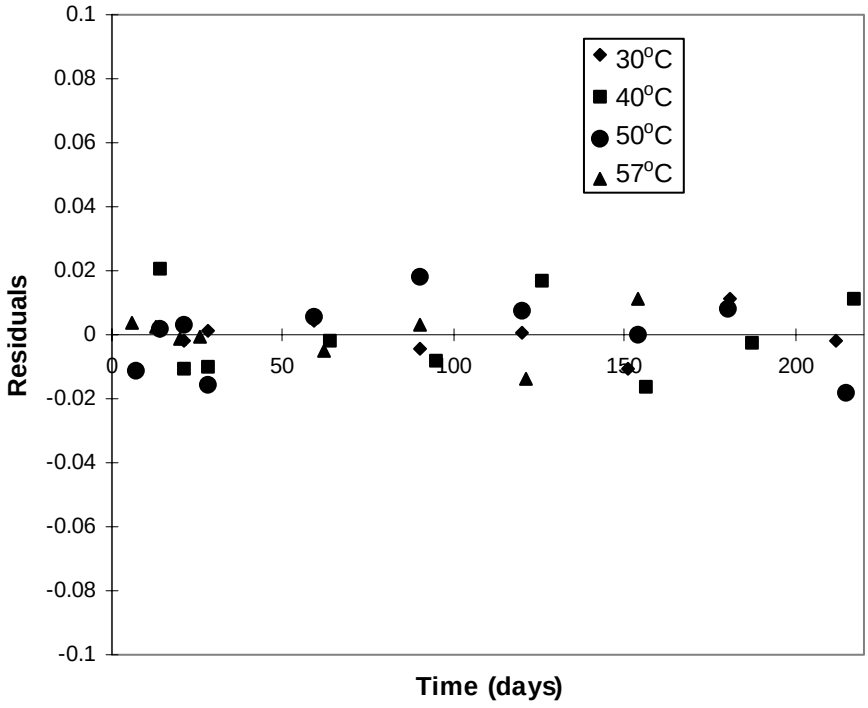

Figure K.1 Residual plot for the regressions of the lime consumption data for the treatments with air at the different temperatures.

Table K.9 ANOVA of the regression of the lime consumption for fresh bagasse for the treatment with air, 50°C.

	df	SS	MS	F	P-value
Regression	1	0.0049	0.0049	257.29	<0.0001
Residual	4	7.652E-05	1.913E-05		
Total	5	0.0050			

Table K.10 Regression statistics, parameters and standard errors for the regression of lime consumption for fresh bagasse for treatment with air, 50°C.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.9923	Intercept	0.041	0.003	14.24	0.0001
R^2	0.9847	Slope	9.970E-04	6.22E-05	16.04	<0.0001
Adjusted R^2	0.9809					
Standard Error	0.0044					

APPENDIX L

DELIGNIFICATION MODEL STATISTICAL ANALYSIS

The parameters of the non-linear regression with their standard errors and the regression statistics were computed using SAS® statistical software. Table L.1 through L.20 show the ANOVA tables and the regression statistics and parameters with their standard errors for the delignification model for the treatments with and without air for all the different temperatures for old stored bagasse (Figures 4.45 through 4.49). The data fits the model remarkably well, with R^2 values > 0.87 and all the regressions are significant with a P-value of <0.0001. Except for the k_r for the treatment at 23°C without air (Figure 4.45) and k_b for the treatment at 30°C without air (Figure 4.46), all parameters are significant with P-values < 0.1.

Table L.1 ANOVA of the delignification model for lime treatment without air at 23°C.

	df	SS	MS	F	Approx. P-value
Model	4	7.6622	1.9156	1628.74	<0.0001
Error	8	0.00941	0.00118		
Uncorrected Total	12	7.6717			

Table L.2 Regression statistics, parameters and standard errors for the delignification model for lime treatment without air at 23°C.

Regression Statistics		Parameter	Coefficients	Approx. Standard Error	t-Stat	Approx. P-value
R^2	0.8783	a_b	0.202	0.043	4.66	0.0016
Adjusted R^2	0.8327	k_b	0.115	0.057	2.01	0.0797
		a_r	0.795	0.030	26.16	<0.0001
		k_r	0.000410	0.000251	1.63	0.1409

Table L.3 ANOVA of the delignification model for lime treatment without air at 30°C.

	df	SS	MS	F	Approx. P-value
Model	4	7.3546	1.8386	2271.47	<0.0001
Error	7	0.00567	0.000809		
Uncorrected Total	11	7.3602			

Table L.4 Regression statistics, parameters and standard errors for the delignification model for lime treatment without air at 30°C.

Regression Statistics		Parameter	Coefficients	Approx. Standard Error	t-Stat	Approx. P-value
R^2	0.9302	a_b	0.151	0.038	4.01	0.0051
Adjusted R^2	0.9003	k_b	0.120	0.070	1.71	0.1309
		a_r	0.846	0.028	30.49	<0.0001
		k_r	0.000876	0.000248	3.54	0.0095

Table L.5 ANOVA of the delignification model for lime treatment without air at 40°C.

	df	SS	MS	F	Approx. P-value
Model	4	7.4257	1.8564	14417.8	<0.0001
Error	7	0.000901	0.000129		
Uncorrected Total	11	7.4266			

Table L.6 Regression statistics, parameters and standard errors for the delignification model for lime treatment without air at 40°C.

Regression Statistics		Parameter	Coefficients	Approx. Standard Error	t-Stat	Approx. P-value
R^2	0.9846	a_b	0.181	0.015	12.01	<0.0001
Adjusted R^2	0.9779	k_b	0.111	0.021	5.21	0.0012
		a_r	0.818	0.011	72.14	<0.0001
		k_r	0.000450	0.000098	4.58	0.0025

Table L.7 ANOVA of the delignification model for lime treatment without air at 50°C.

	df	SS	MS	F	Approx. P-value
Model	4	6.3033	1.5758	2689.53	<0.0001
Error	7	0.00410	0.000586		
Uncorrected Total	11	6.3074			

Table L.8 Regression statistics, parameters and standard errors for the delignification model for lime treatment without air at 50°C.

Regression Statistics		Parameter	Coefficients	Approx. Standard Error	t-Stat	Approx. P-value
R^2	0.9473	a_b	0.253	0.029	8.82	<0.0001
Adjusted R^2	0.9247	k_b	0.290	0.123	2.36	0.0502
		a_r	0.748	0.016	48.07	<0.0001
		k_r	0.000367	0.000172	2.14	0.0695

Table L.9 ANOVA of the delignification model for lime treatment without air at 57°C.

	df	SS	MS	F	Approx. P-value
Model	4	7.8666	1.9666	1309.05	<0.0001
Error	10	0.0150	0.00150		
Uncorrected Total	14	7.8816			

Table L.10 Regression statistics, parameters and standard errors for the delignification model for lime treatment without air at 57°C.

Regression Statistics		Parameter	Coefficients	Approx. Standard Error	t-Stat	Approx. P-value
R^2	0.8881	a_b	0.258	0.040	6.48	<0.0001
Adjusted R^2	0.8545	k_b	0.451	0.158	2.85	0.0172
		a_r	0.719	0.023	31.81	<0.0001
		k_r	8.76E-4	4.08E-4	2.15	0.0573

Table L.11 ANOVA of the delignification model for lime treatment with air at 23°C.

	df	SS	MS	F	Approx. P-value
Model	4	6.5405	1.6351	6063.01	<0.0001
Error	8	0.00216	0.000270		
Uncorrected Total	12	6.5427			

Table L.12 Regression statistics, parameters and standard errors for the delignification model for lime treatment with air at 23°C.

Regression Statistics		Parameter	Coefficients	Approx. Standard Error	t-Stat	Approx. P-value
R^2	0.9898	a_b	0.172	0.021	8.26	<0.0001
Adjusted R^2	0.9860	k_b	0.152	0.046	3.30	0.0109
		a_r	0.826	0.014	58.69	<0.0001
		k_r	0.00181	0.00013	14.27	<0.0001

Table L.13 ANOVA of the delignification model for lime treatment with air at 30°C.

	df	SS	MS	F	Approx. P-value
Model	4	5.9233	1.4808	4637.25	<0.0001
Error	7	0.00224	0.000319		
Uncorrected Total	11	5.9255			

Table L.14 Regression statistics, parameters and standard errors for the delignification model for lime treatment with air at 30°C.

Regression Statistics		Parameter	Coefficients	Approx. Standard Error	t-Stat	Approx. P-value
R^2	0.9891	a_b	0.256	0.028	9.05	<0.0001
Adjusted R^2	0.9844	k_b	0.0699	0.015	4.59	0.0025
		a_r	0.742	0.025	29.47	<0.0001
		k_r	0.00142	0.00024	5.90	0.0006

Table L.15 ANOVA of the delignification model for lime treatment with air at 40°C.

	df	SS	MS	F	Approx. P-value
Model	4	5.0555	1.2639	6510.92	<0.0001
Error	7	0.00136	0.000194		
Uncorrected Total	11	5.0568			

Table L.16 Regression statistics, parameters and standard errors for the delignification model for lime treatment with air at 40°C.

Regression Statistics		Parameter	Coefficients	Approx. Standard Error	t-Stat	Approx. P-value
R^2	0.9962	a_b	0.189	0.018	10.43	<0.0001
Adjusted R^2	0.9946	k_b	0.194	0.051	3.79	0.0068
		a_r	0.809	0.012	66.04	<0.0001
		k_r	0.00336	0.00014	23.73	<0.0001

Table L.17 ANOVA of the delignification model for lime treatment with air at 50°C.

	df	SS	MS	F	Approx. P-value
Model	4	3.7397	0.9349	813.58	<0.0001
Error	7	0.00804	0.00115		
Uncorrected Total	11	3.7477			

Table L.18 Regression statistics, parameters and standard errors for the delignification model for lime treatment with air at 50°C.

Regression Statistics		Parameter	Coefficients	Approx. Standard Error	t-Stat	Approx. P-value
R^2	0.9814	a_b	0.329	0.046	7.23	0.0002
Adjusted R^2	0.9734	k_b	0.172	0.062	2.79	0.0269
		a_r	0.666	0.032	20.55	<0.0001
		k_r	0.00386	0.00047	8.22	<0.0001

Table L.19 ANOVA of the delignification model for lime treatment with air at 57°C.

	df	SS	MS	F	Approx. P-value
Model	4	5.8926	1.4732	885.05	<0.0001
Error	10	0.0166	0.00166		
Uncorrected Total	14	5.9092			

Table L.20 Regression statistics, parameters and standard errors for the delignification model for lime treatment with air at 57°C.

Regression Statistics		Parameter	Coefficients	Approx. Standard Error	t-Stat	Approx. P-value
R^2	0.9735	a_b	0.379	0.047	8.12	<0.0001
Adjusted R^2	0.9656	k_b	0.198	0.054	3.66	0.0044
		a_r	0.589	0.041	14.48	<0.0001
		k_r	0.00502	0.00095	5.29	0.0004

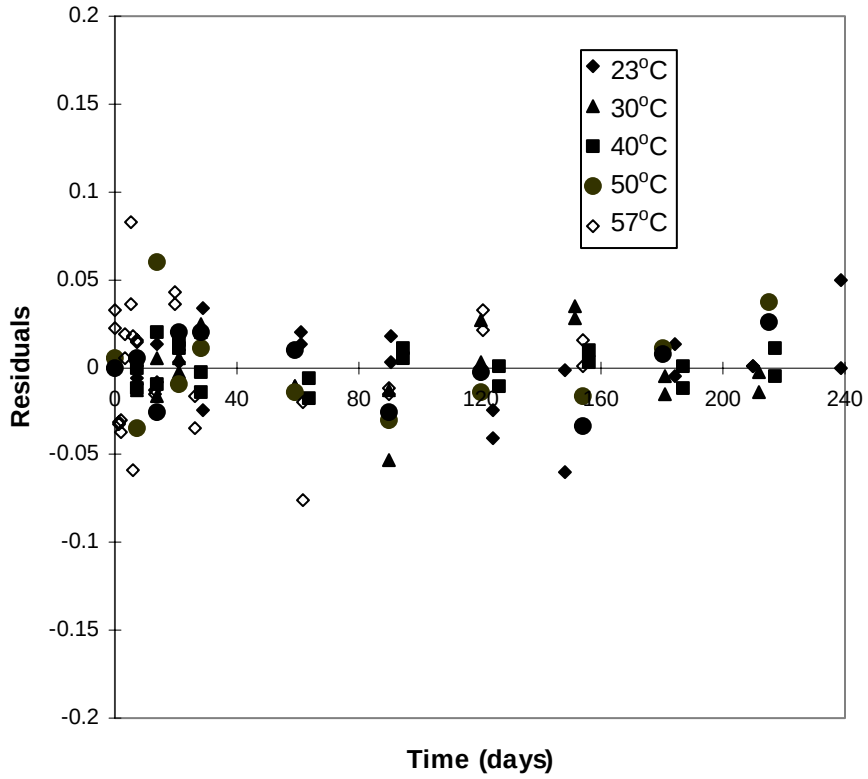

Figure L.1 Residual plot of the regression of the data to the delignification model for the treatments with and without air for all the temperatures (old bagasse).

Tables L.21 through L.24 show the ANOVA and the regression statistics and parameters with their standard errors for the regression of the delignification model for the treatment of fresh bagasse at 50°C (Figure 4.68). All the regressions and parameters are significant (i.e., P-values are small).

Table L.21 ANOVA of the delignification model for lime treatment of fresh bagasse without air at 50°C.

	df	SS	MS	F	Approx. P-value
Model	4	3.4479	0.8620	5662.61	<0.0001
Error	3	0.000457	0.000152		
Uncorrected Total	7	3.4483			

Table L.22 Regression statistics, parameters and standard errors for the delignification model for lime treatment of fresh bagasse without air at 50°C.

Regression Statistics		Parameter	Coefficients	Approx. Standard Error	t-Stat	Approx. P-value
R^2	0.9961	a_b	0.343	0.017	20.20	0.0003
Adjusted R^2	0.9923	k_b	0.3057	0.0574	5.32	0.0130
		a_r	0.657	0.012	55.97	<0.0001
		k_r	0.001163	0.000346	3.36	0.0437

Table L.23 ANOVA of the delignification model for lime treatment of fresh bagasse with air at 50°C.

	df	SS	MS	F	Approx. P-value
Model	4	2.8855	0.7214	2067.94	<0.0001
Error	3	0.00105	0.000349		
Uncorrected Total	7	2.8866			

Table L.24 Regression statistics, parameters and standard errors for the delignification model for lime treatment of fresh bagasse with air at 50°C.

Regression Statistics		Parameter	Coefficients	Approx. Standard Error	t-Stat	Approx. P-value
R^2	0.9952	a_b	0.353	0.028	12.46	0.0011
Adjusted R^2	0.9904	k_b	0.2615	0.0656	3.99	0.0282
		a_r	0.647	0.022	29.88	<0.0001
		k_r	0.005130	0.000706	7.27	0.0054

For the Arrhenius plots (Figures 4.52 and 4.53), the data were analyzed by taking the natural log (ln) of the rate constants and fitting a linear regression to their correlation

with the reciprocal of the temperature (i.e., 1/temperature, where the temperature is in Kelvin). Then, in the Arrhenius equation (Equation 4.8), the intercept would be the ln A and the slope would be equal to $-\frac{E_a}{R}$.

Tables L.25 through L.32 show the ANOVA, the regression statistics, parameters and standard errors for the Arrhenius plots for the bulk and residual phase rate constants (k_b and k_r) for the treatments with and without air. The analysis shows that regressions for k_r for the treatment without air (Figure 4.52) and k_b for the treatment with air (Figure 4.53) are not significant; therefore, their parameters are not conclusive. For these regressions, even though influence diagnostics might suggest the presence of potential outliers, because the number of data points in the correlation is small, outlier detection is not easy and it might lead to some erroneous conclusions.

Table L.25 ANOVA of the regression of the Arrhenius plot for the bulk phase rate constant (k_b) for the treatment without air.

	df	SS	MS	F	P-value
Regression	1	1.285	1.285	10.03	0.0506
Residual	3	0.384	0.128		
Total	4	1.670			

Table L.26 Regression statistics, parameters and standard errors of Arrhenius plot for the bulk phase rate constant (k_b) for the treatment without air.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.8774	Intercept	11.0	4.0166	2.74	0.0713
R^2	0.7698	Slope	-3975	1254.8	-3.17	0.0506
Adjusted R^2	0.6931					
Standard Error	0.3579					

Table L.27 ANOVA of the regression of the Arrhenius plot for the bulk phase rate constant (k_b) for the treatment with air.

	df	SS	MS	F	P-value
Regression	1	0.2313	0.2313	1.3507	0.3292
Residual	3	0.5136	0.1712		
Total	4	0.7449			

Table L.28 Regression statistics, parameters and standard errors of Arrhenius plot for the bulk phase rate constant (k_b) for the treatment with air.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.5572	Intercept	3.4795	4.6432	0.749	0.5080
R^2	0.3105	Slope	-1685.8	1450.5	-1.16	0.3292
Adjusted R^2	0.0806					
Standard Error	0.4138					

Table L.29 ANOVA of the regression of the Arrhenius plot for the residual phase rate constant (k_r) for the treatment without air.

	df	SS	MS	F	P-value
Regression	1	0.0215	0.0215	0.0917	0.7818
Residual	3	0.7023	0.2341		
Total	4	0.7238			

Table L.30 Regression statistics, parameters and standard errors of Arrhenius plot for the residual phase rate constant (k_r) for the treatment without air.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.1722	Intercept	-5.8561	5.4294	-1.08	0.3598
R^2	0.0297	Slope	-513.7	1696.2	-0.30	0.7818
Adjusted R^2	-0.2938					
Standard Error	0.4838					

Table L.31 ANOVA of the regression of the Arrhenius plot for the residual phase rate constant (k_r) for the treatment with air.

	df	SS	MS	F	P-value
Regression	1	0.9577	0.9577	16.92	0.0260
Residual	3	0.1698	0.0566		
Total	4	1.1275			

Table L.32 Regression statistics, parameters and standard errors of Arrhenius plot for the residual phase rate constant (k_r) for the treatment with air.

Regression Statistics		Parameter	Coefficients	Standard Error	t-Stat	P-value
Multiple R	0.9216	Intercept	5.0882	2.6697	1.91	0.1527
R^2	0.8494	Slope	-3430.6	834.0	-4.11	0.0260
Adjusted R^2	0.7992					
Standard Error	0.2379					

APPENDIX M

DATA FOR THE BAGASSE LONG-TERM LIME PRETREATMENT STUDIES

Tables M.1 through M.14 show the data necessary to generate all the correlations shown in the figures in Chapter IV. Although some of the parameters necessary to generate the plots in Chapter IV are not explicitly listed, they can be calculated from the given data. For instance, the holocellulose content can be found by subtracting from 100 the sum of the lignin (g lignin/100 g treated bagasse) and acid-insoluble ash content (g A.I. ash/100 g treated bagasse) given below. Also, the total 3-day digestibility sugar yield is the sum of the glucose and xylose yields given below.

The experimental procedures, calculations, and nomenclature for the parameters shown in Tables M.1 through M.14 and other parameters needed to generate the correlations in Chapter IV, are given in Chapter IV and in Appendix I. The overall yield (Y) is given in g treated bagasse/g untreated bagasse (dry weight basis).

Table M.1 Lime consumption values for old stored bagasse treatment at 23°C.

Air

n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	$W_{Ca(OH)2}$ (g)	W_{left} (g)	W_{corr} (g)	g Ca(OH)2/g untreated bagasse
0	7/18/2001	0	3.2109	3.0252	1.5345	1.4493	1.5421	0.0000†
1	7/25/2001	7	3.2131	3.0459	1.5027	1.3334	1.4188	0.0276
2	8/1/2001	14	3.2113	3.0442	1.5210	1.3204	1.4050	0.0381
3	8/8/2001	21	3.2131	3.0459	1.5122	1.3056	1.3892	0.0404
4	8/16/2001	29	3.2065	3.0397	1.5091	1.3064	1.3900	0.0392
5	9/17/2001	61	3.2094	3.0424	1.5223	1.2778	1.3597	0.0535
6	10/17/2001	91	3.2018	3.0352	1.5142	1.1871	1.2631	0.0827
7	11/19/2001	124	3.2076	3.0407	1.5251	1.1993	1.2761	0.0819
8	12/13/2001	148	3.2080	3.0411	1.5162	1.0389	1.1055	0.1351
9	1/18/2002	184	3.2008	3.0343	1.5189	1.1804	1.2560	0.0866
10	2/21/2002	210	3.2137	3.0167	1.5119	0.7712	0.8205	0.2292
11	3/22/2002	239	3.2085	3.0118	1.5188	0.3426	0.3645	0.3832

No Air (Capped)

n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	$W_{Ca(OH)2}$ (g)	W_{left} (g)	W_{corr} (g)	g Ca(OH)2/g untreated bagasse
0	7/18/2001	0	3.2042	3.0098	1.5173	1.4190	1.5098	0.0000†
1	7/25/2001	7	3.2122	3.0451	1.5197	1.3419	1.4278	0.0302
2	8/1/2001	14	3.2057	3.0389	1.5203	1.3278	1.4129	0.0354
3	8/8/2001	21	3.2158	3.0485	1.5233	1.3219	1.4066	0.0383
4	8/16/2001	29	3.2089	3.0420	1.5219	1.3390	1.4247	0.0320
5	9/17/2001	61	3.2051	3.0384	1.5149	1.2749	1.3565	0.0521
6	10/17/2001	91	3.2126	3.0455	1.5296	1.3338	1.4192	0.0363
7	11/19/2001	124	3.2198	3.0523	1.5194	1.2990	1.3821	0.0450
8	12/13/2001	148	3.2083	3.0414	1.5188	1.2253	1.3037	0.0707
9	1/18/2002	184	3.2236	3.0559	1.5187	1.3130	1.3971	0.0398
10	2/21/2002	210	3.2490	3.0800	1.5129	1.2378	1.3171	0.0636
11	3/22/2002	239	3.2283	3.0604	1.5126	1.2908	1.3735	0.0455

C_f = 1.0640 g $Ca(OH)_2$ before titration/g $Ca(OH)_2$ after titration (see Equation I.2)

C_f , in this case, is the average from 0 – Air and 0 – No Air, which are duplicates of the same untreated material

† Average from 0 – Air and 0 – No Air

Table M.2 Data for lime-treatment of old stored bagasse at 23°C.

	Air									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	W_2 (g)	$W_2(1-X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
0	7/18/2001	0	3.2081	3.0226	3.0328	2.9865	0.9902†	23.98†	12.84†	0.0647	0.0108
1	7/25/2001	7	3.2169	3.0495	2.7349	2.6397	0.866	20.77	15.19	0.1731	0.0557
2	8/1/2001	14	3.2087	3.0418	2.6804	2.6050	0.856	20.14	13.30	0.1889	0.0561
3	8/8/2001	21	3.2035	3.0368	2.5568	2.4889	0.820	19.47	13.94	0.2038	0.0588
4	8/16/2001	29	3.2047	3.0380	2.5611	2.4696	0.813	18.27	11.09	0.2086	0.0571
5	9/17/2001	61	3.2037	3.0370	2.4844	2.3956	0.789	18.23	16.02	0.2188	0.0568
6	10/17/2001	91	3.2234	3.0557	2.4934	2.4244	0.793	16.88	13.85	0.2506	0.0620
7	11/19/2001	124	3.2092	3.0422	2.4059	2.3469	0.771	15.24	17.27	0.2734	0.0642
8	12/13/2001	148	3.2077	3.0408	2.3998	2.3496	0.773	15.12	14.84	0.2470	0.0604
9	1/18/2002	184	3.208	3.0411	2.3095	2.2649	0.745	14.52	15.86	0.2559	0.0587
10	2/21/2002	210	3.2011	3.0048	2.2207	2.1772	0.725	13.56	14.36	0.2631	0.0572
11	3/22/2002	239	3.2086	3.0119	2.2035	2.1452	0.712	12.86	11.11	0.2148	0.0502
	No Air (Capped)									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	W_2 (g)	$W_2(1-X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
0	7/18/2001	0	3.2015	3.0073	3.0457	2.9839	0.9902†	23.98†	12.84†	0.0616	0.0104
1	7/25/2001	7	3.2138	3.0466	3.1574	2.3881	0.784	21.04	13.04	0.1786	0.0557
2	8/1/2001	14	3.2106	3.0436	2.6748	2.5901	0.851	19.74	18.83	0.1800	0.0558
3	8/8/2001	21	3.2023	3.0357	2.5904	2.4895	0.820	19.42	14.07	0.1901	0.0559
4	9/10/2002	29	3.2084	3.0060	2.5467	2.4929	0.829	19.83	11.98	0.1805	0.0575
5	9/17/2001	61	3.2086	3.0417	2.5302	2.4253	0.797	18.91	14.16	0.2061	0.0584
6	10/17/2001	91	3.2102	3.0432	2.5331	2.4720	0.812	18.79	14.10	0.1897	0.0564
7	11/19/2001	124	3.2201	3.0526	2.3935	2.3255	0.762	17.15	16.66	0.2197	0.0599
8	12/13/2001	148	3.209	3.0421	2.3905	2.3384	0.769	16.51	17.26	0.2484	0.0627
9	1/18/2002	184	3.2135	3.0463	2.338	2.2902	0.752	17.57	13.75	0.2114	0.0578
10	2/21/2002	210	3.2346	3.0663	2.3705	2.3268	0.759	17.53	14.24	0.2202	0.0593
11	3/22/2002	239	3.2075	3.0406	2.4545	2.3818	0.783	18.47	14.11	0.1965	0.0600

Abbreviations: A.I. ≡ acid-insoluble, unt ≡ untreated, treated ≡ treated bagasse, for other nomenclature see Appendix I

Table M.3 Lime consumption values for old stored bagasse treatment at 30°C.

Air

n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	$W_{Ca(OH)2}$ (g)	W_{left} (g)	W_{corr} (g)	g Ca(OH)2/g untreated bagasse
0(1)	1/23/2003	0	3.2248	3.0489	1.5094	1.438595	1.50831	0.0004
0(2)	1/23/2003	0	3.2219	3.0462	1.5143	1.440076	1.509863	0.0015
0(3)	1/23/2003	0	3.2201	3.0445	1.5024	1.438224	1.507921	-0.0018
1	1/30/2003	7	3.2364	3.0584	1.7677	1.6056	1.6835	0.0275
2	2/6/2003	14	3.2292	3.0516	1.5042	1.2953	1.3580	0.0479
3	2/13/2003	21	3.2027	3.0265	1.5060	1.2964	1.3592	0.0485
4	2/20/2003	28	3.2137	3.0369	1.5143	1.2856	1.3479	0.0548
5	3/23/2003	59	3.2556	3.0765	1.5019	1.2204	1.2796	0.0723
6	4/23/2003	90	3.2149	3.0381	1.5051	1.2086	1.2672	0.0783
7	5/23/2003	120	3.2077	3.0313	1.5225	1.1701	1.2268	0.0976
8	6/23/2003	151	3.2118	3.0351	1.5078	1.1456	1.2011	0.1010
9	7/23/2003	181	3.2234	3.0461	1.5024	1.0349	1.0850	0.1370
10 (1)	8/23/2003	212	3.2156	3.0387	1.5042	1.0345	1.0846	0.1381
10 (2)	8/23/2003	212	3.2042	3.0280	1.5268	1.0619	1.1134	0.1365
11 (3)	8/23/2003	212	3.2409	3.0626	1.5028	1.0208	1.0703	0.1412

No Air (Capped)

n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	$W_{Ca(OH)2}$ (g)	W_{left} (g)	W_{corr} (g)	g Ca(OH)2/g untreated bagasse
1	1/30/2003	7	3.2345	3.0566	1.5034	1.3360	1.4007	0.0336
2	2/6/2003	14	3.2060	3.0297	1.5058	1.3416	1.4066	0.0328
3	2/13/2003	21	3.2040	3.0278	1.5097	1.3286	1.3930	0.0386
4	2/20/2003	28	3.2082	3.0317	1.5050	1.3301	1.3945	0.0364
5	3/23/2003	59	3.2156	3.0387	1.5139	1.3316	1.3961	0.0388
6	4/23/2003	90	3.2041	3.0279	1.5185	1.3212	1.3852	0.0440
7	5/23/2003	120	3.2097	3.0332	1.5288	1.3227	1.3868	0.0468
8	6/23/2003	151	3.2246	3.0472	1.5017	1.3175	1.3813	0.0395
9	7/23/2003	181	3.2655	3.0859	1.5062	1.2953	1.3580	0.0480
10(1)	8/23/2003	212	3.2116	3.0349	1.5194	1.3167	1.3805	0.0458
10(2)	8/23/2003	212	3.2518	3.0729	1.5240	1.3082	1.3716	0.0496
10(3)	8/23/2003	212	3.2051	3.0288	1.5054	1.3064	1.3697	0.0448

C_f = 1.0485 g $Ca(OH)_2$ before titration/g $Ca(OH)_2$ after titration (see Equation I.2)

C_f , in this case, is the average from 0(1), 0(2), and 0(3), which are triplicates of the same untreated material

Table M.4 Data for lime-treatment of old stored bagasse at 30°C.

Air										3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	W_2 (g)	$W_2(1-X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
0(1)	1/23/2003	0	3.2226	3.0469	2.9280	2.8663	0.9407	23.04	19.66	0.0846	0.0171
0(2)	1/23/2003	0	3.2272	3.0512	2.9429	2.8828	0.9448	23.61	16.05	0.0854	0.0171
0(3)	1/23/2003	0	3.2257	3.0498	2.9634	2.9137	0.9554	23.51	16.24	0.0848	0.0174
1	1/30/2003	7	3.2126	3.0359	2.6357	2.5694	0.8463	20.95	12.82	0.1975	0.0598
2	2/6/2003	14	3.2057	3.0294	2.5380	2.5213	0.8323	18.87	13.43	0.2146	0.0615
3	2/13/2003	21	3.2354	3.0574	2.5225	2.4549	0.8029	18.17	12.96	0.2112	0.0564
4	2/20/2003	28	3.2262	3.0487	2.4528	2.4046	0.7887	18.11	14.73	0.2228	0.0597
5	3/23/2003	59	3.2078	3.0314	2.3404	2.2656	0.7474	15.82	16.58	0.2345	0.0598
6	4/23/2003	90	3.205	3.0287	2.2673	2.1904	0.7232	14.98	19.70	0.2488	0.0602
7	5/23/2003	120	3.2348	3.0569	2.2198	2.1520	0.7040	14.70	16.48	0.2614	0.0606
8	6/23/2003	151	3.2274	3.0499	2.2735	2.2006	0.7215	14.66	13.96	0.2651	0.0582
9	7/23/2003	181	3.2317	3.0539	2.1426	2.0949	0.6860	13.07	16.28	0.2628	0.0567
10(1)	8/23/2003	212	3.2152	3.0384	2.1300	2.0684	0.6808	13.01	17.48	0.2821	0.0584
10(2)	8/23/2003	212	3.2321	3.0543	2.1110	2.0595	0.6743	12.70	19.44	0.2663	0.0547
10(3)	8/23/2003	212	3.2122	3.0355	2.0721	2.0119	0.6628	12.67	18.43	0.2546	0.0529

No Air (Capped)										3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	W_2 (g)	$W_2(1-X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
1	1/30/2003	7	3.2051	3.0288	2.6321	2.5730	0.8495	20.87	15.04	0.1993	0.0601
2	2/6/2003	14	3.2044	3.0281	2.5732	2.5608	0.8457	20.30	13.33	0.1957	0.0585
3	2/13/2003	21	3.2041	3.0279	2.5369	2.4641	0.8138	19.81	13.04	0.2045	0.0598
4	2/20/2003	28	3.2075	3.0311	2.5253	2.4739	0.8162	19.88	11.71	0.2003	0.0608
5	3/23/2003	59	3.2049	3.0286	2.4585	2.3779	0.7851	18.54	15.25	0.2000	0.0592
6	4/23/2003	90	3.2038	3.0276	2.296	2.2268	0.7355	17.04	16.36	0.2163	0.0595
7	5/23/2003	120	3.204	3.0278	2.3965	2.3381	0.7722	18.42	14.99	0.2074	0.0613
8	6/23/2003	151	3.2112	3.0346	2.4476	2.3759	0.7830	18.15	15.41	0.2187	0.0643
9	7/23/2003	181	3.2096	3.0331	2.2126	2.1777	0.7180	16.76	15.57	0.2065	0.0561

Table M.4 Continued

	No Air (Capped)									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1\text{-}X_1)$ (g)	W_2 (g)	$W_2(1\text{-}X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
10(1)	8/23/2003	212	3.2103	3.0337	2.1403	2.0921	0.6896	15.71	19.90	0.2239	0.0572
10(2)	8/23/2003	212	3.2209	3.0437	2.09	2.0401	0.6702	15.33	15.51	0.2227	0.0570
10(3)	8/23/2003	212	3.2903	3.1093	2.4548	2.3889	0.7683	17.26	17.96	0.2163	0.0625

Abbreviations: A.I. ≡ acid-insoluble, unt ≡ untreated, treated ≡ treated bagasse, for other nomenclature see Appendix I

Table M.5 Lime consumption values for old stored bagasse treatment at 40°C.

Air								
n	Date	Time (days)	W_1 (g)	$W_1(1\text{-}X_1)$ (g)	$W_{Ca(OH)2}$ (g)	W_{left} (g)	W_{corr} (g)	g Ca(OH)2/g untreated bagasse
0(1)	5/01/2002	0	3.2248	3.0489	1.5094	1.4386	1.5083	0.0004
0(2)	5/01/2002	0	3.2219	3.0462	1.5143	1.4401	1.5099	0.0015
0(3)	5/01/2002	0	3.2201	3.0445	1.5024	1.4382	1.5079	-0.0018
1	5/8/2002	7	3.2165	3.0316	1.5089	1.3138	1.3774	0.0434
2	5/15/2002	14	3.2113	3.0267	1.5095	1.2853	1.3475	0.0535
3	5/22/2002	21	3.2064	3.0220	1.5062	1.2697	1.3312	0.0579
4	5/29/2002	28	3.2194	3.0343	1.5093	1.2678	1.3293	0.0593
5	7/4/2002	64	3.2232	3.0379	1.5035	1.1864	1.2439	0.0855
6	8/4/2002	95	3.2101	3.0255	1.5028	1.0667	1.1184	0.1270
7	9/4/2002	126	3.2124	3.0277	1.5077	0.9952	1.0435	0.1533
8	10/4/2002	156	3.2098	3.0252	1.5060	0.9775	1.0248	0.1591
9	11/4/2002	187	3.2136	3.0288	1.5086	0.7497	0.7860	0.2386
10	12/4/2002	217	3.2076	3.0232	1.5089	0.6008	0.6299	0.2908

Table M.5 Continued.

No Air (Capped)

n	Date	Time (days)	W_1 (g)	$W_1(1\text{-}X_1)$ (g)	$W_{Ca(OH)2}$ (g)	W_{left} (g)	W_{corr} (g)	g Ca(OH)2/g untreated bagasse
1	5/8/2002	7	3.2079	3.0235	1.5015	1.3267	1.3910	0.0365
2	5/15/2002	14	3.2067	3.0223	1.5036	1.3308	1.3953	0.0358
3	5/22/2002	21	3.2040	3.0198	1.5047	1.3256	1.3899	0.0380
4	5/29/2002	28	3.2083	3.0238	1.5016	1.3290	1.3934	0.0358
5	7/4/2002	64	3.2109	3.0263	1.5061	1.3208	1.3848	0.0401
6	8/11/2002	95	3.2077	3.0233	1.5013	1.2915	1.3541	0.0487
7	9/4/2002	126	3.2136	3.0288	1.5030	1.2671	1.3285	0.0576
8	10/4/2002	156	3.2272	3.0416	1.5036	1.3241	1.3883	0.0379
9	11/4/2002	187	3.2120	3.0273	1.5014	1.3001	1.3631	0.0457
10	12/4/2002	217	3.2043	3.0201	1.5096	1.3064	1.3697	0.0463

C_f = 1.0485 g $Ca(OH)_2$ before titration/g $Ca(OH)_2$ after titration (see Equation I.2)
C_f , in this case, is the average from 0(1), 0(2), and 0(3), which are triplicates of the same untreated material

Table M.6 Data for lime-treatment of old stored bagasse at 40°C.

	Air									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1\text{-}X_1)$ (g)	W_2 (g)	$W_2(1\text{-}X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
0(1)	5/1/2002	0	3.2226	3.0469	2.9280	2.8663	0.9407	23.04	19.66	0.0846	0.0171
0(2)	5/1/2002	0	3.2272	3.0512	2.9429	2.8828	0.9448	23.61	16.05	0.0854	0.0171
0(3)	5/1/2002	0	3.2257	3.0498	2.9634	2.9137	0.9554	23.51	16.24	0.0848	0.0174
1	5/8/2002	7	3.2114	3.0268	2.5491	2.4831	0.8204	19.35	16.80	0.1969	0.0577
2	5/15/2002	14	3.2167	3.0318	2.4193	2.3540	0.7764	18.82	11.28	0.2087	0.0617
3	5/22/2002	21	3.2052	3.0209	2.408	2.3440	0.7759	17.96	13.01	0.2285	0.0627
4	5/29/2002	28	3.2145	3.0297	2.3195	2.2669	0.7482	16.90	14.18	0.2294	0.0627

Table M.6 Continued.

	Air									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	W_2 (g)	$W_2(1-X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
5	7/4/2002	64	3.2133	3.0285	2.1703	2.1159	0.6987	14.84	13.62	0.2543	0.0630
6	8/4/2002	95	3.2073	3.0229	2.1391	2.0672	0.6838	13.88	17.86	0.2662	0.0622
7	9/4/2002	126	3.2069	3.0225	2.2139	2.1187	0.7010	12.41	17.43	0.2949	0.0649
8	10/4/2002	156	3.215	3.0301	2.063	2.0010	0.6604	11.45	17.80	0.2704	0.0595
9	11/4/2002	187	3.2098	3.0252	1.9117	1.8480	0.6109	10.11	17.83	0.2345	0.0481
10	12/4/2002	217	3.2076	3.0232	2.3803	2.3218	0.7680	9.03	17.03	---	---
6 NL	8/19/2002	94	3.2061	3.0047	2.8045	2.7599	0.9185	25.10	9.93	0.0639	0.008

	No Air (Capped)									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	W_2 (g)	$W_2(1-X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
1	5/8/2002	7	3.2383	3.0521	2.6343	2.5519	0.8361	21.02	12.28	0.1782	0.0565
2	5/15/2002	14	3.2368	3.0507	2.5528	2.4885	0.8157	19.69	13.55	0.1711	0.0545
3	5/22/2002	21	3.2264	3.0409	2.5254	2.4475	0.8049	19.72	11.96	0.1968	0.0606
4	5/29/2002	28	3.2249	3.0395	2.4787	2.4246	0.7977	19.02	14.12	0.2022	0.0632
5	7/4/2002	64	3.2301	3.0444	2.3564	2.3104	0.7589	18.44	12.94	0.1947	0.0613
6	8/4/2002	95	3.2283	3.0427	2.4394	2.3644	0.7771	18.60	16.70	0.2077	0.0650
7	9/4/2002	126	3.2037	3.0195	2.3664	2.2985	0.7612	17.83	16.90	0.2116	0.0660
8	10/4/2002	156	3.2167	3.0318	2.3512	2.2819	0.7527	17.92	12.21	0.2101	0.0655
9	11/4/2002	187	3.226	3.0405	2.298	2.2075	0.7260	17.30	15.72	0.2072	0.0661
10	12/4/2002	217	3.2223	3.0370	2.3023	2.2524	0.7416	17.61	11.48	0.2102	0.0671
6 NL	8/19/2002	94	3.2094	3.0078	2.9371	2.8921	0.9615	26.12	9.66	0.0575	0.007

Abbreviations: A.I. ≡ acid-insoluble, unt ≡ untreated, treated ≡ treated bagasse, NL ≡ no lime, for other nomenclature see Appendix I

Table M.7 Lime consumption values for old stored bagasse treatment at 50°C.

Air

n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	$W_{Ca(OH)2}$ (g)	W_{left} (g)	W_{corr} (g)	g Ca(OH)2/g untreated bagasse
0	6/12/2001	0	3.2109	3.0252	1.5345	1.4493	1.5421	0.0000†
1	6/19/2001	7	3.2148	3.0496	1.5107	1.2519	1.3321	0.0586
2	6/26/2001	14	3.2330	3.0668	1.5552	1.2230	1.3013	0.0828
3	7/3/2001	21	3.2169	3.0516	1.5682	1.2001	1.2769	0.0955
4	7/10/2001	28	3.2081	3.0432	1.5265	1.1834	1.2592	0.0878
5	8/10/2001	59	3.2356	3.0693	1.5297	0.9797	1.0424	0.1588
6	9/10/2001	90	3.2641	3.0963	1.5321	0.7967	0.8477	0.2210
7	10/10/2001	120	3.2274	3.0170	1.5548	0.7278	0.7744	0.2587
8	11/13/2001	154	3.2467	3.0351	1.5578	0.5923	0.6302	0.3056
9	12/9/2001	180	3.2386	3.0275	1.5252	0.4211	0.4481	0.3558
10	1/13/2001	215	3.2295	3.0190	1.5346	0.3489	0.3712	0.3853

No Air (Capped)

n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	$W_{Ca(OH)2}$ (g)	W_{left} (g)	W_{corr} (g)	g Ca(OH)2/g untreated bagasse
0	6/12/2001	0	3.2042	3.0098	1.5173	1.4190	1.5098	0.0000†
1	6/19/2001	7	3.2024	3.0378	1.5033	1.3186	1.4030	0.0330
2	6/26/2001	14	3.2026	3.0380	1.5388	1.3408	1.4267	0.0369
3	7/3/2001	21	3.2440	3.0773	1.5605	1.3519	1.4385	0.0396
4	9/9/2002	29	3.2061	3.0038	1.5691	1.3041	1.3876	0.0604
5	8/10/2001	59	3.2299	3.0639	1.5144	1.3186	1.4030	0.0364
6	9/10/2001	90	3.2256	3.0153	1.5261	1.3216	1.4062	0.0398
7	10/10/2001	120	3.2131	3.0037	1.5243	1.3112	1.3951	0.0430
8	11/13/2001	154	3.2377	3.0266	1.5383	1.3145	1.3987	0.0461
9	12/9/2001	180	3.2039	2.9951	1.5587	1.3375	1.4231	0.0453
10	1/13/2001	215	3.2266	3.0163	1.5602	1.3241	1.4089	0.0502

C_f = 1.0640 g $Ca(OH)_2$ before titration/g $Ca(OH)_2$ after titration (see Equation I.2)

C_f , in this case, is the average from 0 – Air and 0 – No Air, which are duplicates of the same untreated material

† Average from 0 – Air and 0 – No Air

Table M.8 Data for lime-treatment of old stored bagasse at 50°C.

	Air									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	W_2 (g)	$W_2(1-X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
0	6/12/2001	0	3.2081	3.0226	3.0328	2.9865	0.9902[†]	23.98	12.84	0.0647	0.0108
1	6/19/2001	7	3.2060	3.0412	2.4713	2.4033	0.7902	17.08	13.67	0.1809	0.0523
2	6/26/2001	14	3.1999	3.0354	2.2872	2.2413	0.7384	17.27	13.67	0.2341	0.0678
3	7/3/2001	21	3.2008	3.0363	2.4194	2.3747	0.7821	14.71	16.26	0.2965	0.0753
4	7/10/2001	28	3.2031	3.0385	2.4373	2.3837	0.7845	14.66	15.41	0.2776	0.0730
5	8/10/2001	59	3.2084	3.0435	2.2490	2.1795	0.7161	12.37	14.16	0.2735	0.0622
6	9/10/2001	90	3.2231	3.0130	2.7192	2.6324	0.8737	10.56	14.12	0.3140	0.0707
7	10/10/2001	120	3.2058	2.9968	2.0807	2.0031	0.6684	9.71	14.80	0.2785	0.0584
8	11/13/2001	154	3.2020	2.9933	2.0719	2.0133	0.6726	8.41	18.98	0.2475	0.0506
9	12/9/2001	180	3.2359	3.0250	2.0995	2.0471	0.6768	8.23	17.25	0.2313	0.0486
10	1/13/2002	215	3.2028	2.9940	2.3172	2.2872	0.7639	7.84	15.31	0.2403	0.0517

	No Air (Capped)									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	W_2 (g)	$W_2(1-X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
0	6/12/2001	0	3.2015	3.0073	3.0457	2.9839	0.9902[†]	23.98	12.84	0.0616	0.0104
1	6/19/2001	7	3.2239	3.0582	2.5619	2.4900	0.8142	18.81	13.89	0.3053	0.0923
2	6/26/2001	14	3.2236	3.0579	2.5745	2.4978	0.8168	17.33	15.92	0.2372	0.0712
3	7/3/2001	21	3.2338	3.0676	2.5187	2.4656	0.8037	18.29	12.73	0.2108	0.0654
4	7/10/2001	28	3.2366	3.0702	2.5237	2.4573	0.8004	18.24	15.97	0.2119	0.0666
5	8/10/2001	59	3.2561	3.0887	2.4824	2.4026	0.7779	17.78	13.25	0.2112	0.0663
6	9/10/2001	90	3.2351	3.0242	2.4814	2.4069	0.7959	16.73	17.11	0.2367	0.0756
7	10/10/2001	120	3.2151	3.0055	2.3823	2.3064	0.7674	17.09	14.88	0.2342	0.0757
8	11/13/2001	154	3.2268	3.0165	2.3660	2.3093	0.7656	16.13	18.86	0.2261	0.0742
9	12/9/2001	180	3.2118	3.0024	2.3585	2.2975	0.7652	16.96	13.58	0.2287	0.0757
10	1/13/2001	215	3.2263	3.0160	2.2813	2.2340	0.7407	17.18	11.47	0.2343	0.0772

Abbreviations: A.I. ≡ acid-insoluble, unt ≡ untreated, treated ≡ treated bagasse, for other nomenclature see Appendix I

[†] Average yield from 0 – air and 0 – No Air, which are simply the same untreated sample run in duplicate

Table M.9 Lime consumption values for old stored bagasse treatment at 57°C.

Air

n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	$W_{Ca(OH)2}$ (g)	W_{left} (g)	W_{corr} (g)	g Ca(OH)2/g untreated bagasse
0	7/11/2000	0	3.2149	3.0489	1.5077	1.4167	1.5077	0
1	7/17/2000	6	3.2184	3.0662	1.5213	1.1982	1.2751	0.0803
2	7/24/2000	13	3.2253	3.0728	1.5202	1.1630	1.2377	0.0919
3	7/31/2000	20	3.2198	3.0675	1.5158	1.1323	1.2050	0.1013
4	8/6/2000	26	3.2088	3.0570	1.5132	1.0978	1.1683	0.1128
5	9/11/2000	62	3.2023	3.0508	1.5211	0.9289	0.9886	0.1745
6	10/9/2000	90	3.2186	3.0664	1.5123	0.7467	0.7946	0.2340
7	11/9/2000	121	3.2210	3.0687	1.5111	0.6297	0.6701	0.2741
8	12/12/2000	154	3.2073	3.0556	1.5268	0.4019	0.4277	0.3597

No Air (Capped)

n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	$W_{Ca(OH)2}$ (g)	W_{left} (g)	W_{corr} (g)	g Ca(OH)2/g untreated bagasse
1	7/17/2000	6	3.2201	3.0678	1.5049	1.3334	1.4190	0.0280
2	7/24/2000	13	3.2195	3.0672	1.5279	1.3075	1.3914	0.0445
3	7/31/2000	20	3.2140	3.0620	1.5078	1.3186	1.4032	0.0341
4	8/6/2000	26	3.2150	3.0629	1.5199	1.3264	1.4115	0.0354
5	2/12/2001	59	3.2029	2.9806	1.5040	1.2478	1.3280	0.0591
6	10/9/2000	90	3.2172	3.0650	1.5210	1.3175	1.4021	0.0388
7	11/9/2000	121	3.2127	3.0608	1.5282	1.3212	1.4060	0.0399
8	12/12/2000	154	3.2095	3.0577	1.5018	1.2908	1.3737	0.0419

C_f = 1.0642 g $Ca(OH)_2$ before titration/g $Ca(OH)_2$ after titration (see Equation I.2)

Table M.10 Data for lime-treatment of old stored bagasse at 57°C.

	Air									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	W_2 (g)	$W_2(1-X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
0	7/11/2000	0	3.2112	3.0701	3.0872	3.0264	0.9858	24.14	15.26	0.0777	0.0036
1-d	11/24/2000	1	3.2508	3.0516	2.7115	2.6859	0.8802	20.89	14.04	0.1967	0.0670
2-d	11/25/2000	2	3.2615	3.0616	2.6683	2.5898	0.8459	19.35	14.57	0.2010	0.0693
3-d	11/26/2000	3	3.2471	3.0481	2.6229	2.5723	0.8439	19.18	12.66	0.2196	0.0738
5-d	11/28/2000	5	3.2397	3.0411	2.5663	2.3686	0.7789	19.25	10.23	0.1986	0.0642
6-d	7/17/2000	6	3.2145	3.0625	2.4385	2.3686	0.7734	15.16	18.22	0.3234	0.0712
1	2/28/2001	7	3.2090	3.0650	2.3803	2.3028	0.7513	16.36	16.34	0.2465	0.0710
2	7/24/2000	13	3.2050	3.0534	2.2695	2.2121	0.7245	13.66	17.46	0.3474	0.0748
3	7/31/2000	20	3.2176	3.0654	1.9751	1.9176	0.6256	13.92	17.07	0.3000	0.0632
4	8/6/2000	26	3.2219	3.0695	2.2708	2.2109	0.7203	12.13	20.87	0.3275	0.0735
5	9/11/2000	62	3.2066	3.0549	2.1339	2.0706	0.6778	9.94	21.23	0.3095	0.0610
6	10/9/2000	90	3.2218	3.0694	2.1728	2.1210	0.6910	8.76	18.50	0.3033	0.0656
7	11/9/2000	121	3.2212	3.0689	2.0457	2.0309	0.6618	8.26	20.37	0.2528	0.0521
8	12/12/2000	154	3.2173	3.0651	2.4826	2.4085	0.7858	6.58	14.36	0.2447	0.0511

	No Air (Capped)									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	W_2 (g)	$W_2(1-X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
1-d	11/24/2000	1	3.2239	3.0263	2.6644	2.6294	0.8689	20.55	14.90	0.1876	0.0660
2-d	11/25/2000	2	3.2172	3.0200	2.6458	2.5777	0.8535	19.15	16.57	0.1884	0.0665
3-d	11/26/2000	3	3.2216	3.0242	2.6220	2.5159	0.8319	19.39	10.83	0.1943	0.0670
5-d	11/28/2000	5	3.2388	3.0403	2.5553	2.5074	0.8247	18.82	12.72	0.2131	0.0717
6-d	7/17/2000	6	3.2192	3.0669	2.5187	2.4377	0.7948	18.12	11.87	0.2249	0.0432
1	2/28/2001	7	3.2075	3.0635	2.5068	2.4392	0.7962	17.90	14.31	0.2296	0.0730
2	7/24/2000	13	3.2078	3.0561	2.4369	2.3747	0.7771	16.87	16.86	0.3160	0.0670
3	7/31/2000	20	3.2199	3.0676	2.4616	2.3721	0.7733	18.11	15.87	0.2850	0.0663
4	8/6/2000	26	3.2223	3.0699	2.3850	2.3177	0.7550	16.14	17.56	0.2779	0.0681
5	9/11/2000	62	3.2191	3.0669	2.4051	2.3417	0.7636	14.63	21.04	0.2513	0.0823

Table M.10 Continued.

	Air									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1\text{-}X_1)$ (g)	W_2 (g)	$W_2(1\text{-}X_2)$ (g)	Y	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
6	10/9/2000	90	3.2116	3.0597	2.3597	2.3048	0.7533	15.69	19.20	0.2552	0.0845
7	11/9/2000	121	3.2100	3.0582	2.3293	2.3083	0.7548	16.40	15.03	---	---
8	12/12/2000	154	3.2093	3.0575	2.3230	2.2493	0.7357	15.54	17.40	0.2422	0.0785

Abbreviations: A.I. ≡ acid-insoluble, unt ≡ untreated, treated ≡ treated bagasse, d ≡ days, for other nomenclature see Appendix I

Table M.11 Lime consumption values for fresh bagasse treatment at 50°C.

Air								
n	Date	Time (days)	W_1 (g)	$W_1(1\text{-}X_1)$ (g)	$W_{Ca(OH)2}$ (g)	W_{left} (g)	W_{corr} (g)	g Ca(OH)2/g untreated bagasse
0	7/11/2003	0	3.2257	3.0264	1.6447	1.5164	1.6447	0
1	7/18/2003	7	3.2025	3.0112	1.5169	1.2753	1.3832	0.0444
2	7/25/2003	14	3.1866	2.9962	1.5163	1.2560	1.3623	0.0514
3	8/1/2003	21	3.1868	2.9964	1.5102	1.2023	1.3040	0.0688
4	8/8/2003	28	3.1920	3.0013	1.5194	1.2056	1.3076	0.0706
5	9/8/2003	59	3.1823	2.9922	1.5245	1.1312	1.2269	0.0995
6	10/8/2003	89	3.1896	2.9991	1.5111	1.0375	1.1253	0.1287
No Air (Capped)								
n	Date	Time (days)	W_1 (g)	$W_1(1\text{-}X_1)$ (g)	$W_{Ca(OH)2}$ (g)	W_{left} (g)	W_{corr} (g)	g Ca(OH)2/g untreated bagasse
1	7/18/2003	7	3.1858	2.9955	1.5198	1.3108	1.4217	0.0327
2	7/25/2003	14	3.1920	3.0013	1.5146	1.3016	1.4117	0.0343
3	8/1/2003	21	3.1965	3.0055	1.5268	1.3045	1.4149	0.0372
4	8/8/2003	28	3.1887	2.9982	1.5237	1.3056	1.4161	0.0359
5	9/8/2003	59	3.1833	2.9931	1.5231	1.3064	1.4169	0.0355
6	10/8/2003	89	3.1835	2.9933	1.5121	1.2960	1.4057	0.0356

C_f = 1.0846 g $Ca(OH)_2$ before titration/g $Ca(OH)_2$ after titration (see Equation I.2)

Table M.12 Data for lime-treatment of fresh bagasse at 50°C.

	Air									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	W_2 (g)	$W_2(1-X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
0	7/11/2003	0	3.2205	3.0215	2.9589	2.9079	0.9624	21.03	1.59	0.0721	0.0227
1	7/18/2003	7	3.1797	2.9897	2.4289	2.3613	0.7898	14.25	1.15	0.2474	0.1139
2	7/25/2003	14	3.1811	2.9911	2.3167	2.2341	0.7469	13.08	1.17	0.2777	0.1179
3	8/1/2003	21	3.2014	3.0102	2.2706	2.2042	0.7322	12.15	1.20	0.2807	0.1163
4	8/8/2003	28	3.1814	2.9913	2.2104	2.1755	0.7272	11.47	1.29	0.2975	0.1195
5	9/8/2003	59	3.1894	2.9989	2.1726	2.1002	0.7003	10.53	1.30	0.3327	0.1199
6	10/8/2003	89	3.1810	2.9910	2.0140	1.9679	0.6580	8.36	1.33	0.3343	0.1105
1-sh	7/18/2003	7	6.3652	5.9849	4.5647	4.4498	0.7435	9.56	0.45	0.2595	0.1367
4-sh	8/8/2003	28	6.3690	5.9885	4.2905	4.2251	0.7055	7.08	0.26	0.2931	0.1393
6-sh	10/8/2003	89	6.3645	5.9843	3.8936	3.8051	0.6358	4.32	0.27	0.3350	0.1344

	No Air (Capped)									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	W_2 (g)	$W_2(1-X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
1	7/18/2003	7	3.2171	3.0249	2.5054	2.4268	0.8023	14.49	1.11	0.2389	0.1133
2	7/25/2003	14	3.1942	3.0034	2.4402	2.3591	0.7855	13.99	1.11	0.2579	0.1190
3	8/1/2003	21	3.1810	2.9910	2.4062	2.3305	0.7792	13.51	0.96	0.2481	0.1170
4	8/8/2003	28	3.1838	2.9936	2.3927	2.3391	0.7814	13.05	1.18	0.2423	0.1150
5	9/8/2003	59	3.1824	2.9923	2.3681	2.2937	0.7665	12.95	1.04	0.2594	0.1235
6	10/8/2003	89	3.2002	3.0090	2.3191	2.2899	0.7610	12.49	0.98	0.2539	0.1216

Abbreviations: A.I. ≡ acid-insoluble, unt ≡ untreated, treated ≡ treated bagasse, sh ≡ NaOH-treated bagasse, for other nomenclature see Appendix I

Table M.13 Lime consumption values for old stored bagasse treatment at 75°C.

Air

n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	$W_{Ca(OH)2}$ (g)	W_{left} (g)	W_{corr} (g)	g Ca(OH)2/g untreated bagasse
0	7/9/2003	0	6.4463	6.0530	3.0321	2.8742	3.0321	0
1	7/16/2003	7	6.3317	5.9931	3.2481	2.6509	2.7965	0.0754
2	7/23/2003	14	6.3363	5.9975	3.2213	2.5349	2.6742	0.0912
3	7/30/2003	21	6.3134	5.9758	3.2363	2.5994	2.7422	0.0827
4	8/6/2003	28	6.3362	5.9974	3.2276	2.5124	2.6504	0.0962
5	9/5/2003	58	6.3450	6.0057	3.2365	2.2031	2.3241	0.1519
6	10/7/2003	90	6.3385	5.9996	3.2310	1.8723	1.9752	0.2093

Oxygen

n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	$W_{Ca(OH)2}$ (g)	W_{left} (g)	W_{corr} (g)	g Ca(OH)2/g untreated bagasse
1	7/16/2003	7	6.3575	6.0176	3.2032	2.4709	2.6066	0.0991
2	8/7/2003	14	6.3567	6.0091	3.2331	2.4931	2.6300	0.1004
3	8/14/2003	21	6.3257	5.9798	3.2243	2.2557	2.3796	0.1413
4	8/21/2003	28	6.3294	5.9833	3.2089	2.0379	2.1498	0.1770
5	9/5/2003	58	6.3497	6.0102	3.4468	1.9705	2.0787	0.2276
6	10/7/2003	90	6.3033	5.9663	3.3328	0.9556	1.0081	0.3896

Nitrogen

n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	$W_{Ca(OH)2}$ (g)	W_{left} (g)	W_{corr} (g)	g Ca(OH)2/g untreated bagasse
1	7/16/2003	7	6.3428	6.0036	3.2013	2.8024	2.9563	0.0408
2	7/23/2003	14	6.3143	5.9767	3.2263	2.7927	2.9461	0.0469
3	7/30/2003	21	6.3240	5.9859	3.2062	2.7694	2.9215	0.0476
4	8/6/2003	28	6.3315	5.9929	3.2162	2.7794	2.9321	0.0474
5	9/5/2003	58	6.3127	5.9752	3.3912	2.8813	3.0395	0.0589
6	10/7/2003	90	6.3465	6.0071	3.2011	2.5650	2.7058	0.0824

C_f = 1.0549 g $Ca(OH)_2$ before titration/g $Ca(OH)_2$ after titration (see Equation I.2)

Table M.14 Data for lime-treatment of old stored bagasse at 75°C.

	Air									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	W_2 (g)	$W_2(1-X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
0	7/9/2003	0	6.4463	6.0530	6.0467	6.0128	0.9934	22.44	21.32	0.0860	0.0168
1	7/16/2003	7	6.3317	5.9931	4.6894	4.6107	0.7693	15.17	21.93	0.2136	0.0616
2	7/23/2003	14	6.3363	5.9975	4.7752	4.6504	0.7754	14.61	22.77	0.2308	0.0664
3	7/30/2003	21	6.3134	5.9758	4.7465	4.6131	0.7720	15.53	20.33	0.2144	0.0639
4	8/6/2003	28	6.3362	5.9974	4.7756	4.6763	0.7797	13.10	28.59	0.2510	0.0726
5	9/5/2003	58	6.3450	6.0057	4.8533	4.7327	0.7880	11.36	22.60	0.2478	0.0686
6	10/7/2003	90	6.3385	5.9996	4.9926	4.8826	0.8138	9.90	21.02	0.2692	0.0732

	Oxygen									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	W_2 (g)	$W_2(1-X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
1	7/16/2003	7	6.3575	6.0176	4.8046	4.6928	0.7799	14.09	22.26	0.2293	0.0633
2	8/7/2003	14	6.3567	6.0091	4.8573	4.7248	0.7863	15.17	20.86	0.2437	0.0681
3	8/14/2003	21	6.3257	5.9798	4.7761	4.6349	0.7751	11.65	26.31	0.2402	0.0625
4	8/21/2003	28	6.3294	5.9833	4.6863	4.5623	0.7625	9.35	24.11	0.2591	0.0631
5	9/5/2003	58	6.3497	6.0102	4.9264	4.8084	0.8000	7.31	26.15	0.2738	0.0707
6	10/7/2003	90	6.3033	5.9663	5.6623	5.5498	0.9302	4.94	17.78	0.2496	0.0569

	Nitrogen									3-day Enzyme Digestibility	
n	Date	Time (days)	W_1 (g)	$W_1(1-X_1)$ (g)	W_2 (g)	$W_2(1-X_2)$ (g)	*Y*	g lignin/100 g treated	g A.I. Ash/ 100 g treated	Glucose Yield (g/g unt bagasse)	Xylose Yield (g/g unt bagasse)
1	7/16/2003	7	6.3428	6.0036	4.7960	4.6887	0.7810	17.92	21.29	0.2185	0.0653
2	7/23/2003	14	6.3143	5.9767	4.7861	4.6411	0.7765	18.54	18.09	0.2000	0.0619
3	7/30/2003	21	6.3240	5.9859	4.7906	4.6699	0.7802	16.85	24.08	0.1949	0.0595
4	8/6/2003	28	6.3315	5.9929	4.6826	4.5924	0.7663	17.96	19.52	0.2261	0.0681
5	9/5/2003	58	6.3127	5.9752	4.7244	4.6351	0.7757	14.65	31.43	0.2102	0.0633
6	10/7/2003	90	6.3465	6.0071	4.6549	4.5219	0.7528	16.96	15.29	0.2253	0.0668

Abbreviations: A.I. ≡ acid-insoluble, unt ≡ untreated, treated ≡ treated bagasse, for other nomenclature see Appendix I

APPENDIX N

QUALITY ASSESSMENT REPORT FOR BAGASSE PULP FROM BATCH # 1

	UNIVERSIDAD DE COSTA RICA INSTITUTO DE INVESTIGACIONES EN INGENIERÍA LABORATORIO DE PRODUCTOS FORESTALES (Institute for Engineering Research, Forest Products Laboratory) Teléfono: 207-5354, Facsímil: 224-2619, Apartado postal: 36-2060, Correo electrónico: lpf@fing.ucr.ac.cr	**LPF-R-15** (cuarta versión)
	INFORME DE ENSAYO **Test Report**	

The Forest Products Laboratory accredited the assays :"Thickness of paper and cardboard" and "Humidity level of wood", under regulations ISO IEC 25:1990 and NCR EN 45 001 on October 2000.

November 28th, 2002

REPORT SERIAL NUMBER: LPF-S-INF-046-02

TYPE: CP-2-46/AN-1-05

REPORT: A morphometric study of the fibers, refining, and sugar-cane pulp handsheets formation. Sheet characterization was based on physical, chemical, mechanical and optical properties of pulp from sugar-cane bagasse (*Saccharum officinarum),* taken from a sugar-cane processing plant in Southern Texas.

CUSTORMER: **TEXAS A&M UNIVERSITY**
Ph. D. Mark Holtzapple
College Station, Texas

Telephone: (979) 845-9708
Fax: (979) 845-6446
E-mail: mth4500@chemail.tamu.edu

SAMPLE DATE OF ARRIVAL: August, 2002

DELIVERY OF SAMPLES: Via airmail

NUMBER OF PAGES: 11

DESCRIPTION:

The customer requested, via airmail, that the Forest Products Laboratory carry out 1) the morphometric study of the fibers, 2) refining, and laboratory sheet formation, and 3) the characterization of these sheets based upon physical, chemical, mechanical, and optical properties of the pulp from sugar-cane bagasse (*Saccharum officinarum*), which was taken from a sugar-cane processing plant located in Southern Texas.

The customer sent the pulp samples with the following procedural detail: fresh bagasse was collected from a sugar mill in South Texas. No size reduction was performed on the collected bagasse. The bagasse was treated with lime and then extensively washed to remove any residual calcium carbonate that might be present. The washed, lime-treated bagasse was dried in an oven and formed hard 2-cm-thick mats. The mats were broken apart by hand, and by rubbing mats against a 4-mesh screen allowing the finer material to fall through. After the clumps were broken apart, all the materials was sieved to separate it into various particle sizes. The sieves were stacked on top of each other, coarse on top, fine on bottom. A small amount of material was placed on the top sieve, enough to fill about 25% of the sieve volume. To separate the particles, the sieve stack was tapped with a rubber mallet for about 5 minutes. The following size classifications were obtained:

Number	Fraction	Description	Mass (g)
1	Handpicking	Chunks that were removed by visual inspection	27,4
2	Coarse fiber	Portions that would not go through the 4-mesh screen during rubbing.	21,4
3	+4	Retained on 4-mesh screen during sieving	81,0
4	-4 +10	Pass 4-mesh, retained on 10-mesh	34,1
5	-10 +16	Pass 10-mesh, retained on 16-mesh	23,9
6	-16 +30	Pass 16-mesh, retained on 30-mesh	40,1
7	-30 +40	Pass 30-mesh, retained on 40-mesh	13,0
8	-40 +50	Pass 40-mesh, retained on 50-mesh	15,4
9	-50	Pass 50 mesh	39,8

After considering the amounts collected, a set of fractions were selected and mixed. These were identified as: #2 coarse fibre; #3 +4 hand picked; #4 –4/+10; y #5 -10/+16. Humidity of the mixed material was determined at 105 °C.

Morphological measurements were made on the sugar-cane bagasse fibers: length, tangential diameter, lumen thickness, wall thickness. They were classified based upon their length.

The Runkel Factor, the Flexibility Coefficient and the length-diameter ratio were parameters determined for the classification of the fibers. The experimental procedures are described by Carpio (1996). The results are in Tables 1 and 2. Figure 1 shows the fiber-sample percent distribution in the sugar-cane bagasse sample that was analyzed. Figure 2 is a micrograph of the bagasse fibers taken with a 10x zoom lens.

A sample of 121,9 g of the original material was used for pulping. This sample was hydrated for 24 hours in water and passed through a laboratory beater (holander beater) where water was added to a consistency of 1,2%.

Refining began within 10 minutes without weights for mixture homogenization. 11,9 kg of weights were installed to start the curve of refining. It took 21 minutes to reach the desired beating degree. See Figure 3.

Pulp handsheets (approximate grammage 60 g/m^2) were made from the pulp using the procedure T-200 described by TAPPI (1996). Other properties were measured following the procedures described by Blanco (1998, 2002) and TAPPI (1996): grammage, thickness, apparent density, paper air resistance (Gurley Method), pH hot extraction method, lignin Klason content, ash content at 525 °C and 900 °C, burst index, tensile index and tear index, opacity white backing, opacity paper backing, brightness, and the color (L, a, b) and (x, y, z). The conditions were of 50% ± 2% relative humidity and 23 ± 2 °C. Average results of the tests and their standard deviations are included in Table 3.

TEST DATES: 12-25 November, 2002

ANATOMY RESULTS

LABORATORIO DE PRODUCTOS FORESTALES
SECCION DE ANATOMÍA Y MORFOLOGÍA DE LA MADERA

Forest Products Laboratory
Wood Anatomy and Morphology Section
Table 1

Characteristics of Sugar-Cane Bagasse Fibers
LPF-S-INF-046-02

FIBER CHARACTERISTICS	SUGAR-CANE BAGASSE				
	Mean	Minimum	Maximum	Standard Deviation	Variation Coefficient (%)
FIBER DIMENSIONS					
Average length (µm)	1 820	737	3 775	643	35
Average tangential diameter (µm)	23	12	39	6	26
Diámetro promedio del lumen (µm)	11	2	29	5	49
Average wall thickness (µm)	6	2	11	1	28
IMPORTANT RATIOS					
Runkel Factor	1				
Flexibility coefficient (%)	49				
Ratio L/D	81				
FIBER CLASSIFICATION					
based on length	long fiber				
based on tangential diameter	fine fiber				
based on wall thickness	thick fiber				
Test date: November 26, 2002					

LABORATORIO DE PRODUCTOS FORESTALES
SECCION DE ANATOMÍA Y MORFOLOGÍA DE LA MADERA

Forest Products Laboratory
Wood Anatomy and Morphology Section
Table 2

Fiber Percent Distribution
LPF-S-INF-046-02

SUGAR CANE BAGASSE					
CLASSIFICATION	**RANGE**	**MEDIA**	**Standard Deviation**	**Variation Coefficient**	**Frequency**
	(µm)	**(µm)**	**(µm)**	**(%)**	**(%)**
Short fibers	0 a 900	801	64	8	2
Medium fibers	901 a 1 600	1 274	182	14	40
Long fibers	1 601 a 2 000	1 780	1	5	23
Very long fibers	2 001 a 3 000	2 338,61	263	11	30
Extra-long fibers	>3 000	3 386	513	15	5
					100
Test date: November 26, 2002					

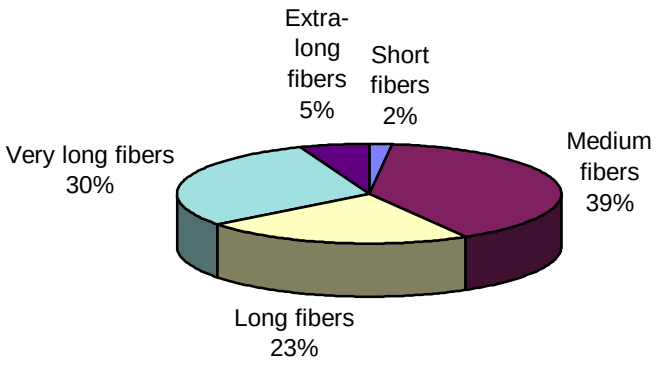

Figure 1. Percent distribution of sugar-cane bagasse fibers (*Saccharum officinarum*)

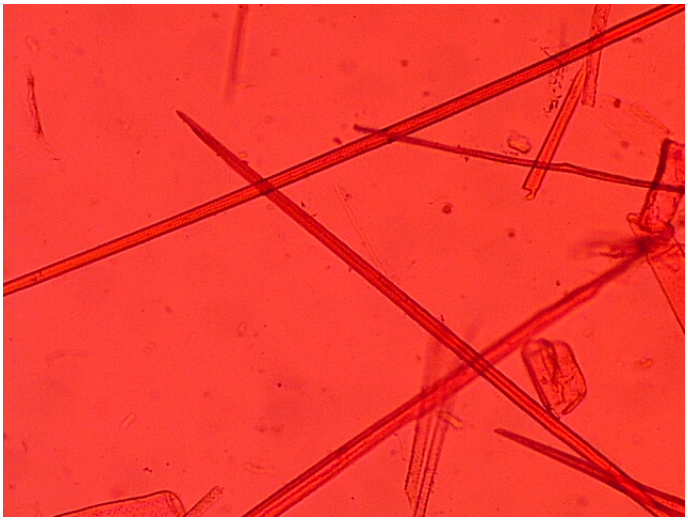

Figure 2. Microphotograph of sugar-cane bagasse fibers (*Saccharum officinarum*) (Zoom lens 10X)

PULPING RESULTS

1. The sugar-cane sample had a humidity content of 5,62% with a standard deviation of 0,06%.

2. The curve of refining was obtained using a laboratory beater type hollander beater.

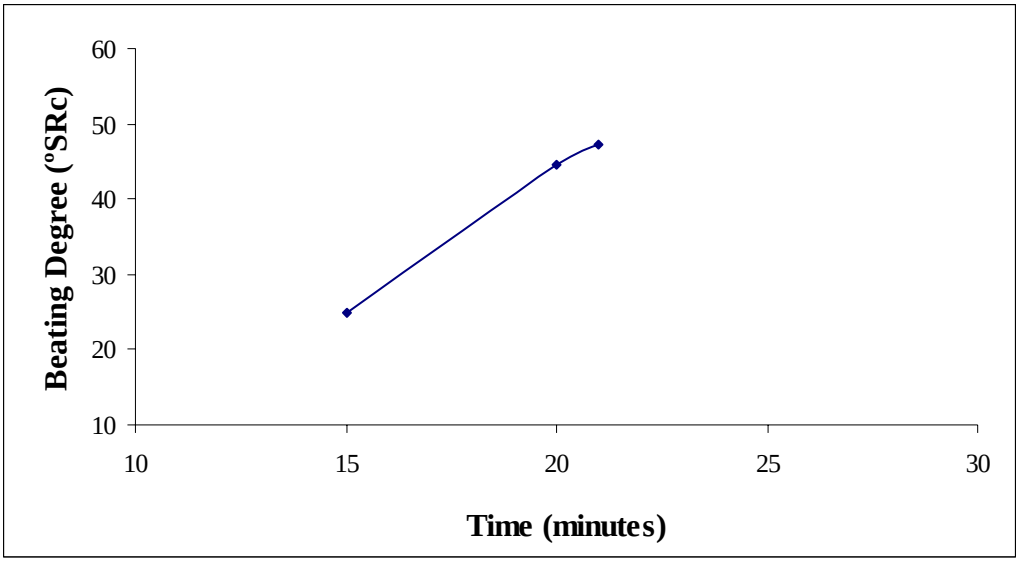

Figure 3. Beating degree profile for sugar-cane bagasse pulp (*Saccharum officinarum*)

LABORATORIO DE PRODUCTOS _mall_ALES
SECCION DE CELULOSA Y PAPEL
CUADRO N. 3

SUGAR-CANE BAGASSE PULP HANDSHEET

PROPERTIES (*Saccharum officinarum*) REFINED AT 47,3 °SR_C

LPF-S-INF-046-02

BAGASSE PULP HANDSHEET (*Saccharum officinarum*) REFINED AT 47,3 °SR_C	**Results**	
	Mean (x)	**Standard Deviation (s)**
PHYSICAL PROPERTIES		
Grammage on a conditioned weight basis (g/m^2)	68,5	0,2
Percent moisture content on a conditioned weight basis (%)	5,79	0,10
Thickness average (mm)	0,146	0,003
Thickness _mall (mm)	0,133	---
Thickness large (mm)	0,164	---
Apparent density on a conditioned weight basis (kg/m^3)	469	23
SURFACE PROPERTIES		
Air resistance of paper (Gurley Method) (s/100ml)	61,6	3,4
Air resistance of paper (Gurley Method) ($\mu m/Pa \bullet s$)	2,14	0,13
CHEMICAL PROPERTIES		
pH in hot (dimensionless)	9,40	0,02
Ash at 525 ºC (% dry basis)	11,02	0,11
Ash at 900 ºC (% dry basis)	7,57	0,03
Lignin Klason (% dry basis)	12,16	0,14
MECHANICAL PROPERTIES		
Bursting strength (kPa)	105,8	3,7
Burst index ($kPa \bullet m^2/g$)	1,5	0,1
Tensile strength (kN/m)	2,33	0,05
Breaking length (km)	3,46	0,09
Tensile index ($N \bullet m/g$)	33,92	0,87
Tearing resistance (mN)	235,4	5,1
Tear index ($mN \bullet m^2/g$)	3,4	0,1

OPTICAL PROPERTIES		
Opacity (white backing) (%)	98,9	0,8
Opacity (paper backing) (%)	102,0	0,5
Brightness (%)	28,5	0,3
Color (%)		
• L	71,18	0,13
• a	10,56	0,08
• b	18,56	0,13
Color (%)		
• X	51,19	0,20
• Y	42,46	0,19
• z	10,08	0,08
MEAN RELATIVE-HUMIDITY: 48,77% **MEAN TEMPERATURE:** 23,44 °C		
SR_c: Schopper Riegler degree		
TEST DATES: 12-25 November, 2002		

REFERENCES:

CARPIO, I. M. **Análisis morfométrico de fibras vegetales. LPF-AN-001.** Laboratorio de Productos Forestales, San José, 1996. TAPPI.

TAPPI**. Tappi. Test Methods 1996-1997**, Atlanta, 1996.

BLANCO, M. L**. Bitácora del densímetro Gurley CPE-19**. Laboratorio de Productos Forestales, San José. 1998. 47p.

BLANCO, M. L. **Espesor en papel y cartón LPF-CP-005.** Laboratorio de Productos Forestales, San José. Segunda versión, 2002. 3p.

SCOPE: The results in this report refer exclusively to the items tested under the procedures that are specified.

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TIME FOR DISPOSAL OF ASSAYED SAMPLES: 90 natural days from the date on this report.

TIME FOR DISPOSAL OF BACK-UP SAMPLES: 365 natural days from the date on this report.

SECTION: Cellulose and Paper

PRINCIPAL INVESTIGATOR:

Licda. Isabel Ma. Carpio Malavassi
Section Head. Wood Anatomy and Morphology

Ing. María Lorena Blanco Rojas, M.Sc.
Section Head. Celulosa and Paper

SUPERVISOR:

Licda. Isabel María Carpio Malavassi
Head
Forest Products Laboratory

APPENDIX O

QUALITY ASSESSMENT REPORT FOR BAGASSE PULP FROM BATCH # 2

Report to: Mr. Cesar Granda
Graduate Research Assistant
Chemical Engineering Department
Texas A & M University
M.S. 3122 Room 337
College Station, TX 77843

Sample identification: One Unbleached Bagasse Pulp Sample

Date received: September 29, 2003

Tests requested: Valley Beater Curve (Including Freeness, Handsheets, Basis Weight, Caliper, Bulk, Density, Tear, Burst, Tensile, and Gurley Porosity), Dirt Count, Ash at 525^{o}C and 900^{o}C, Klason Lignin, Brightness, Color, Opacity, MorFi Fiber Length, and Digital Microphotographs

Refining Study

Integrated Paper Services, Inc. received one pulp sample for a Valley beater curve. The pulp was separated into fiber length classes at Texas A&M prior to shipment to IPS. A MorFi fiber length analysis was run on each fiber class for comparison to a typical fiber length distribution of copy paper. The MorFi fiber length data is summarized in Table 1 on page 2. The fiber lengths of the bagasse pulp fractions were too low to simulate the fiber found in typical copy paper. The fractions listed in table 1 were blended for refining.

After refining the pulp with the Valley beater, handsheets were prepared and tested for basis weight, caliper, bulk, density, tear, burst, tensile, and Gurley porosity, dirt count, ash at 525^{o}C and 900^{o}C, Klason lignin, brightness, color, and opacity. Digital microphotographs were also taken of the pulp sample. Physical test results are summarized in Table 2 on pages 3-5.

Fiber Length Distributions

Enclosed are the results of the fiber length distribution testing performed on 6 samples. The samples were run on the Techpap MorFi LB01 system. The sample labels can be found on the top of each data page. Please note that the coarseness values listed in the results are not correct, as a known weight of the sample is needed to obtain accurate coarseness results. A known weight of sample was not run through the MorFi and 0.2 grams was entered as the weight for each sample.

Table 1. Summary of fiber length and width data for the six samples

Sample ID	Average Length Weighted in Length (mm)	Arithmetical Average (mm)	Width (micrometers)
Copy Paper	1.07	0.854	21.2
16 mesh - 20 mesh	0.69	0.507	28.1
20 mesh - 30 mesh	0.691	0.515	27.3
30 mesh - 40 mesh	0.695	0.525	27.4
40 mesh - 50 mesh	0.634	0.493	26.6
Greater than 50 mesh	0.566	0.447	28.5

The physical properties of handsheets of this pulp compared with commercial

bagasse (article attached) are low. This pulp could probably find use in filler applications such as corrugating medium or inside layers of a liner grade.

If you have any questions, please do not hesitate to call.

Signed_____

Sally A. Berben
Group Leader, Analytical Services
(920) 749-3040, Ext. 114

SAB/pas
Enclosures

Table 2. Physical Test Data

Sample ID	0 minutes	5 minutes	7 minutes	9 minutes	11 minutes
Freeness (mL)	550	306	263	245	217
Basis Wt (g/m^2)	71.1	67.4	68.9	69.1	67.1
Caliper - 5 ply (mm)					
Average	0.703	0.620	0.628	0.600	0.573
St. Dev.	0.039	0.011	0.012	0.009	0.007
Max	0.756	0.656	0.659	0.614	0.583
Min	0.653	0.603	0.615	0.579	0.560
Density (g/cm^3)	0.506	0.544	0.548	0.575	0.585
Bulk (cm^3/g)	1.98	1.84	1.82	1.74	1.71
Brightness (%)					
Average	33.70	32.58	32.49	31.68	31.53
St. Dev.	0.19	0.12	0.25	0.17	0.10
Max	33.93	32.79	32.96	31.89	31.67
Min	33.29	32.39	32.26	31.42	31.40
Color					
L	71.00	70.22	70.05	69.06	68.88
a	1.56	1.59	1.59	1.63	1.64
b	16.99	17.18	17.07	16.72	16.66
Opacity (%)					
Average	92.6	92.5	93.4	93.5	93.2
St. Dev.	0.5	0.3	0.5	0.3	0.4
Max	93.2	93.0	94.3	93.9	93.5
Min	91.6	92.1	92.9	93.0	92.2
Burst (kPa)					
Average	20.7	38.6	41.4	48.3	48.3
St. Dev	5.5	3.8	4.2	4.2	4.2
Max	27.6	41.4	44.8	55.2	51.7
Min	13.8	34.5	34.5	44.8	41.4

Table 2. Physical Test Data (continued)

Sample ID	0 minutes	5 minutes	7 minutes	9 minutes	11 minutes
Burst Index (kPa-m^2/g)	0.291	0.573	0.601	0.699	0.720
Tear (g)					
Average	9.60	11.52	12.16	12.80	11.52
St. Dev.	0.00	1.75	1.43	0.00	1.75
Max	9.60	12.80	12.80	12.80	12.80
Min	9.60	9.60	9.60	12.80	9.60
Tear Index (mN-m^2/g)	1.32	1.68	1.73	1.82	1.68
Gurley Porosity (s/100 mL)					
Average	1.9	10.3	15.5	25.3	48.8
St. Dev.	0.2	2.3	1.0	4.6	7.5
Max	2.2	14.2	17.7	30.7	60.9
Min	1.6	5.8	14.4	15.7	35.2
Tensile Strength (kN/m)					
Average	0.0857	1.134	1.373	1.464	1.379
St. Dev.	0.0377	0.110	0.034	0.232	0.211
Max	0.134	1.262	1.416	1.615	1.649
Min	0.0480	0.964	1.337	1.060	1.080
Stretch (%)					
Average	0.175	0.638	0.746	0.776	0.666
St. Dev.	0.037	0.070	0.039	0.137	0.114
Max	0.220	0.720	0.810	0.870	0.850
Min	0.130	0.530	0.710	0.540	0.550
TEA* (Joule/m^2)					
Average	0.07	4.12	6.02	6.89	5.25
St. Dev.	0.04	0.95	0.52	2.32	1.92
Max	0.12	5.39	6.81	8.61	8.27
Min	0.03	2.73	5.53	2.99	3.19

* TEA ≡ Tensile Energy Absorption

Table 2. Physical Test Data (continued)

Sample ID	0 minutes	5 minutes	7 minutes	9 minutes	11 minutes
Breaking Length (km)					
Average	0.12	1.72	2.03	2.16	2.10
St. Dev.	0.05	0.17	0.05	0.34	0.32
Max	0.19	1.91	2.10	2.38	2.51
Min	0.07	1.46	1.98	1.56	1.64
Tensile Index (N-m/g)					
Average	1.2	16.8	19.9	21.2	20.6
St. Dev.	0.5	1.6	0.5	3.4	3.1
Max	1.9	18.7	20.6	23.4	24.6
Min	0.7	14.3	19.4	15.3	16.1
Ash 525^{o}C (%)	7.41				
Ash 900^{o}C (%)	5.36				
Klason Lignin (%)	8.8				

Methods:

TAPPI T 227 om-99
Freeness of pulp (Canadian standard method)

TAPPI T 220 sp-01
Physical testing of pulp handsheets

TAPPI T 525 om-02
Diffuse brightness of pulp

TAPPI T 527 om-02
Color of paper and paperboard (d/0, C/2)

TAPPI T 425 om-01
Opacity of paper (15/d, illuminant A/2^{o}, 89% reflectance backing and paper backing)

TAPPI T 460 om-02
Air resistance of paper (Gurley method)

TAPPI T 211 om-93
Ash in wood, pulp, paper and paperboard: combustion at 525^{o}C

TAPPI T 413 om-02

Ash in wood, pulp, paper and paperboard: combustion at 900^{o}C
Lignin – Klason (acid insoluble lignin) Tappi 60(10):143-144 (October 1977).

Analysis by LAH and JPA
Quality review by SAB and JRS
Date tested: October 3 through 17, 2003

Notes: These results relate only to the items tested. This test report shall not be reproduced, except in full, without written consent of IPS. See the TAPPI test methods cited above for estimate of measurement uncertainty.

APPENDIX P

STANDARD ERROR, STANDARD DEVIATION AND PROPAGATION OF ERROR

The standard error for all the regressed parameters, as mentioned, were calculated using SAS® statistical software.

The standard deviations for the average of several observations were calculated using the "stdev" function in EXCEL™, which uses the following formula:

$$\sigma = \sqrt{\frac{\sum (x - \bar{x})^2}{n-1}} \qquad \text{(P.1)}$$

where

σ	=	The estimated standard deviation
x	=	The value for the observation
$\bar{x}$	=	The average of all the observations
n	=	The number of observations

Whenever applicable, the propagation of error in the result of two or more values being added or subtracted were calculated as follows:

Let the parameters $x_1 \pm S_1$, $x_2 \pm S_2$, …, $x_N \pm S_N$, where S is either the standard deviation or the standard error, be added or subtracted to obtain the parameter $y \pm S_y$ (i.e., $x_1(+/-)x_2(+/-)...(+/-)x_N = y$), then,

$$S_y^{\,2} = S_1^{\,2} + S_2^{\,2} + ... + S_N^{\,2} \qquad \text{(P.2)}$$

In the case of multiplication or division, the standard deviation or standard error of the result was calculated as follows:

Let $x_1(\times/\div)x_2(\times/\div)...(\times/\div)x_N = y$, then,

$$\left(\frac{S_y}{y}\right)^2 = \left(\frac{S_1}{x_1}\right)^2 + \left(\frac{S_2}{x_2}\right)^2 + ... + \left(\frac{S_N}{x_N}\right)^2 \qquad \text{(P.3)}$$

VITA

Cesar Granda Cotlear was born May 21, 1976, in Macará, province of Loja, Ecuador. He was raised in Ecuador until 1993, when he came to the United States to complete his high-school studies. In January 1995, Cesar started college in Binghamton, NY at Broome Community College. He was accepted at Texas A&M in May 1995, and received his B.S. in chemical engineering from this school in 1998. In January 1999, he started his Ph.D. in chemical engineering at Texas A&M, completing this degree in 2004.

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