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Solid-liquid separation technologies in the conversion of bagasse to liquid fuel

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SOLID-LIQUID SEPARATION TECHNOLOGIES IN THE CONVERSION OF BAGASSE TO LIQUID FUEL

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
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Master of Science in
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Engineering

in

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by

Keith Miller
B.S., Louisiana State University, 2008
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Abstract

Development of liquid biofuels has entered a new phase of large scale pilot demonstrations. A number of plants in operation or under construction face the engineering challenges of creating a viable plant design, scaling up, and optimizing various unit operations. It is well-known that separation technologies account for 50-70% of both capital and operating costs. Processes vary in terms of selection of unit operations; however, solid-liquid separations are likely to be a major contributor to the overall project costs. A typical process for ethanol production from biomass includes several solid-liquid separation steps. The nature of biomass derived materials makes it either difficult or uneconomical to accomplish complete separation in a single step.

Material balance models were developed for two bagasse-to-ethanol processes utilizing alkaline-pretreatment, and applied to evaluate the sensitivities of the process yields to separation performance. This aided in setting realistic efficiency targets for solid-liquid separations. Results from material balance calculations revealed that 10% of solid feed material can be lost to liquid streams, with an equivalent process yield reduction. Both filtration and sedimentation processes were found to have low separation efficiencies, due to small particle sizes, low density, and the fibrous nature of bagasse.

Because of low concentrations of suspended solids in the liquid stream (0.1-0.15%), recovery of solids by centrifugation may require high capital and operating costs. The efficiency of a dissolved air flotation process (DAF) for recovery of suspended solids from liquid stream derived from dilute-ammonia pretreatment process was investigated. DAF was evaluated for suspended solids recovery from the liquid stream obtained from alkaline pretreated cane bagasse. A continuous bench scale DAF clarifier was constructed and tested. The effect of additives at various chemical addition rates, air-to-solids ratios and hydraulic loadings on the DAF process was determined. Small quantities of lime were found to enhance flotation of particles and minimize the use of flocculants. Recoveries of suspended solids were in the range of 50-57% and were accompanied by a greater volume reduction than could be achieved by conventional sedimentation. The DAF process effectively concentrated solids from 0.1% in the feed material to 8-9% in the floated fraction.

Chapter 1 Introduction

1.1 Fuels from Renewable Resources

As global population grows, the demand for petroleum for power, industrial, and residential utilization will only increase, putting a greater strain on supply. This spike alone will cause more rapid petroleum depletion as a result of power production. However, transportation will also require more fuel. Population growth results in more commercial and personal transportation. Based on a 1996 review, 97% of transportation fuels were petroleum based (Mielenz, 2001). Additionally, 68% of petroleum utilized in the U.S. is for transportation purposes (Davis, Diegel and Boundy, 2008). The need for alternative fuels is becoming even more apparent since countries with unstable governments control a large percentage of petroleum supply.

To reduce the dependence on petroleum, research has been focused on the development of biofuels from renewable resources. Due to abundance to corn in the U.S., ethanol has been considered as a viable alternative to gasoline as a transportation fuel or as an additive. Based on a U.S. Department of Energy report (2007), gasoline consumption was estimated at 390 million gallons per day. Assuming the blending of ethanol at 10% (E10), 39 million gallons of ethanol should be produced daily. As of 2005, the total annual ethanol production in the U.S. was 3.9 billion gallons, or 10.7 million gallons per day—with most produced from corn. This production capacity could satisfy only ~2.5% of total gasoline utilization. U.S. Department of Energy has projected that ethanol production in 2030 will be sufficient to account for only 7.6% of all the gasoline (in 2007 the ethanol production was 4.3%). The recent introduction of automobile engines which can efficiently burn fuels with 85% ethanol concentration (E85) furthers the need increased ethanol production.

1.2 Feedstocks Used for Ethanol Production

Currently, most ethanol produced in the U.S. for transportation purposes is derived from corn (Lin and Tanaka, 2006). Increased ethanol demand for fuels has resulted in a rise in corn prices. In fact, from January 2006 to January 2007, the price of corn has almost doubled, raising concerns over the use of food crops for fuel (Nash, 2007). This increase in the price of corn has had ramifications on global food supply. These considerations have created additional pressure on production of biofuels from alternative sources. Thus, emphasis has switched to finding more sustainable feedstocks for ethanol production.

To avoid the use of food sources for fuel, research has been focused on developing new technology for conversion of agricultural byproducts, municipal wastes, and other non-food biomass into ethanol. These materials contain cellulose and hemicelluloses, which can be hydrolyzed to monomeric sugars and fermented to ethanol. Herein, the term ‘cellulosic ethanol’ will refer to ethanol produced from this type of biomass. Cellulose is a long chain of glucose molecules while hemicellulose is composed of various 5-carbon sugars—mainly xylose, but also mannose, arabinose, galactose, and rhamnose. The presence of lignin in cellulosic biomass makes the conversion to ethanol difficult. Lignin binds the cellulose and hemicellulose together, making it difficult to hydrolyze the sugars efficiently. Figure 1 illustrates the composition of cellulosic biomass and the effect that lignin has.

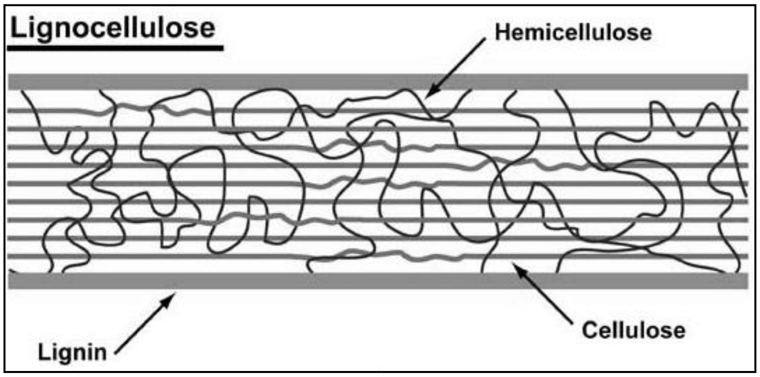

Figure 1 Structure of cellulosic biomass.

Research in the cellulosic ethanol process has shown promise for technical feasibility. However, the technology had several process-limitations slowing the expansion to large-scale production. Some of these factors include feedstock harvesting and shipment costs, pretreatment and bioconversion difficulties, processing costs, and high capital investment requirements. Researchers are currently developing solutions, which help advance processes to pilot-scale. For example, microorganisms are being genetically altered to convert multiple sugars into ethanol. Researchers at the University of Florida have altered a species to efficiently convert both hemicellulose and cellulose sugars into ethanol, where as generally these must be fermented separately (Ingram, Aldrich, Borges, Causey, Martinez, Morales, Saleh, Underwood, Yomano, York, Zaldivar and Zhou, 1999). Such advances in technology will help lower costs of producing ethanol, making it a more viable option.

Sugarcane bagasse is one example of an agricultural by-product which can be converted to ethanol. Bagasse is the residue after sugar is extracted from sugarcane (Figure 2).

Figure 2 Sugarcane bagasse.

At present, bagasse is burned to provide steam and power the sugar factories (Rein, 2007). Because of its high cellulose content, it is a viable source of cellulosic biomass for ethanol production. Even with low-efficiency boilers in raw sugar factories, all bagasse from a given sugar mill is not burned, leading to a surplus at the end of the season. Factories could increase boiler efficiencies, resulting in more excess bagasse. With changes, a typical raw sugar factory could potentially save up to 40% of bagasse.

In Louisiana, cellulosic ethanol may be a viable option, where the grinding season for raw sugar factories is generally around three months, from October to December. Due to the short milling season, factories could potentially produce ethanol from bagasse during the off-season.

1.3 General Process for Cellulosic Ethanol Production

A general flow diagram of the unit operations for cellulosic ethanol production is shown in Figure 3. Because lignin molecules bind the sugar polymers (cellulose and hemicellulose) in cellulosic biomass together, the first step in the process is to make these sugar molecules available for hydrolysis. This is accomplished using a pretreatment process.

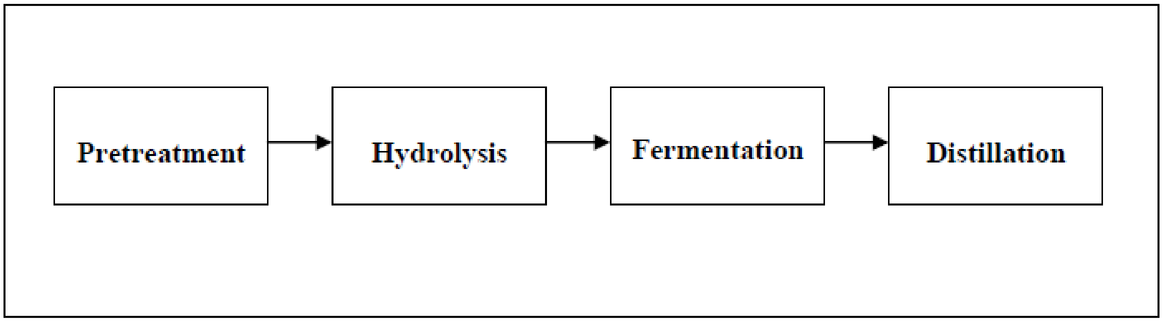

Figure 3 Block diagram of cellulosic ethanol production process.

After pretreatment the sugar polymers are more accessible for enzymatic hydrolysis, which fractures the biomass into sugars. Fermentation then produces a slurry containing ethanol mixed with the remaining liquor and residual solids. A distillation step separates the ethanol from the remaining residue.

1.4 Pretreatment Processes

Pretreatment processes disrupt the bonds between lignin, cellulose, and hemicellulose molecules. Figure 4 is an illustration of the effect of pretreatment on cellulosic biomass.

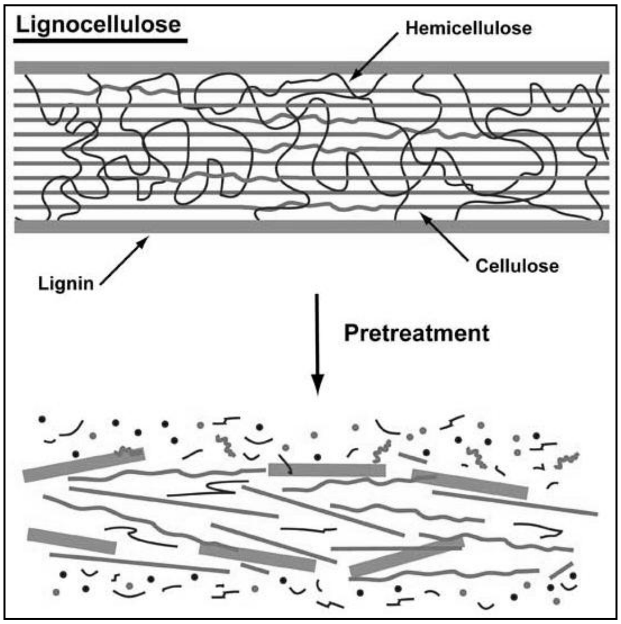

Figure 4 Effect of pretreatment processes on the structure of cellulosic biomass (Hector, Hughes and Liang-Li, 2008).

Several pretreatment methods have been developed that efficiently deconvolute cellulosic biomass. Steam explosion (Schultz, Blermann and McGinnis, 1983; Playne, 1984; Laser, Schulman, Allen, Lichwa, Antal and Lynd, 2002), Ammonia Fiber Explosion (AFEX) (Holtzapple, Lundeen, Sturgis, Lewis and Dale, 1992), lime (Chang, Burr and Holtzapple, 1997), dilute acid (Torget, Himmel, Wright and Grohmann, 1988; Aden, Ruth, Ibsen, Jechura, Neeves, Sheehan, Wallace, Montague, Slayton and Lukas, 2002) and concentrated acid (Cuzens and Miller, 1997) technologies have been tested on a pilot scale for cellulosic feedstocks. Pretreatment operations target specific components of the biomass for downstream processing. Dilute acid pretreatment solubilize lignin and hemicellulose. Concentrated acid solubilizes most of the components of the biomass. Alkaline pretreatment processes solubilize lignin, leaving cellulose and hemicellulose mostly intact.

At the Louisiana State University AgCenter's Audubon Sugar Institute (ASI), research has been focused on alkaline-based methods for pretreatment of sugarcane bagasse—using ammonium hydroxide and calcium hydroxide respectively. These processes have been proven to effectively pretreat other grassy feedstocks, such as energy cane and sweet sorghum, as well (Salvi, Aita, Robert and Bazan, 2010).

1.4.1 Dilute-Ammonia Pretreatment

ASI dilute-ammonia pretreatment involves treating biomass with heat and dilute ammonia in the pressurized reactor shown in Figure 5. This pretreatment process has proven to efficiently remove lignin and improve hydrolysis and fermentation yields. Composition of untreated bagasse is 37% glucans with approximately 21% xylans. The remaining 42% of bagasse consist of ash, lignin, and other extractives. The pretreated biomass composed of 54% glucans, 31% xylan, and 15% lignin and other non-sugars.

In the ammonia based pretreatment, cellulose is the target for conversion to ethanol. After pretreatment, the process incorporates a simultaneous saccharification and fermentation (SSF) process which combines hydrolysis and fermentation, performing both in one unit. (Ooshima, Ishitani and Harano, 1985; Szczodrak and Targonski, 1989; Philippidis, Smith and Wyman, 1993). Enzymes hydrolyze the cellulose and anaerobic microorganisms (e.g. *S. cerevisiae*) simultaneously ferment glucose to ethanol. By employing SSF in place of separate hydrolysis and fermentation steps, the amount of end-product inhibition of enzymatic hydrolysis is reduced, better yield of ethanol is obtained, enzyme requirements are decreased, and processing time is shortened (Sun and Cheng, 2002). After fermentation is complete, liquid and the remaining solids (mainly xylans and a minimal amount of unconverted cellulose) are separated. A simplified block diagram illustrating the main steps of the ASI dilute-ammonia pretreatment process is presented in Figure 6. In addition to the pretreatment, SSF, and distillation steps, several solid-liquid separations are required.

Figure 5 Dilute-ammonia pretreatment reactor.

All pretreatment processes produce fermentation-inhibiting compounds. Hydroxycarboxylic acids (e.g. glycolic acid and lactic acid) are common carbohydrate degradation products from alkaline-pretreatment processes (Klinke, Thomsen and Ahring, 2004). Depending on concentration and type of inhibitors present, fermentation of glucose by *S. cerevisiae* at common process conditions can be inhibited as much as 60% (Larsson, Palmqvist, Hahn-Hagerdal, Tengborg, Stenberg, Zacchi and Nilvebrant, 1999; Panagiotou and Olsson, 2007). To remove inhibitory components from the biomass prior to SSF, solids are washed in the same screening device (Figure 7).

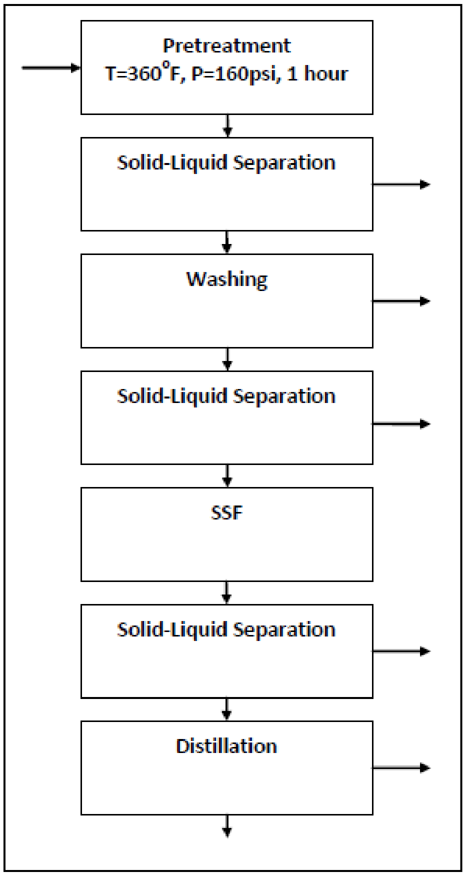

Figure 6 Block diagram of ethanol production process using ASI dilute-ammonia pretreatment.

Figure 7 Screening device used for Separation 1 and Washing.

To decrease solids moisture content for following saccharification and fermentation (SSF) step, washed solids are milled in the three-roller sample mill in Figure 8. After SSF, the residual solids, mainly xylans, are separated from the reaction mixture. Finally, ethanol is distilled from the liquid phase, and the solid phase is used for further processing.

Figure 8 Three roll sample mill used for Separation 3.

1.4.2 Calcium Hydroxide Pretreatment

Another alkaline-based pretreatment at ASI utilizes calcium hydroxide (lime) to treat sugar yields prior to enzymatic hydrolysis. This process requires 0.2g $Ca(OH)_2$ mixed with 8g distilled water per 1g biomass (dry basis). The bagasse is then autoclaved for 1 hour at 121^oC.

Lime pretreated bagasse is composed of approximately 50% glucans, 29% xylans, and 21% lignin, ash, and extractives. Hydrolysis of lime-treated bagasse resulted in digestion of up to 90% of available glucans. Fermentation converts 95% of available glucose into ethanol.

The general process for conversion of the pretreated bagasse to ethanol is similar to that of the dilute-ammonium process. However, instead of being subjected to an SSF step, pretreated bagasse is instead enzymatically hydrolyzed and then fermented in separate stages. A generalized flow sheet of this process is presented in Figure 9. As with the dilute-ammonia pretreatment process, several solid-liquid separation steps are required. A washing stage is implemented before hydrolysis to remove inhibitory components.

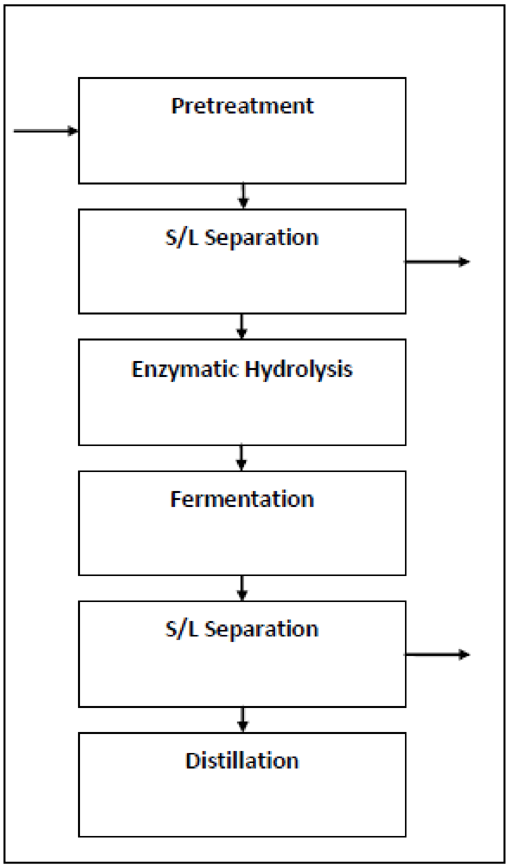

Figure 9 Block diagram of ethanol production process using ASI calcium hydroxide pretreatment process.

1.5 Process Yield

Ethanol yield from pretreated biomass is affected by the efficiency of hydrolysis and fermentation steps. Commercial enzymes are available which can hydrolyze alkali-pretreated cellulose. These cellulase enzymes have been employed in laboratory and pilot scale processes (Prior and Day, 2008). Results indicate that hydrolysis of nearly 95% of cellulose is possible. Organisms that can ferment glucose effectively at conditions found in processing cellulosic ethanol has led to high-efficiency fermentation. For example, Alterthum and Ingram report 95% efficiency in glucose fermentation by a strain of *E. Coli* (1989). Other researchers have identified process conditions and organisms (e.g. *S. cerevisiae, Z. mobilis*) which can ferment biomass-derived glucose at high efficiency (>90%).

Theoretical ethanol yield is calculated based on the stoichiometric balance for fermentation of glucose shown in Equation 1 and

Table 1.

$$C_6H_{12}0_6 \longrightarrow 2(CH_3CH_2OH) + 2(CO_2)$$

Equation 1

Table 1 Stoichiometric balance for fermentation of glucose.

	Glucose ($C_6H_{12}0_6$)	**Ethanol (CH_3CH_2OH)**	**Carbon Dioxide (CO_2)**
Molar Mass (g/mol)	180.16.	46.07	44.01
Moles	1	2	2
Mass (g)	180.16	92.14	88.02

Fermentation of one gram of glucose can potentially yield 0.51 g ethanol and 0.49 g carbon dioxide. Density of ethanol is 0.79 g/ml. Based on composition of sugarcane bagasse (approximately 37-45% glucans), theoretical yield per ton of sugar cane bagasse is 47.3-57.6 gallons of ethanol.

1.6 Process Scale-Up Limitations

A transition from laboratory experiments to pilot-scale and commercial demonstration phase processing is now in progress. The core-technologies of pretreatment, hydrolysis, and fermentation have been studied, optimized, and are available for scale-up. However, to realize a full-scale process, several separation steps are required. This presents engineering challenges in process design, scale-up, and equipment selection. Few systematic studies have been presented with respect to solid-liquid separations in cellulosic ethanol production (Kochergin, Kearney, Herbst, Mann, Garn and Hess, 2004; Burke, Andersen, Gilcrease and Menkhaus, 2009; Gertenbach and Cooper, 2009; Monavari, Galbe and Zacchi, 2009). Following features of agricultural biomass-derived feedstocks complicate the development of reliable and consistently operating solid-liquid separations.

- Variability in biomass properties throughout the processing season.
- Differences in growing areas and storage conditions drastically change filterability of pretreated biomass.
- Presence of low density particles requires stronger driving forces for effective separation
- Initial particle size reduction, which increases the available surface area and facilitates chemical reactions and mass transfer, makes the task of downstream separation of biomass components more difficult.

Separation technologies can account for 50-70% of both capital and operating costs of an industrial process(Humphrey and Keller, 1997). Therefore, cost of solid-liquid separations is is expected to have significant influence overall process operation.

Solid-liquid separation are used to recover the solids for further processing and discard the liquid, recover the liquid fraction and discard the solids, recover both the solids and the liquid, or discard both the solids and the liquid (Svarovsky, 1977). Complete isolation of the two phases is virtually impossible. A diagram is presented in Figure 10 showing the composition of two-phase systems that result from solid-liquid separations.

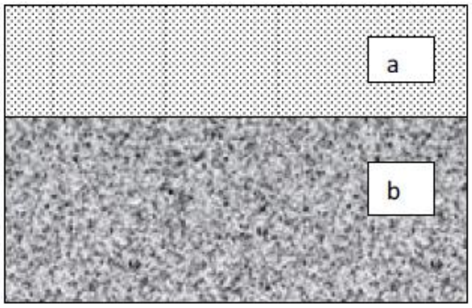

Figure 10 Solid-liquid separations (a- liquid phase with entrained solids, b- solid phase with entrained liquid).

Solid phase contains liquid, and some solid particles are entrained with the liquid fraction. Due to this, realistic separation targets for each step in the process must be established. These separation targets should be determined experimentally, based on available technologies and scale-up considerations.

1.7 Solid-Liquid Separation Efficiency Parameters

By convention, separation efficiency is expressed as the percentage of dry solids recovered during the separation. The moisture content of the solid fraction (MC_{db}) is calculated as a percentage on a dry basis using Equation 2, where m_{H_2O} and m_{dm} are the masses of water and dry matter respectively:

$$MC_{db} = \frac{m_{H_2O}}{m_{dm}}$$

Equation 2

It is important that separation efficiency targets are identified for each step of the process, and technologies are properly selected and designed to meet these goals. An inefficient separation can negatively affect the economics and yield of the process. For example, if solids are the targeted fraction for downstream processing, and the separation is inefficient, solids entrained in the liquid phase reduce the overall process yield.

The importance of separation processes for ASI sugarcane bagasse to ethanol process using dilute-ammonium pretreatment is illustrated in Figure 11.

Four solid-liquid separations are required in the process. Efficiency parameters of each will influence the yield of ethanol. In Figure 11, the targeted fraction for downstream processing is solids for Separations 1, 2, and 3. However, the liquid phase is the desired product from Separation 4. Due to differences in separation requirements, it is vital, prior to process scale-up, to identify the critical parameters for each step and evaluate their influence on overall process yield. This will allow for selection of target separation efficiencies to maximize process yield and minimize waste stream generation.

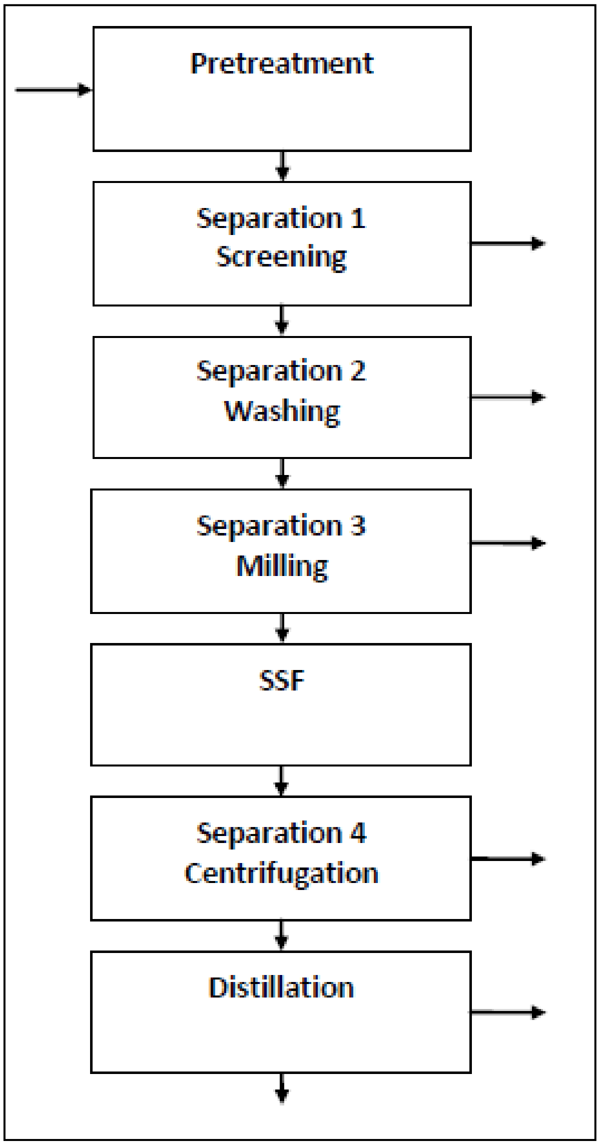

Figure 11 Simplified process flow diagram of ASI dilute-ammonia bagasse-to-ethanol process including separation steps.

1.8 Process Stream Characterization

Characteristics of process streams—such as particle size, solids concentrations, and viscosities—have an effect on separation efficiencies. To illustrate this point, the general equations governing common separations are presented in Table 2. Filtration, sedimentation, and centrifugation are affected by the size of the particles. For sedimentation, particle settling velocity is proportional to the diameter. During centrifugation, the velocity at which the liquid phase is spun off through the packed solids is proportional to the square of the particle size. For filtration, particle size affects the cake resistance term (R_c). In general, for a particular filter media at a given differential pressure and fluid viscosity, a decrease in particle size will reduce flow through the filter due to a higher cake resistance.

Table 2 Design equations for common separation techniques.

Separation Method	General Equation
Sedimentation	$V_s = \frac{g(\rho_p - \rho_l)d_p}{18\mu}$
Filtration	$\frac{1}{A}\frac{dV}{dt} = \frac{\Delta p}{\mu(R_m + R_c)}$
Centrifugation	$V_f = \frac{\rho g d^2}{150\mu}\left(\frac{\varepsilon^3}{(1-\varepsilon)^2}\right)$

Reduction of biomass size provides more surface area to facilitate chemical reactions. Some alkaline pretreatment processes operate more efficiently with smaller particle sizes. For instance, the ammonia based AFEX process was found to be more effective when treating finely ground particles (<80 μm) than coarser particles (500-800 μm) (Chundawat, Venkatesh and Dale, 2007).

To select suitable separation techniques, it is important to determine the particle sizes in the process streams. An accurate characterization is obtained by measuring the particle size distribution (PSD).

Suspended solids concentration and range of particle sizes in the feed material are known to influence settling processes. Particles larger than 200-300 μm with specific gravities higher than water (1.0) can efficiently settle out of the slurry, while smaller, low-density particles are typically lost with the supernatant. Filtration media selection is governed chiefly by the particle size; the separation efficiency attained is affected by the distribution of particle sizes. The particle retention rate—and the separation efficiency—are negatively influenced by a broad distribution of particle sizes (Kaminski, Vescan and Adin, 1997; Chang, Vigneswaran, Kandasamy and Tsai, 2008).

The physical characteristics of sugarcane bagasse make separations in the ASI processes difficult. The broad particle size distribution and low density (~120-180 kg/m^3) render common separation techniques, such as settling and filtration, inefficient. More efficient centrifugal separations require significantly higher capital and operating investments (Møller, Lund and Sommer, 2000; Gertenbach and Cooper, 2009). Thus, centrifugation should be avoided where possible, and other methods should be investigated.

1.9 Objectives

It is known that process yield loss can occur due to solid-liquid separations. However, there was no available data on the quantity of these losses for the ASI bagasse-to-ethanol processes. Realistic separation efficiency targets must be established which minimize yield loss and waste generation. Additionally, solid-liquid separation of slurries containing biomass-derived solids can be difficult, requiring multiple steps to reach the target efficiencies. Thus, three goals were identified for this project:

- Identify process stream characteristics in the ASI sugarcane bagasse-to-ethanol processes which allow for development of full material balances.
- Develop material balances, based on experimentally-determined input parameters and analyze the models to set realistic solid-liquid separation targets for the process.
    - Evaluate the sensitivities of the material balances to quantify the effects of solid-liquid separation parameters on the overall process yields and waste generation.
- Develop and test a dissolved air flotation (DAF) process for recovery of suspended solids in a dilute-ammonia pretreated bagasse process stream.

Chapter 2 Materials and Methods

2.1 Preparation of Pretreated Biomass

The following procedures specify the conditions at which biomass is treated at ASI using each of the alkaline-based pretreatments. Specific procedures for each are found in the Appendices.

2.1.1 Dilute-Ammonia Pretreated Bagasse

Ammonia pretreatment is carried out in a steam-jacketed reactor fitted to a chain-driven tumbling mechanism. Prior to pretreatment, moisture content of the bagasse is measured. In the ASI dilute-ammonia pretreatment process, dry bagasse, ammonium hydroxide, and water are required in the ratio of 1.0:0.5:8.0. Bagasse and water are initially loaded into the reactor and the reactor is sealed. One liter of water is excluded from the reactor at this point, and is loaded into a pressure vessel with the required amount of ammonium hydroxide. The pressure vessel is pressurized to 30-40 psi, then connected and discharged into to the reactor.

The biomass is then treated at 140-160 psi at approximately 320^{o}F for one hour. After the reactor has cooled, and pressure is approximately 80 psi, pretreated biomass from the tumbling reactor is discharged into a stainless steel cylindrical screen with opening size of 0.5 mm. The screen retains the pretreated bagasse while the liquid fraction drains by gravity for 10 minutes. This allows for reduction of moisture content to approximately 80%. The liquid and solid fractions are collected. A set of detailed procedures for operating the dilute-ammonia pretreatment reactor is presented in Appendix A.

2.1.2 Calcium Hydroxide Pretreated Bagasse

Calcium hydroxide pretreatment is carried out in 500 ml Erlenmeyer flasks. Calcium-hydroxide pretreatment requires dry bagasse, calcium hydroxide, and water in the ratio of 1.0:0.2:8.0. Moisture content of the bagasse is measured prior to pretreatment. Calcium hydroxide is mixed in the water, and the suspension is then mixed with the bagasse. The flask is then placed in an autoclave at 121^{o}C for one hour.

After one hour, the bagasse is separated from liquid under vacuum through a commercial screen with 0.44 mm x 5 mm slots. Filtrate from this separation was collected for further analysis. Specific procedures for calcium hydroxide pretreatment are found in Appendix B.

2.2 Experimental Procedures

Samples of process streams were taken from various stages of conversion of sugarcane bagasse into ethanol. Performance of various separation techniques were evaluated to provide information for generating a complete process material balance.

2.2.1 Settling

Settling tests were performed in a 100-ml clear graduated cylinder. Samples were heated to a temperature of 95°C, stirred well, poured into the cylinder, and allowed to settle for 10 minutes. Settling time was selected based on empirical scale-up factors for commercial clarifiers used in the sugar industry. Formation of a solid-liquid interface was observed, and the interface level was recorded every 30 seconds. The process temperature was monitored. After 10 minutes of settling, the supernatant was carefully decanted and analyzed for suspended and dissolved solids. Solids concentration and moisture content of the settled mud (underflow) were also measured.

2.2.2 Centrifugation

A Hermle Z320 centrifuge fitted with a swinging bucket rotor was used for centrifugation experiments. Samples were preheated to 95°C, placed into 50-ml Corning centrifuge tubes, and spun at 3200 rpm for four minutes. The overflow was then carefully decanted. Solid phase moisture content was measured. Concentrations of dissolved and suspended solids in the liquid phase were analyzed. The centrifugal force was selected at about 1000 G which is typical of commercially available decanter centrifuges. It is understood that the laboratory results would not directly match the separation efficiencies of commercial centrifuges, mainly due to the difference in residence time. Scale-up of centrifugation was not possible with the available quantities of feed material.

2.3 Analytical Procedures

Presented in the following sections are the procedures utilized for process stream characterization. The characteristics were selected to develop material balances for ASI dilute-ammonia and calcium hydroxide processes.

2.3.1 Suspended Solids

Suspended solids concentration was measured using a Sartorius Mark 3 moisture analyzer. A Whatman No. 4 filter paper (with a nominal particle retention size of 20-25μm) was dried and weighed on the analyzer's scale. Five milliliter samples of slurries were carefully measured then filtered. The filters were placed in the moisture analyzer for drying at 110°C until constant weight was reached (see procedure in the following chapter). The total weight of the filter, suspended solids, and water are thus calculated. The moisture analyzer is programmed to report the concentration of the total solids in mg/l. Dissolved solids concentration must be determined and subtracted from total solids to obtain the suspended solids concentration as shown in Equation 3.

$$SS = TS - DS$$

Equation 3

It is understood that a certain amount of fine particles may be carried through the filter paper during the initial phase of filtration. However, the volume of "breakthrough" particles is negligible compared to the total volume retained on the filter paper. Using paper with smaller pore size is possible but the total volume of filtered sample is reduced due to fouling. This in turn reduces the accuracy of measurement.

2.3.2 Moisture Content

Moisture contents of solid phases were determined using a Sartorius Mark 3 moisture analyzer. Samples weighing approximately 2 grams were homogenized and placed on the moisture analyzer's balance and dried at 100°C until a constant weight was obtained. The analyzer was programmed to report the moisture content as a percent dry basis.

2.3.3 Dissolved Solids Retained in Solid Phase

Refractometric dry solids were measured using a Reichert AR200 digital refractometer for streams with relatively low concentrations of suspended solids. The instrument reports the dry substance as a percentage and the concentration of dissolved solids is then calculated using Equation 4

$$DS = W_{H_2O} * \frac{RDS}{(100 - RDS)} * \frac{1000}{V}$$

Equation 4

where W_{H2O} is the mass of evaporated water from the filter in grams, *RDS* is the refractometric dry solids (in percent) measured by the instrument, and *V* is the sample volume in ml. The factor of 1000 converts the concentration into mg/l. by measuring moisture content of solid phase and dissolved solids content in the liquor, it is possible to estimate the amount of dissolved solids retained by the solid phase.

The refractometer wave length is 589 nm and it was calibrated for sugar solutions. The instrument reading may not be exact due to the presence of soluble lignins that have refractive indices different than that of solubilized sugars. The effect of lignin measurement error on overall concentration was estimated by adding lignin solution to the prepared sugar solution. Because of poor lignin solubility, at 3-4% DS, the effect of lignin was negligible (within 5%).

Solubility of 20,000MW lignin at room temperature was measured at 1.4 g/l. When suspended solids concentrations exceed 2-5 % (depending on the type of suspensions) the accuracy of dissolved solids measurements tends to decrease. For thicker suspensions, the samples should be filtered. Corrections should be made for the weight of removed suspended solids. If this is neglected, analytical errors can lead to significant discrepancies in material balance calculations (Kochergin, Olmstead and Jacob, 2001).

2.3.4 Particle Size Analysis

Particle size distribution of the streams was characterized using CILAS 1180L laser diffraction analyzer. The samples were initially prescreened through an 18 mesh (1 mm) sieve to avoid plugging of the analyzer cell. The analyzer reports the median particle size, the mean particle size, and the coefficient of variation. Three diameters were recorded—d10, d50 and d90—where 10%, 50%, and 90%, respectively, of the volume distribution falls below the measured value. A graphical distribution of the particle sizes in the slurries was also obtained.

2.3.5 pH Measurement

The pH of samples was measured using a Thermo Scientific Orion 2 Star bench-top pH meter with refillable Ag/AgCl electrodes. Because pH is temperature dependent, measurements were taken at operating conditions. A temperature increase can lead to a dissociation of molecules, especially in weak bases, such as ammonium hydroxide (Barron, Ashton and Geary, 2005). Thus, an increase in temperature may result in a decrease in pH by as much as one pH unit.

Chapter 3 Evaluation of Target Efficiencies for Solid-Liquid Separation Steps in Biofuels Production

3.1 Methodology for Selecting Target Separation Efficiency for Process Design

Material balances were developed for dilute-ammonium and calcium hydroxide pretreatment processes. Process yields were then calculated with various separation efficiencies. Reliable process scale-up requires that efficiency targets be defined for each solid-liquid separation. For example, the goal of pretreatment in the ASI processes is to partially solubilize lignin and facilitate enzymatic hydrolysis and saccharification of the cellulose fraction at high solids loading. Therefore, removal of inhibitors and subsequent cake moisture reduction must be achieved through solid-liquid separations. By utilizing the developed material balance, it was possible to evaluate the sensitivity of the process yields to separation efficiencies for each step in both processes. This allowed for the selection of realistic separation efficiencies to optimize process yields.

3.2 Material Balance Constraints and Development

The methodology applied in the present work required input parameters to be measured directly from process streams derived from pilot installations. Table 3 contains input data needed to calculate solid and liquid balances in each step of the ASI dilute-ammonia process.

Separation efficiency was defined as the fraction of suspended solids recovered from the liquid phase. Washing efficiency was calculated as the percentage of dissolved solids removed from the solid phase.

3.2.1 Effect of Separation Efficiencies on Process Yield

Results of mass balance calculations were used to model the influence of separation parameters throughout the process on ethanol yield and the volume of effluent streams. The results from these calculations for each separation are presented individually in the following sections.

Table 3 Input parameters for material balance.

Unit Operation	Measured Parameters			
	Dissolved Solids, %	**Moisture Content, %**	**Suspended Solids, %**	**Separation Efficiency, %**
Pretreatment				
Solid Biomass		x		
Pretreated Slurry	x		x	
Separation 1-Screening				X
Liquid Phase	x		x	
Solid Phase		x		
Separation 2-Washing				
Liquid Phase	x			
Solid Phase		x		
Separation 3-Milling				
Liquid Phase	x			
Solid Phase		x		
Enzymatic Hydrolysis and Fermentation				
Fermentation Slurry	x		x	
Separation 4-Centrifugation				X
Liquid Phase	x		x	
Solid Phase		x		

3.2.1.1 Separation 1—Screening

Pretreated biomass from the pretreatment reactor was discharged into a stainless steel cylindrical screen with opening size about 0.5 mm. The screen surface area was oversized to avoid pressure buildup during reactor discharge. The 80 psi discharge pressure was released instantaneously. The screen held the pretreated bagasse while the liquid fraction drained by gravity for 10 minutes. This allowed for reduction of moisture content to approximately 80%. A portion of fine suspended solids was lost in the liquid phase flowing through the screen during pressure release.

A portion of fine solid particles was carried with the liquid stream during pressure release. Measurements of volume and suspended solids concentration of collected liquid fraction showed that the loss of biomass at this step may reach as high as 3-4% of the total feed load. The screening process step described above is designated as Separation 1 in Figure 6.

A variety of separation methods may be considered for suspended solids recovery from the liquid fraction from Separation 1 and reduction of BOD and COD of the waste stream. Results of settling and centrifugal separation tests are discussed below.

Based on particle size analysis data, settling without the addition of flocculants was not expected to perform at high efficiency due to the presence of very fine particles (about 35% of particles were smaller than 100 microns). Settling tests were carried out according to the description in the Experimental Procedures section above. Due to the high turbidity of the solution, no noticeable interface was detected for the first few minutes of settling. Temperature drop was observed during the settling period, which would not be typical for operation of commercial clarifiers. Maintaining constant temperature is expected to improve settling characteristics. The average separation efficiency of the settling process was calculated at 43%. The overflow was not clear and contained a significant amount of suspended solids (concentration of 22,600 mg/l). Despite the low separation efficiency, a settling process may still be applied in combination with another more efficient method to recover suspended solids lost during Separation 1.

The experimental results of settling and centrifugation are presented in Table 4. Values of ethanol yield were calculated using the developed material balance program. Maximum theoretical yield was calculated based on the measured value of 37% glucans in raw bagasse prior to pretreatment. These data were corroborated by various researchers (Saska and Gray, 2006; Prior and Day, 2008).

Under the assumptions that 5% solids are carried with the liquid phase after Separation 1 and solids in the liquid phase are of similar composition to pretreated biomass, recovery at 43.4% efficiency could increase the ethanol recovery from 94.6% to 96.7% of theoretical yield. At 72.6% recovery measured in centrifugation tests, the yield increases from 94.6% to 98.2%.

Table 4 Effect of separation efficiencies on ethanol yield loss.

	Feed suspended solids, (mg/l)	**Overflow suspended solids, (mg/l)**	**Underflow suspended solids, (mg/l)**	**Separation Efficiency, %**	**Increase in ethanol yield, points**
Settling	35,826	22,643	57,081	43.4%	2.1
Centrifugation	25,397	8,105	97,075	72.6%	3.6

Recovery of suspended solids from the liquid fraction of Separation 1, even at relatively low efficiencies, results in a reduction of overall ethanol loss. Thus it is critical to maximize the recovery of solids entrained with the liquid phase after Separation 1 to increase overall process yield.

3.2.1.2 Separation 2—Washing

Pilot experiments at ASI showed that fermentation of pretreated bagasse in the presence of inhibiting components, such as lignin, furfurals and organic acids, without washing, can reduce the ethanol yield to 0.36 g ethanol/g glucose (De Queiroz and Stradi, 2007). As wash water usage increased, ethanol yield improved in a linear fashion. Calculated ethanol yield as a function of inhibitor removal is presented in Figure 12. Theoretical yields were calculated assuming 5.0, 7.5, and 10.0% solids loss to the liquid streams (separation efficiencies of 90, 92.5 and 95%, respectively).

Significant ethanol losses can be incurred if washing stage is not efficient. Decrease of both cake moisture content and dissolved solids content should lead to improved yields. Consequently, a combination of washing and milling may be required to achieve removal of inhibitors as well as reduce moisture contents of cakes to acceptable levels for an SSF step.

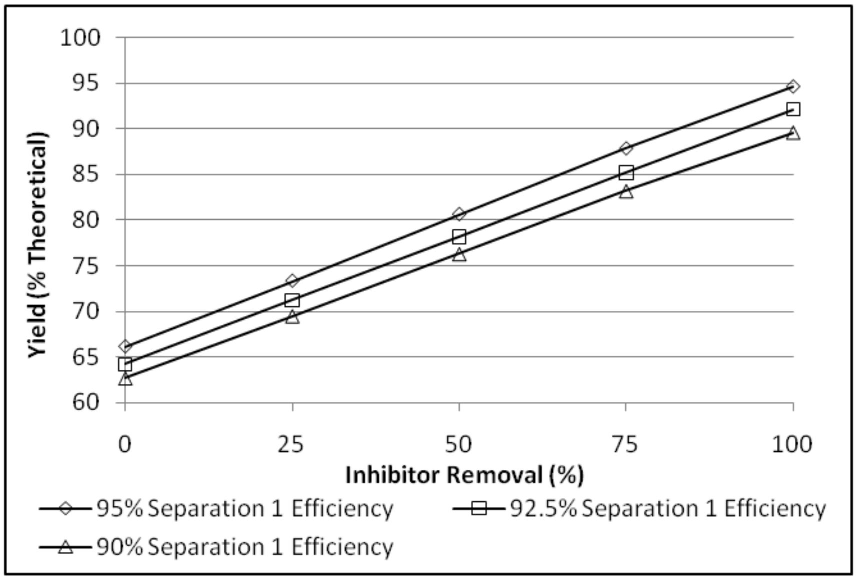

Figure 12 Effect of inhibitors on ethanol yield.

The volume of wash water is an important parameter that affects process economics. High wash water use can improve process yield by reducing concentration of inhibitors, but this will increase the volume of effluent with its concomitant cost of disposal. Single stage washing experiments were performed to obtain additional information on dissolved solids concentration of wash effluent and determine the relationship between wash water use and inhibitor removal. A 200 g sample of ammonia pretreated bagasse was collected and filtered under vacuum using a commercial screen with 0.44 mm x 5 mm slots. Cake moisture content and the concentration of dissolved solids in the filtrate were analyzed before washing. Wash water was then added within the range of 0.5-6.0 g water per g of pretreated bagasse in 0.5 g increments. Effluent from each incremental washing step was analyzed for dissolved solids. Composite effluent samples were also collected and analyzed. Washing efficiencies were calculated for each washing ratio, and results from these experiments are presented in Figure 13.

Results illustrate that complete washing in a single stage required a large volume of water (6.2:1 ratio). A multistage washing procedure will be required in a commercial process to minimize effluent volume and cost of waste handling.

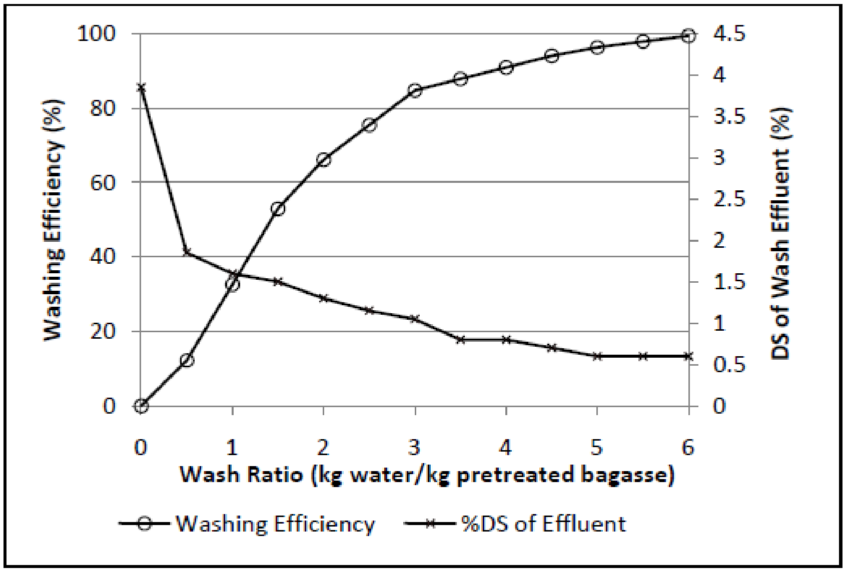

Figure 13 Evaluation of efficiency of a single stage washing step.

The ratio of wash water required to remove inhibitors is a function of both moisture content of solids from Separation 1 and washing efficiency. Cake properties also affect the washing efficiency. For illustration purposes, cake characteristics were considered to be constant. Data obtained in single stage washing experiments were used to calculate water requirements as a function of cake moisture content. Results plotted in Figure 14 are calculated values of wash water requirements at various degrees of inhibitor removal (washing efficiencies).

As a general trend, wash water volumes are reduced at lower moisture content of solid phase. For example, at 100% washing efficiency, reduction of cake moisture content from 80 to 50% results in about 65% water savings. This is especially important considering that the wash water stream must be treated as an effluent. The cost of an additional milling stage to reduce the solid phase moisture content before washing should be considered.

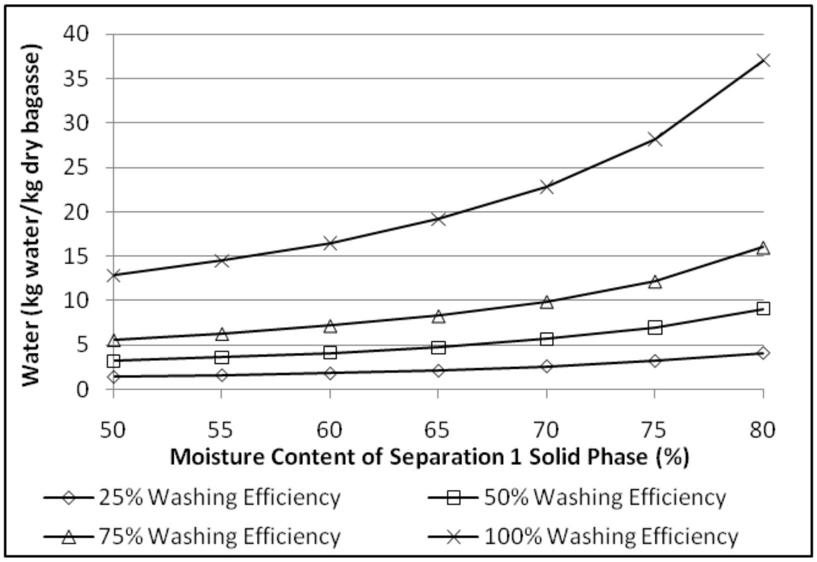

Figure 14 Effect of moisture content of Separation 1 solid phase on wash water requirements.

3.2.1.3 Separation 3—Milling

A milling stage (Separation 3) was introduced to increase solids loading for saccharification and fermentation experiments. A three-roll sample mill was used to reduce moisture content of pretreated bagasse. The major goal of milling equipment, e.g., in sugar production, is to remove liquid from the solid phase in a multistage process. It is usually accompanied by washing. Milling results in certain particle size reduction when fibers go through the mill rollers.

Because the mill does not have a means to capture fine particles and prevent them from being lost with the liquid stream, a portion of solids is always entrained in the liquid phase. Our earlier studies indicate that this loss can be as high as 3-4% of feed solids, which results in a corresponding reduction in ethanol yield. Results from the model material balance are presented in Figure 15 showing the effect of moisture content of milled cake on calculated yield. The washing efficiency at the preceding stage (Separation 2) varied in the calculations between 50 and 100%.

Results demonstrate that reduction of cake moisture is beneficial for waste reduction and improved solids content for the saccharification step. Monavari et al. came to similar conclusions while investigating the effects of washing, pressing, and filtering on the inhibitor content of pretreated biomass (2009). They found unwashed biomass produced higher sugar yields if pressing was incorporated before enzymatic hydrolysis rather than filtration. This is due pressing effectively lowering the solid phase moisture content. Thus, the amount of inhibiting components in the filtered solids was found to be higher than in pressed biomass (Monavari et al., 2009).

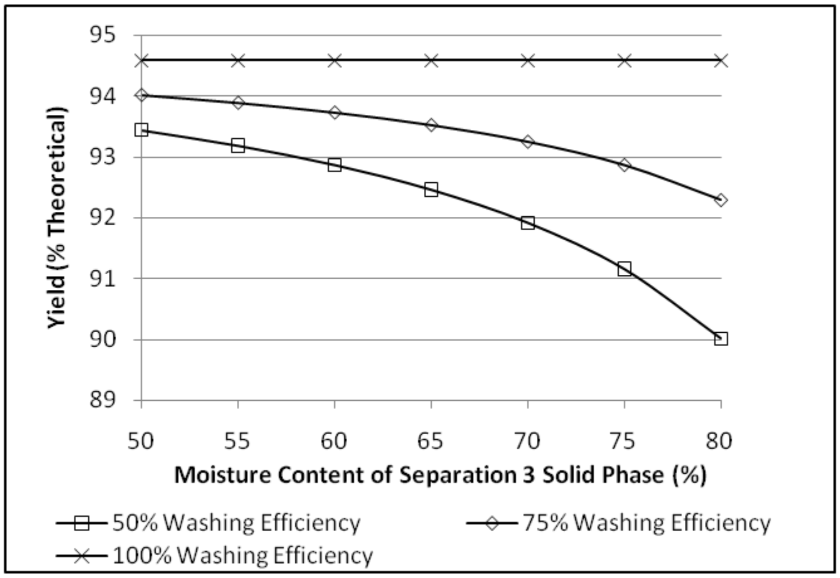

Figure 15 Effect of moisture content of milled solids on ethanol yield at various washing efficiencies at the preceding stage.

3.2.1.4 Separation 4—Centrifugation

Fermentation broth was found to contain suspended solids at a level unacceptable to directly feed a distillation column. Additionally, solid phase containing xylans can be recovered for further processing. A slurry sample after fermentation was subjected to settling and centrifugation using methods described in the Experimental Procedures section.

Virtually no separation of suspended solids was observed during settling of the fermented slurry. An interface was formed within two minutes, but the overflow level was measured at only 9% of the total cylinder height. The suspended solids concentration of the underflow was 35,200 mg/l, which was only slightly higher than the initial concentration of 32,800 mg/l. Centrifugation tests demonstrated relatively high separation efficiency (95.6%). Results representing mean values of four parallel tests are shown in Table 5. The underflow was well packed and represented 27.5% of the total original volume at moisture content of 80%.

Table 5 Separation of suspended solids from fermentation slurry.

	Feed	**Overflow**	**Underflow**	**Separation 4 Efficiency, %**
Volume, ml	40	29	11	
SS Concentration, mg/l	32,854	1,995	139,146	
Mass of Solids, mg	1,314	58	1,256	95.6

The final concentration of ethanol in the solution and the moisture content of the cake define ethanol loss with the solids fraction. Yield was calculated assuming 2.75% ethanol concentration in the liquid phase. The graph in Figure 16 illustrates that ethanol yield is more sensitive to changes in cake moisture than to separation efficiency (within the separation range expected of centrifugal operation).

The separation targets for step 4 will depend on the limitations of suspended solids content in the feed to distillation columns. An additional washing step may be considered to recover ethanol from solid precipitate.

To illustrate the sensitivity of overall process efficiencies on the parameters of solid-liquid separations, two processing scenarios were compared (Table 6).

Process parameters used in Scenario 2 are more typical for larger scale biomass separations (Glasser and Wright, 1998). A 9.7% increase in ethanol yield can be achieved by utilizing more efficient separation techniques leading to lower moisture reduction of solid cake. An additional 40% reduction in wash water requirements is expected.

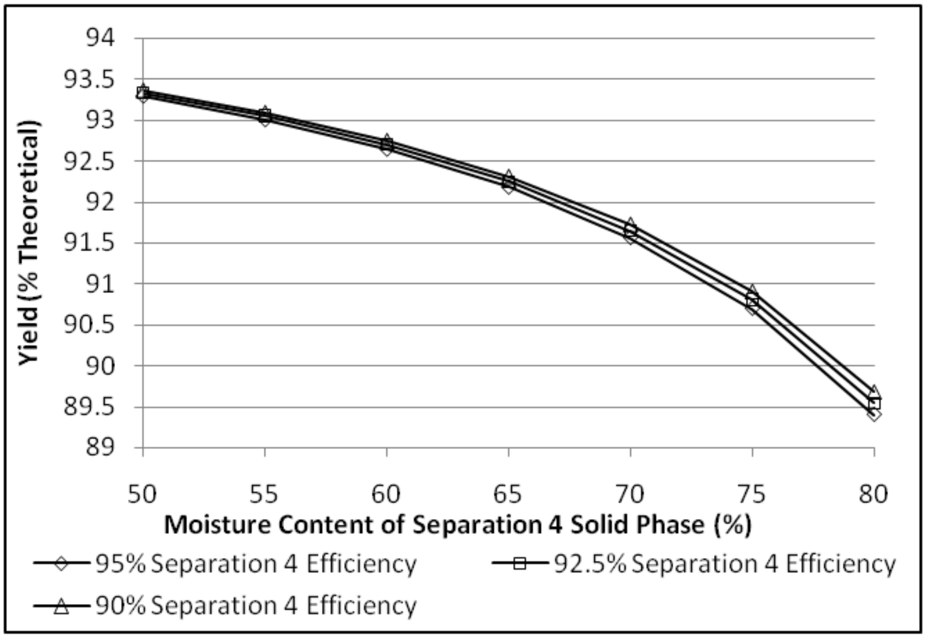

Figure 16 Effect of moisture content of Separation 4 solid phase on yield.

Table 6 Comparison of two separation scenarios.

	Scenario 1	**Scenario 2**
Separation 1		
Separation Efficiency (%)	90	95
Moisture Content (%)	80	65
Separation 2 (Washing)		
Washing Efficiency (%)	75	75
Separation 3 (Milling)		
Moisture Content (%)	70	50
Separation 4 (Centrifugation)		
Separation Efficiency (%)	90	95
Moisture Content (%)	80	65
Yield (% Theoretical)	83.7	92.7
Wash water use (kg water/kg dry bagasse)	13.15	7.89

3.3 Calcium Hydroxide Pretreatment Process

The methodology developed and applied to the dilute-ammonia pretreatment process has been applied to the calcium hydroxide pretreatment process to identify target separation efficiencies. As in the case presented previously with dilute-ammonia pretreatment, the goal of the study was to evaluate the influence of solid-liquid separations on overall process yield. A simplified block diagram outlining the major unit operations of the process is presented in Figure

17. To develop the material balance, process stream characteristics were identified and measured which allowed for full convergence of relevant constituents in the process. Using the results from these measurements, it was possible to analyze the separation performances and to quantify losses associated with separation processes.

Ten grams of dry bagasse were weighed. Moisture content was measured at 57.4% (total mass of 23.5 g). Bagasse was mixed with 80 g additional water and 2 g calcium hydroxide. These were then treated according to the methods in the Experimental Procedures.

Compositional analysis of samples was performed using standard procedures recommended by NREL (Sluiter, Hames, Ruiz, Scarlata, Sluiter and Templeton, 2006). Based on material balance calculations (before and after pretreatment), 3.14 g of dry bagasse is solubilized. Analysis of the solubilized fraction indicated that 1.2 g were glucans, 0.6 g xylans, and 1.3 g were non-fermentable solids. The pretreated bagasse is thus composed of the following: 3.4 g glucans, 1.7 g xylans, and 1.7 g non-fermentable material. Bagasse composition is summarized in Table 7.

Table 7 Mass balance of bagasse components during calcium hydroxide pretreatment.

	Bagasse		
Component	**Raw (g)**	**Pretreated (g)**	**Solubilized (g)**
Glucans	4.59	3.41	1.18
Xylans	2.39	1.75	0.64
Non-Fermentable	3.02	1.71	1.31

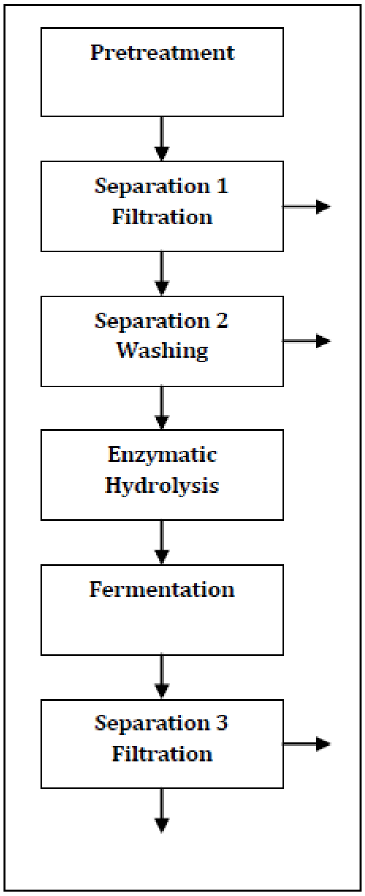

Figure 17 Simplified flow diagram of ASI calcium hydroxide bagasse-to-ethanol process.

3.3.1 Separation 1—Filtration

The effects of separation efficiency and the presence of hydrolysis-inhibiting components were evaluated using complete process material balance. Results are presented in Figure 18. In the model, it was assumed that hydrolysis of all available glucans required complete removal of inhibiting components. Theoretical yield was defined as the maximum amount of ethanol potentially produced from the glucans present in the raw biomass based on stoichiometric ratios. Actual yield will be reduced due to the portion of cellulose which is solubilized during pretreatment. This fraction is lost to the liquid stream after filtration.

Presence of hydrolysis and fermentation inhibiting components can lead to a 6% reduction in process yield. To evaluate the effect of hydrolysis and fermentation-inhibiting components at various washing efficiencies, a washing stage was investigated.

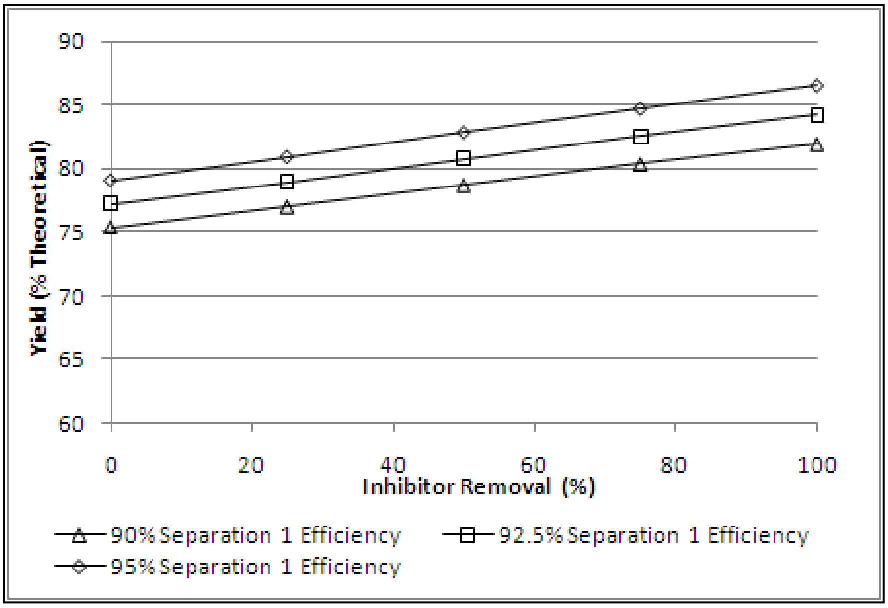

Figure 18 Effect of inhibitor removal on yield.

3.3.2 Separation 2—Washing

To complete the material balance for the calcium hydroxide pretreatment process, data was required for the washing step and its effect on downstream processing. Washing efficiency is defined as the percentage of dissolved solids which are removed from the solid phase after filtration.

To quantify the effects of washing, glucose yields from hydrolysis were evaluated after washing pretreated bagasse with increasing volumes of water. The washed solids were then hydrolyzed and glucose yields were measured. It was found that unwashed, pretreated bagasse yielded lower glucose concentrations, as expected. As wash volume increased to thirteen times the dry mass of pretreated bagasse, glucose concentration approached theoretical yields.

Reducing the moisture content of the solid phase from filtration can lower wash water requirements. Dissolved solids are carried in the filtrate, thus if more liquid is removed from the solid phase during filtration, fewer dissolved solids are present for washing operation to remove. To illustrate this, Figure 19 is a graph of the wash water requirements for washing efficiencies from 25-100% at various moisture contents.

At 75% washing efficiency, producing a solid phase from separation 1 which has moisture content of 55% rather than 80% wash water requirements can be reduced by 45%.

3.3.3 Separation 3—Filtration

The final filtration step is required to remove residual solids which were not hydrolyzed. Separation 3 occurs after fermentation, thus any liquids retained in the cake will negatively affect the overall process yield. Due to this, process yield is especially sensitive to moisture content in the solid phase, more so than to separation efficiency, as illustrated in Figure 20.

Reducing cake moisture from 80% to 50% can improve process yield by 2.5% in the range of separation efficiencies modeled. Thus, requirements of the distillation equipment with respect to solids content will be a major factor in selection of target separation efficiency for Separation 3.

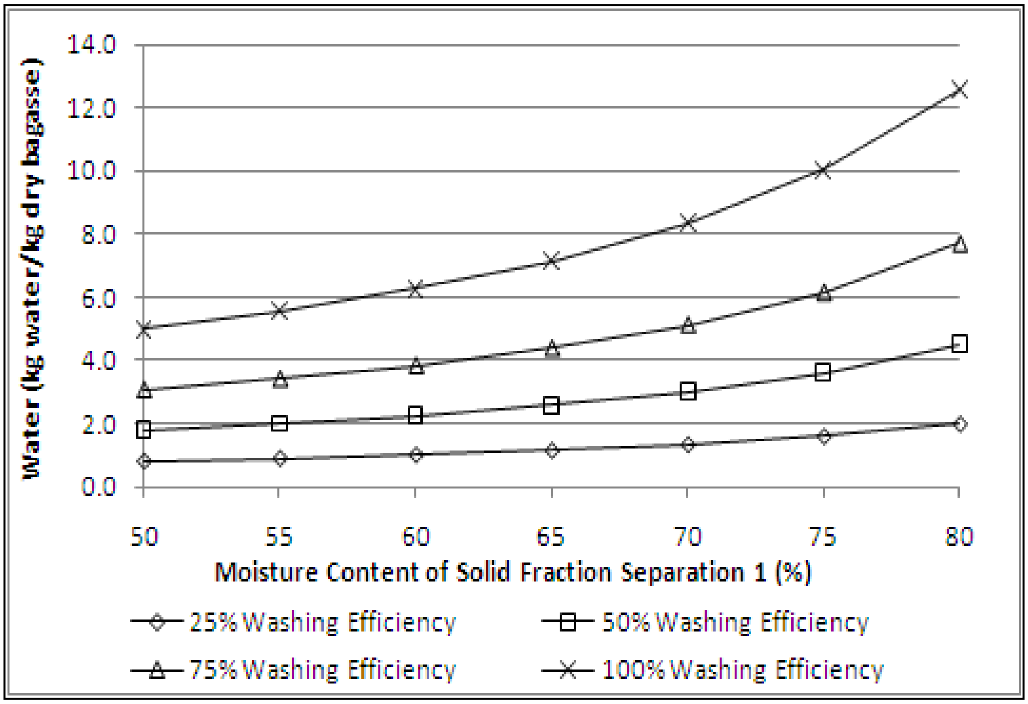

Figure 19 Wash water requirements at various washing efficiencies as a function of moisture content of solid phase from filtration.

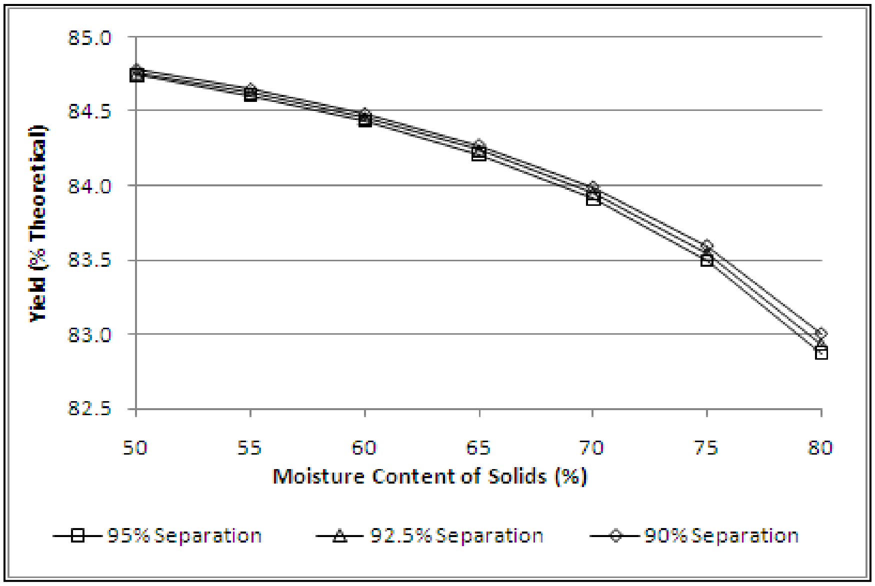

Figure 20 Effect of moisture content of solid phase from Separation 3 on overall yield.

3.4 Summary

Mass balance for a dilute-ammonia pretreatment process for bagasse was established. Input parameters were measured at both bench and pilot scale. The sensitivity of process parameters to reduction of moisture content of solid phase was determined. Separation targets were established to maximize overall process efficiency.

Reduction of both water and dissolved solids content in the solid phase affects the level of inhibitor removal and liquid effluent volume. Up to 30% yield reduction may be expected if inhibitors are not removed completely. Wash water requirements based on a single stage washing are quite high. More efficient countercurrent washing procedures must be considered for process scale-up.

Results from material balance calculations for the calcium hydroxide process suggest inhibiting components from pretreatment had a less significant effect on process yields than those in the dilute-ammonia process. A large volume of water (5-13 kg/kg dry bagasse) is required to completely remove inhibitors. Hydrolysis yields were reduced by only 6% without the use of a washing stage. Incorporating a separation after pretreatment which produces a drier solid phase could reduce the inhibitor content. The necessity of the washing stage could be reevaluated if this is accomplished.

Based on our experimental data and calculations it was concluded that the losses due to solid-liquid separations can reach up to 10% of the total solid biomass, with equivalent ethanol yield reduction. Additional separation steps may be required to recover the lost solids. Though centrifugation can provide high-efficiency separation, the associated capital and operating costs are significantly higher than other technologies. Thus, other methods of recovering biomass lost to the liquid phase during the initial screening process in the dilute-ammonia pretreatment process should be investigated.

Chapter 4 Dissolved Air Flotation (DAF) for Recovery of Suspended Solids from Pretreated Bagasse Streams

4.1 Recovery of Solids by Flotation

Results from previous studies demonstrate that efficient separation methods are critical for maximizing process yields. The broad distribution of particle sizes in pretreated bagasse streams causes settling clarification and filtration to be inefficient methods for recovery of suspended solids. Due to high capital and operational costs of processes like centrifugation, less expensive technologies to improve recoveries are required for economic feasibility of the process. Bagasse particles in the slurry after screening ammonia pretreated bagasse have a propensity to float due to low density of the fibers, the relatively low concentration of suspended solids, and the small particle sizes. Because of these characteristics, a flotation separation may be effective for recovery of suspended solids. Dissolved air flotation (DAF) is a relatively simple process employed in various industries as a means of separating particles with sizes in the range of 10-200 μm.

4.2 Flotation Separation

Flotation has been employed successfully in the mineral industry since the early 1900's as a means of separating ores. Since then, it has been introduced to industries such as wastewater treatment, dairy processing, raw sugar production, and sugar refining (Chuang, Huang and Liu, 2002; Couto, Melo and Massarani, 2004; Bento and Cuddihy, 2006; Briones, 2007). Depending on the influent characteristics and flotation process parameters, separation efficiencies range from 50-95% with floated solids concentrations reported from 0.5% up to 4.5% (de Rijk, Vandergraaf and Denblanken, 1994; Viitasaari, Jokela and Heinanen, 1995).

Flotation is categorized by the method which air is introduced to the slurry. Three main types exist—dispersed air flotation, DAF, and electroflotation (Svarovsky, 1977). In dispersed air flotation systems, bubbles are introduced by mechanical means, typically by forcing air through a porous media. DAF involves saturating liquid with air by initially subjecting the liquid to high pressure, typically in the range of 40-80 psi. Saturated liquid is then released to atmospheric pressure in a flotation cell where micro-bubbles form. Electroflotation consists of supplying current to liquid using electrodes. Anodes provide oxygen while the cathode provides hydrogen to the slurry.

Selection of a flotation method is guided in part by bubble size requirements. Dispersed air flotation generates the largest bubbles of the three methods, depending on the characteristics of the porous media utilized. Bubbles from DAF systems are typically in the range of 10-100 μm, with a mean of 40 μm being common (Edzwald, 1995). The bubbles generated in the electroflotation process are small in comparison to DAF and dispersed air systems, with researchers reporting ranges of 15-45 μm, with average bubble sizes of 30-40 μm (Burns, Yiacoumi and Tsouris, 1997; Chen, Chen and Yue, 2002).

Smaller bubbles have more total surface area for attachment to particles, thus in flotation processes, the bubble size is a critical factor for design. To properly select a flotation method bubble size and the size of the particles to be floated should be known. Recovery by flotation is most efficient for particles in the range of 10-200 μm. Low flotation efficiencies for particles outside of this range is mainly attributed to low probability of bubble-particle collision for small particles, and the high probability of detachment of particles from the bubble surface for larger particles (Tao, 2004).

4.3 Saturation Schemes in DAF

Three forms of DAF are employed industrially, based on the steam which is saturated—full-stream pressurization, split stream pressurization, and recycle-stream pressurization. Figure 21 diagrams the three modes of DAF.

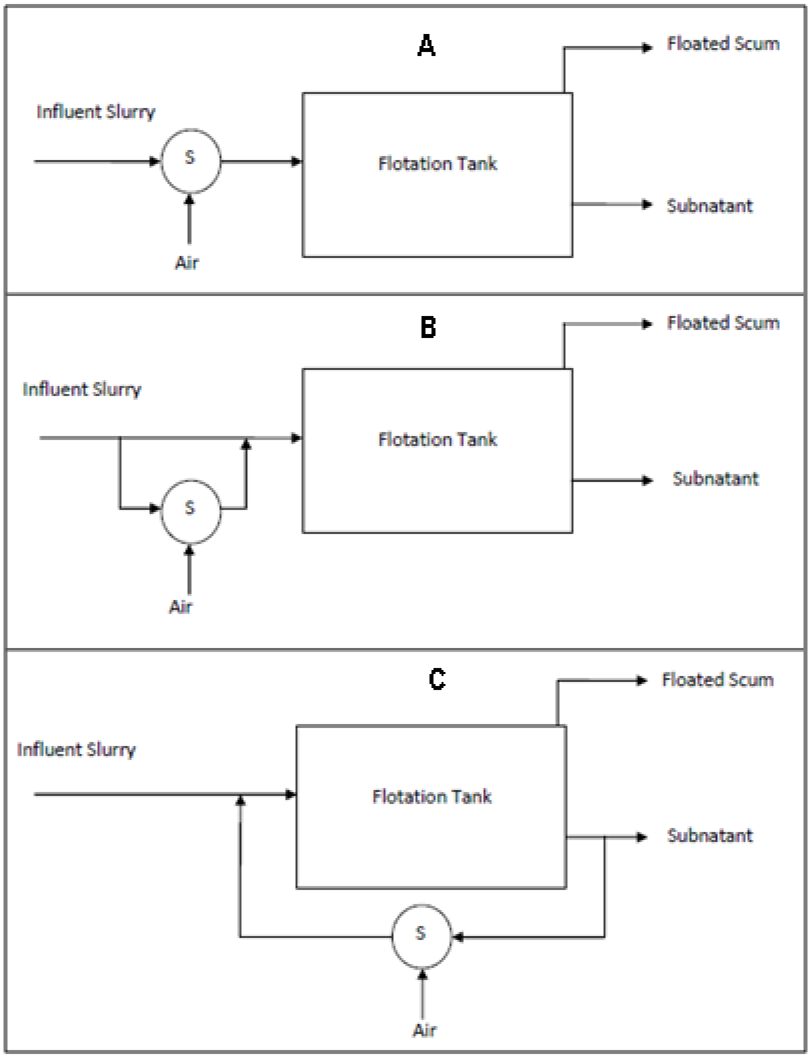

Figure 21 Pressurization schemes utilized for DAF processes. A-Full-stream pressurization. B-Partial-stream pressurization. C-Recycle-stream pressurization.

The first method is full-stream pressurization (Figure 21A), where the entire feed material is pressurized in a tank. The flow is then passed through a pressure reduction valve before entering the flotation cell. One advantage of full-stream pressurization is that the size of the flotation cell is minimized, thus reducing the capital cost for installation. However, it requires a higher head feed pump, larger pressure vessel, and results in more expensive operation compared to split-stream or recycle-stream pressurization (Wang, Shammas, Selke and Aulenbach, 2007). Other disadvantages of full-stream pressurization are the possibility of floc breakage and clogging of the inlet when sludge is passed through the pressure reducing valve.

With partial-stream pressurization (Figure 21B), a part of the fed material is pumped through the pressure vessel while the rest bypasses directly to the flotation cell. The two streams are combined before entering the flotation chamber. Advantages of this system are reductions in size of the pressurizing pump and pressure vessel. The flotation tank size would be the same as in the full-stream pressurization scheme.

For recycle-pressurization (Figure 21C), a portion of the clarified underflow (subnatant) is returned to the pressurization tank. Once saturated with air, it is introduced into the flotation chamber, where it mixes with the influent slurry. Recycle-pressurization minimizes the shear which flocs are subjected to, thus resulting in less breakage. Clogging problems, which can occur in pressurization pumps, pressure retention tanks, and pressure release valves, are also eliminated.

4.4 Design Parameters for DAF Process

Key design parameters for the DAF process include: air-to-solids ratio, recycle ratio, and hydraulic loading. These are described individually below.

4.4.1 Air-to-Solids Ratio

In DAF, the theoretical mass of air available for flotation at atmospheric pressure is dictated by Henry's Law, presented as Equation 5.

$$C_{sat} = K_H P^*$$

Equation 5

where C_{sat} is the mass concentration of air in the pressurized recycle, P^* is the saturator pressure, and K_H is Henry's Law constant for air (24.3 mg l^{-1} atm^{-1}).

Typical range of air-to-solids ratio, abbreviated a_s, in DAF treatment processes is from 0.007 to 0.7 mg/mg (Metcalf and Eddy 1991). The broad range of air-to-solids ratios is due to:

- Saturator inefficiencies, where less air is dissolved than predicted by Henry's Law.
- Broad distribution of bubble sizes where few large bubbles make up a significant fraction of mass of released air.
- Bubble-particle collision probability is not 100%; therefore excess air will be required.

The characteristics of feed material as well as configuration of the DAF unit determine the air-to-solids ratio. Thus, the most effective air-to-solids ratio for a particular feed stream must be determined experimentally. Equation 6 is used to calculate air-to-solids ratio (a_s) where

$$a_s = \frac{kK_H(fP^* - 1)R}{Qc_i}$$

Equation 6

R is the recycle flow rate (ml/min), P^* is the saturator pressure (atm), K_H is Henry's Law constant (24.3 mg l^{-1} atm^{-1}), f is the fraction of air dissolved at pressure P^*, c_i is solids concentration of influent (mg/l), and Q is the influent flow rate (ml/min). In industrial applications, f is generally in the range of 60-70% (Edzwald, 1995). For this study, a conservative f value of 0.6 was selected.

To maximize separation efficiency in a DAF process, uniformly sized bubbles must generated by raising saturator pressure and recycle ratio to increase the probability of bubble-particle attachment. However, a further increase in air-to-solids ratio will provide no improvement in separation and will be detrimental to process economics.

4.4.2 Recycle Ratio

In batch testing, the recycle ratio is defined as the percentage of pressurized liquid within the total influent to the flotation cell. For continuous flotation, the recycle ratio is defined as the percentage of effluent flow which is returned to the pressurization vessel to be saturated. Pressurization of the recycled liquid is the most common form of DAF, with recycle ratios ranging from 30-150% (Arora, Dewolfe, Lee and Grubb, 1995; Wang et al., 2007).

4.4.3 Hydraulic Loading Rate

Hydraulic loading is a measure of the flow rate through the flotation tank and, therefore, influences the liquid residence time. It is calculated using Equation 7 where Q is the total influent flow rate (recycle and feed material) and A is the surface area of the flotation tank.

$$V = \frac{Q}{A}$$

Equation 7

Hydraulic loading rate is measured in terms of $m^3\ m^{-2}\ day^{-1}$. Typical values found in industry range from 10-400 $m^3\ m^{-2}\ day^{-1}$ corresponding to retention times from 15-30 minutes. Variation is due to differences in feed stream characteristics. Dilute streams can be treated at higher hydraulic loading rates, where concentrated streams are limited by the solids loading rates.

4.5 Experimental Procedures

Biomass liquor from the screening separation of the dilute-ammonia pretreatment process was collected (Separation 1 in Figure 11). The suspended solids concentration, dissolved solids concentration, particle size distribution, and pH of slurries were measured using the methods set forth in the Analytical Methods section. The specific procedures required for the development of the DAF unit are presented below.

4.5.1 Coagulation and Flocculation

To improve flotation processes in sugar refineries, a coagulation and flocculation process is employed. Calcium phosphate is precipitated by the addition of phosphoric acid(H_3P0_4) then calcium hydroxide ($Ca(OH)_2$) following the reaction in Equation 8.

$$2H_3P0_4 \quad + \quad 3Ca(OH)_2 \longrightarrow 6H_20 + Ca_3(PO_4)_2$$

Equation 8

In the sugar refining process, this procedure is termed phosphatation (Chen and Chou, 1993; Briones, 2007). When combined with flocculant addition and flotation, it is referred to as phosphoflotation (Briones, 2007).

In the current study, a similar approach was utilized to treat the samples before flotation. The pH was adjusted from about 10 down to 6.5 using 85% phosphoric acid (H_3PO_4). Coagulation was initiated by the addition of calcium hydroxide ($Ca(OH)_2$) and subsequent precipitation of calcium phosphate ($Ca_3(PO_4)_2$). Anionic polyacrylamide polymers, provided by Garratt-Callahan (Burlingame, CA, USA), were then added to agglomerate the slurry. At the pH (6.5) resulting in efficient coagulation, anionic polymers were found to be most effective.

Floc formation was evaluated using a jar testing procedure recommended by Garratt-Callahan (2003). After flocculation, the solids were re-suspended in the sample and then floated with a batch dispersed air apparatus to assess the flotation characteristics. It was understood that a dispersed air process would have lower bubble-particle adhesion efficiency than a DAF, and thus lower separation efficiency, due to bubble size and turbulence created by the introduction of the air. However, it allowed for a quick method of comparison of the floatability of the agglomerates.

High shear forces due to recirculation pumping during particle size analysis reduce the accuracy of the measurement by breaking the floccules. Thus, a qualitative approach was taken to evaluate the characteristics of the agglomerates. After visual inspection, each polymer was assigned a rating based on two parameters: size and shape of the formed floccules and their floatability. These qualities were rated on a scale of 1-10. Each polymer was evaluated against a standard sample. The standard sample was treated with only phosphoric acid and lime and given the value 5 for each characteristic. Values ranging from 6-10 indicated an improvement in the observed characteristic. If no change was observed, a value 5 was assigned. If the desired characteristic was inferior to the standard, a value in the range of 1-5 was given.

4.5.2 Bubble Size Analysis

Bubble sizes were quantified using a CILAS 1180L laser diffraction analyzer following a procedure similar to Cuoto et al. (2009). To measure bubble sizes produced by the dispersed air apparatus utilized in batch testing of polymers, the air stone was placed into sample cell of the analyzer and air was pumped through, generating bubbles continuously during measurement.

Based on data available on the relationship between bubble size and saturation pressure in DAF applications, 60 psi was selected as the operating pressure for this study (Edzwald, 1995; Couto et al., 2009). For analysis of bubbles generated by the DAF saturator, clear water was saturated under pressure, and released into the sample cell of the analyzer at atmospheric pressure, where bubble formation occurred. Water was drawn from the analyzer's cell at the same rate, to avoid over-filling.

During measurement of bubble sizes, some coalescence is likely. Due to this, the distribution is skewed towards the large bubbles to an extent. Therefore, an overestimation of the bubble sizes is possible.

4.5.3 Selection of Recycle Ratio

Recycle ratio was tested first using a batch DAF process. Samples of 400 ml were coagulated and flocculated then poured into a 1000-ml graduated cylinder. Clear water was saturated under 60 psi pressure for fifteen minutes. Increasing volumes of saturated water were then released into the cylinder to test recycle ratios. Solids were allowed to float for five minutes after saturated liquid was introduced. Floated solids were then skimmed, weighed and analyzed for moisture content. A range of recycle ratios were evaluated from 100-150%. Each recycle ratio was evaluated in duplicate with various polymers. Based on these results, a recycle ratio (and thus air-to-solids ratio) was selected for continuous operation.

4.6 Continuous Flotation Unit

Based on parameters obtained from batch testing, a continuous bench-scale recycle-pressurization DAF system was constructed and tested. A picture of the continuous flotation unit is shown in Figure 22. The main components of the system are labeled:

A. 9-liter saturation pressure vessel

B. 2.8 liter flotation tank (20 cm height, 140 cm^2 surface area)

C. Seepex® Model MD 012-12 progressive cavity pump for recycle stream return to pressure vessel

D. Air pressure regulator

E. Cole-Parmer® Model 7520-30 peristaltic pump to recover underflow

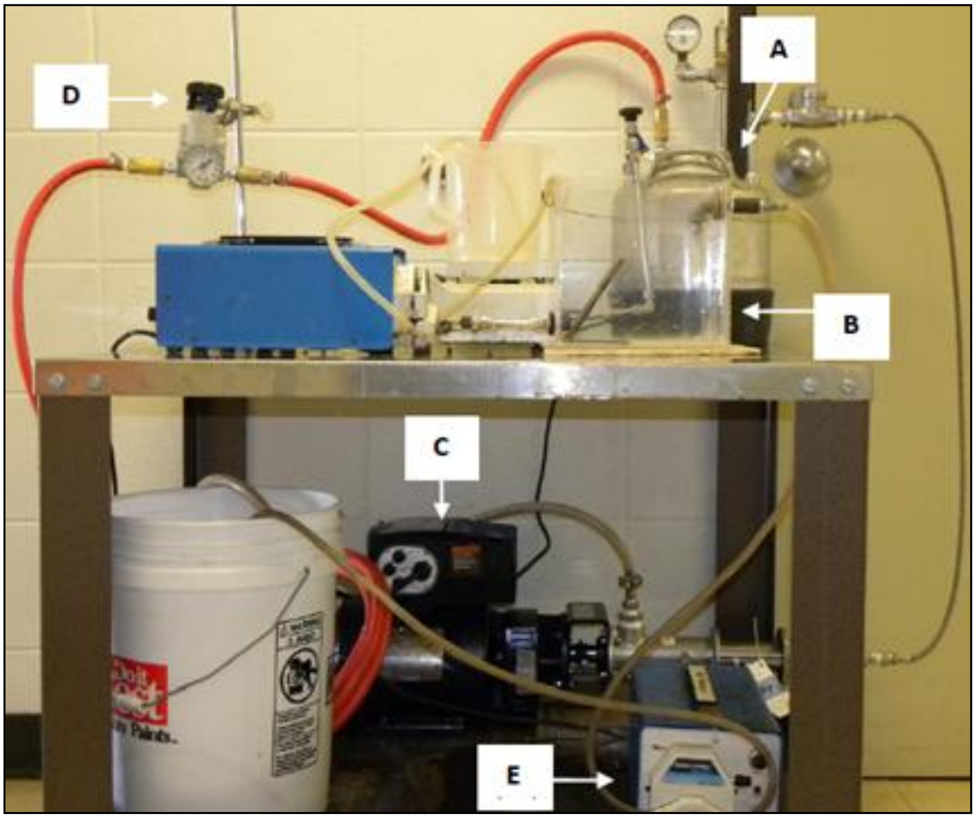

Figure 22 Continuous DAF unit.

This unit was tested for separation efficiency with various polymers which performed well in batch dispersed air flotation. The effect of hydraulic loading rates was also evaluated. Four liter samples were used for continuous testing. Each test was performed in duplicate to validate the results.

4.7 Initial Flotation Testing

A bench-top batch dispersed air flotation unit (Figure 23) was used to test floatability of the solids. It was understood that dispersed air flotation would not achieve the level of separation of DAF due to differences in bubble sizes and turbulence. However, the unit allowed for observation of bubble-particle interaction at various air-to-solids ratios.

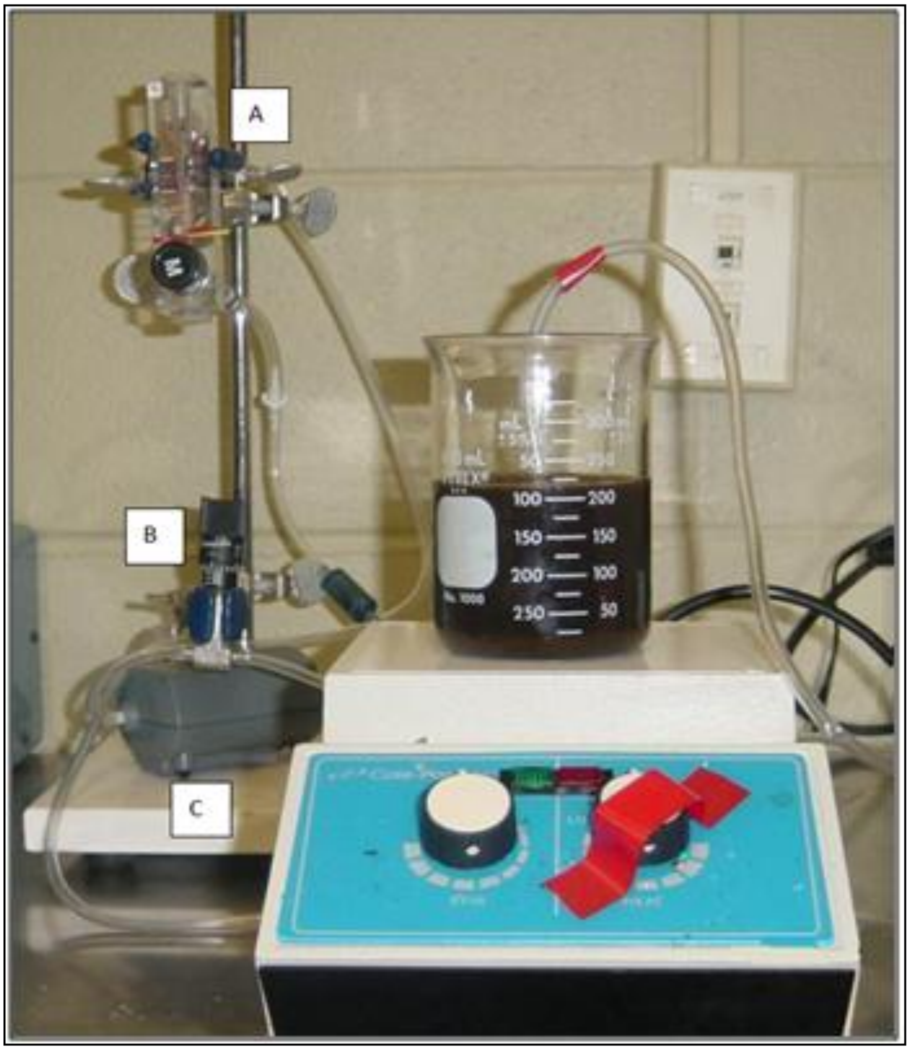

Figure 23 Batch dispersed air flotation. A-Rotameter, B-Needle Valve, C-Air Pump.

4.7.1 Flotation without Chemical Addition

Flotation experiments were first performed without addition of chemicals. Two-hundred milliliter samples of biomass liquor (liquid phase from Separation 1 in dilute-ammonia pretreatment process) were used for testing. Original solids concentration was measured at 10.13 g/l. Particle size analysis was performed prior to flotation. Tests were performed at air flow rates of 220, 280 and 320 mg/min. Air flow was converted to mass flow rates with air density of 1.2 mg/ml to calculate of air-to-solids ratios. Air was distributed through the air stone shown in Figure 24.

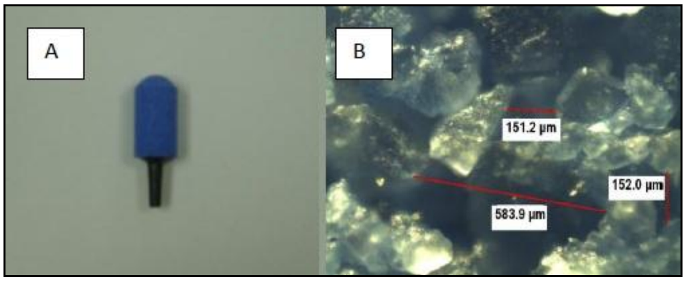

Figure 24 A-Porous air stone used for dispersed air flotation B-microphotograph of air stone with pore measurements.

Batch samples were subjected to the air flow for 2 minutes. Flotation time was selected such that air-to-solids ratios were in the range utilized industrially—0.043, 0.055, and 0.063. The total floated 'scum' was collected (scooped off manually), weighed, and analyzed for solids concentration. The separation efficiency was calculated based on total solids removal. Flotation tests were performed in duplicates for each air flow. Mean values are reported in Table 8.

Table 8 Separation efficiencies at various dispersed air flow rates.

Air Flow (mg/min)	Volume of Floated Scum (ml)	Floated Solids Concentration (g/l)	Separation Efficiency (%)
220	4.1	2.17	4.4
280	20.4	1.27	12.9
320	30.2	1.25	18.7

Little separation occurred with air flow of 220 mg/min. Solids removal did occur, however, these were very fine particles which did not significantly affect the total mass of solids.

With low air flow, flotation did not continually remove solids as with the higher flow rates. Flotation ceased to remove solids after 1 minute during these tests. With the 280 and 320 mg/min air flow, flotation continued to recover solids until the end of 2 minutes.

Low air flow did not provide enough small air bubbles (<200 μm) for efficient bubble-particle adhesion. The air stone which dispersed air into the sample provided non-uniformly sized bubbles. Measurements of the pores in the air stone revealed a range of sizes from 150-600 μm. Bubble size distribution was measured according to the procedure described in the Experimental Procedures section, and is presented in Figure 25.

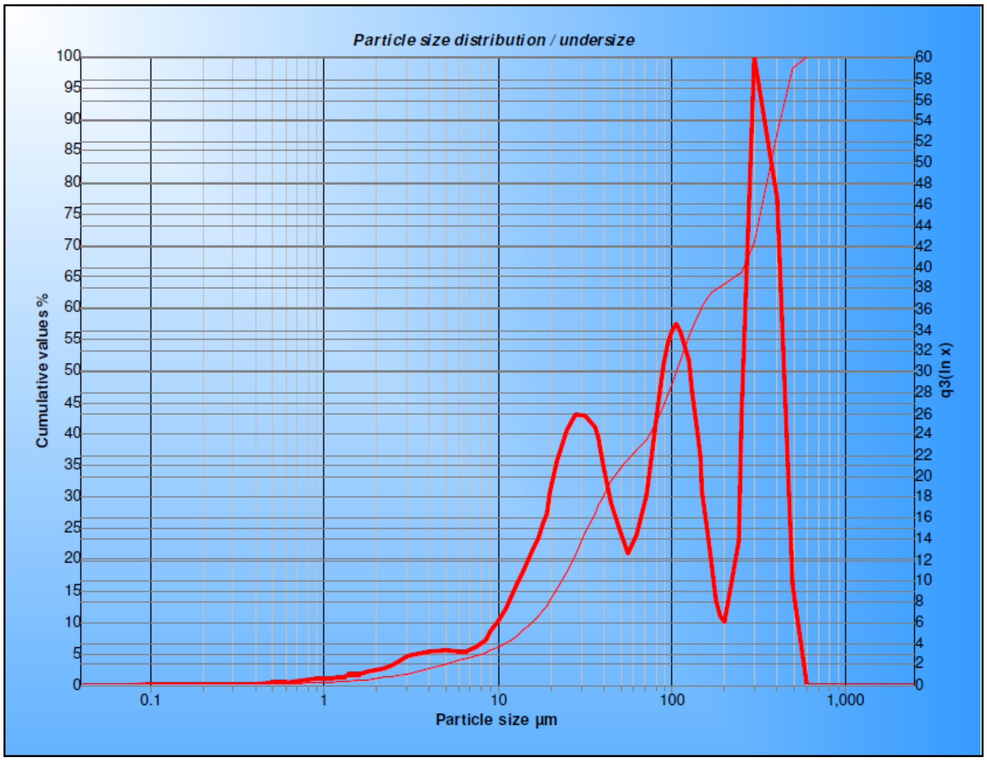

Figure 25 Size distribution of bubbles produced by porous air stone.

Based on the microphotograph of the air stone in Figure 24, it was expected that the bubbles would be non-uniform in size due to the varying pore sizes. Analysis of bubble sizes produced by the air stone revealed a multi-modal distribution. A significant fraction of bubbles were measured above 200 μm. These bubbles do not contribute to efficient flotation, as they are too large for bubble-particle adhesion. Furthermore, the rise velocity of the larger bubbles causes turbulence in the collision zone, which is detrimental to the adhesion of other bubbles to particles. For efficient flotation of slurries with 10-200 µm particle size range it is recommended to use bubbles from 10-200 µm. Particle size distribution of the feed solids in the slurry was measured and is shown in Figure 26.

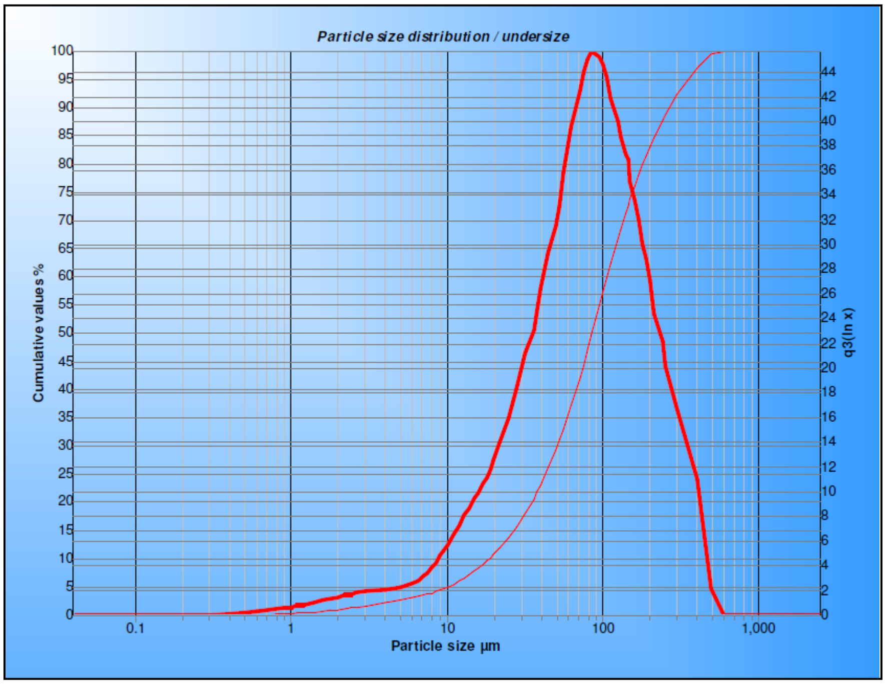

Figure 26 Particle size distribution of biomass liquor.

Results from particle size analysis of the slurry showed a median particle size of 87.0 µm, with a distribution of particles from sub-micron to approximately 650 µm. It was anticipated that the fraction of particles which are smaller than 200 µm could be effectively separated by DAF if bubble-particle attachment is efficient. Thus, a separation efficiency of over 50% should be attainable using a properly designed DAF process. Larger particles may be removed by implementing a settling step before DAF.

The fraction (approximately 12% of the volume) of solids which are smaller than 10 µm will negatively affect the efficiency of the DAF process. Flotation is an ineffective method of separating particles less than 10 µm (Lee and Lee, 2002). Smaller particles decrease the probability of bubble-particle collision and attachment. Therefore it is important to reduce the fraction of particles under 10 μm by agglomeration. This should result in more efficient flotation. Such agglomeration can be accomplished by addition of chemicals as described previously.

4.7.2 Flotation with Coagulation and Flocculation

Coagulation and flocculation were used to adjust the distribution of particle sizes and reduce the portion of fine particles (< 10μm). The pH of samples was adjusted from 10 to approximately 6.5 with phosphoric acid (H_3PO_4). The addition of calcium hydroxide ($Ca(OH)_2$) subsequently precipitated calcium phosphate ($Ca_3(PO_4)_2$), initiating coagulation of the slurry. Calcium hydroxide was weighed and added to the slurry to a concentration of 0.1%.

To encourage flocculation of the particles into larger agglomerates, anionic polyacrylamide flocculants were added to the slurry. Ten anionic polymers were evaluated for flocculation and floatability. Results from the qualitative analysis of the polymers using the procedure described in the Experimental Procedures section are presented in Table 9.

Polyacrylamide flocculants generally perform well in a narrow range of dosing, with flocculation performance dramatically decreasing outside this range. A parabolic relationship exists with flocculant dosing and effectiveness (Wong, Teng, Ahmad, Zuhairi and Najafpour, 2006). Based on recommendations from Garratt-Callahan personnel, polymer addition rates varied from 3 ppm to 10 ppm. It was found that flocculation improved with increasing molecular weight ranges of the polymer.

Flotation performance was enhanced by more strongly charged polymers. The goal was to achieve flocculation and improved flotation at low dosages. Polymers are an additional expense for the process, thus low dosages help the financial viability. Furthermore, polyacrylamide polymers in high concentrations have been shown to inhibit fermentation downstream. However, in the range of dosages applied in this study, fermentation inhibition has not been found (Burke et al., 2009).

Table 9 Results of flocculation testing at various dosages.

		Dosing (ppm)			
Polymer	**Molecular Weight Range (10^6 Daltons)**	**3**	**5**	**7**	**10**
7253	16-27	5,6	6,5	7,7	5,6
7254	18-31	6,5	6,6	6,5	5,5
7274	8-13	5,4	6,5	6,5	5,5
7275	9-16	5,4	5,5	6,5	5,4
7277	12-18	5,3	5,4	6,5	5,5
7282	18-30	7,8	10,10	8,7	6,6
7301	20-35	6,6	8,7	7,8	6,6
7302	20-35	8,8	9,8	8,8	7,6
7303	20-35	7,8	8,9	7,8	6,5
7304	20-35	5,3	7,5	7,6	5,4

Flotation performance was evaluated on the basis of separation efficiency. An increase in separation performance was found for five of the ten polymers at a dosing rate of 3, 5, and 7 ppm. Mean results from duplicate flotation analyses are presented in Table 10. An optimal dose of 5 ppm was determined for five polymers (7282, 7301, 7302, 7303, and 7304). With this dosage, the small, fibrous particles of bagasse readily attached to the phosphates, increasing the size of the agglomerate. This application rate is reasonable compared to the usage of flocculating agents, e.g. in the sugar industry.

Dispersed air flotation of the flocculated samples resulted in separation efficiencies ranging from 11% to 44%. The effect of polymer addition on separation efficiency is presented graphically in Figure 27. For the five polymers presented in Table 10, separation efficiency increased for polymer dosing up to 5 ppm. For 7282 and 7302, increasing polymer dose to 7 ppm did not result in improved flotation. The dispersed air flotation did not result in substantial volume reduction; floated solids concentrations were below 1%. However, results indicated that flotation was a viable option for solids recovery. It was expected that a DAF process would result in higher float solids concentrations and separation efficiencies due to optimized bubble sizes, air-to-solids ratio, and retention time to allow for thickening to occur.

Table 10 Results from flotation with polymer addition.

Polymer	Dosage (ppm)	Volume of Floated Scum (ml)	Floated Solids Concentration (g/l)	Separation Efficiency (%)
7282	3	25	25.9	43.6
7303		26	21.6	33.8
7302		18	21.1	22.8
7301		19	17.8	20.3
7304		17	19.2	19.6
7282	5	14	52.8	44.4
7303		18	35.8	38.7
7302		19	19.7	22.4
7301		20	17.9	21.3
7304		16	21.8	20.9
7282	7	19	36.9	42.1
7303		22	24.0	31.7
7302		24	15.7	22.6
7301		16	22.4	21.5
7304		20	18.7	22.4

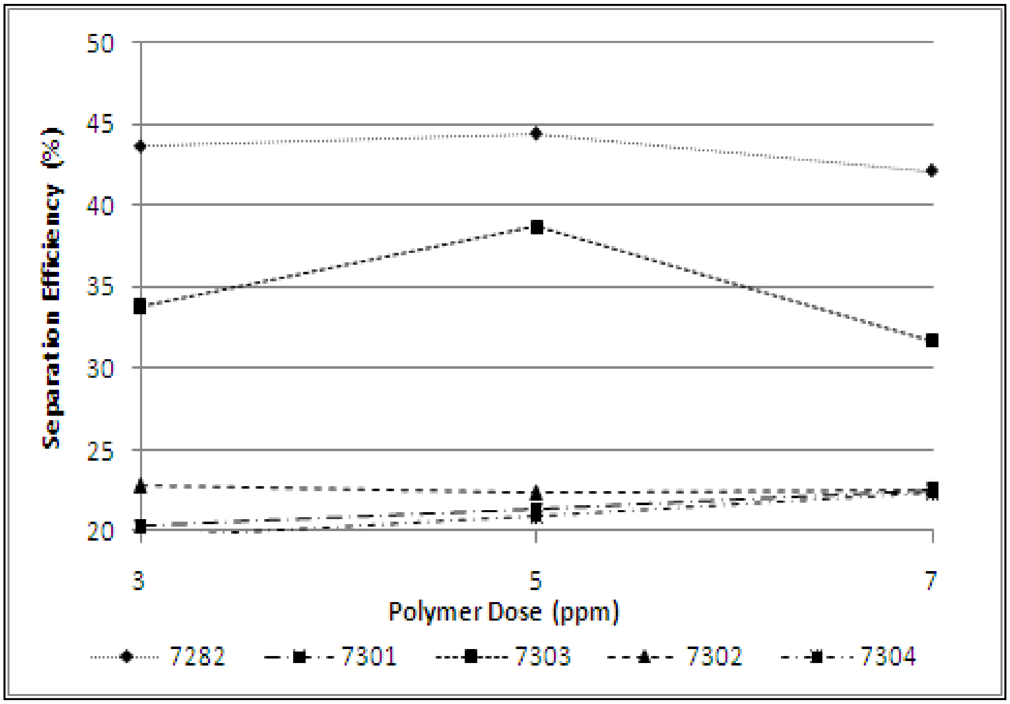

Figure 27 Effect of polymers at various doses on separation efficiency.

Particle size analysis was performed to evaluate the influence of the polymers on the size distribution of particles in the slurry. Three samples were analyzed, pretreatment slurry, a standard coagulated sample treated with phosphoric acid and calcium hydroxide only, and a coagulated flocculated sample dosed with 5ppm of polymer 7282. Results from evaluation of particle size distribution of these samples are presented in Table 11.

Table 11 Comparison of particle size characteristics of biomass liquor, standard sample, and slurry flocculated with polymer.

Sample	d10%	d50%	d90%
Biomass Liquor	9.7	78.3	279.0
Standard	12.1	81.5	300.8
7282, 5ppm	12.7	86.6	294.9

It was understood that the results for flocculated slurry would be distorted to some extent by floc breakage during analysis due to circulation by the peristaltic pump. However, an increase in particle size was measured from the original slurry, indicating flocculation was effective. The d10 measure (particle size at which 10% of the particles are smaller) increased by 31% from the pretreatment slurry to the flocculated sample. Furthermore, a 30% reduction in the fraction of particles under 10 μm was observed. This agglomeration of the biomass particles should lead to an increase in separation efficiency by DAF.

4.8 DAF Testing

Scale-up to continuous DAF required verification that the saturator produced suitable bubble size distribution for DAF. Batch DAF testing allowed for selection of process parameters relevant to scale up to continuous DAF (air-to-solids and recycle ratios).

4.8.1 Bubble Size Distribution from DAF Saturator

In order to facilitate the removal of flocculated particles using DAF process optimal bubble sizes are in the range of 10-200 μm. Bubbles larger than 200 μm rise too quickly for efficient flotation and cause turbulence detrimental to bubble-particle adhesion.

Bubble sizes were characterized following the method set forth in the Experimental Procedures. Clear water was saturated in the pressure vessel at 60 psi. The saturated liquid was transferred into the particle size analyzer's sample cell to evaluate if bubble sizes corresponded to the values recommended for DAF.

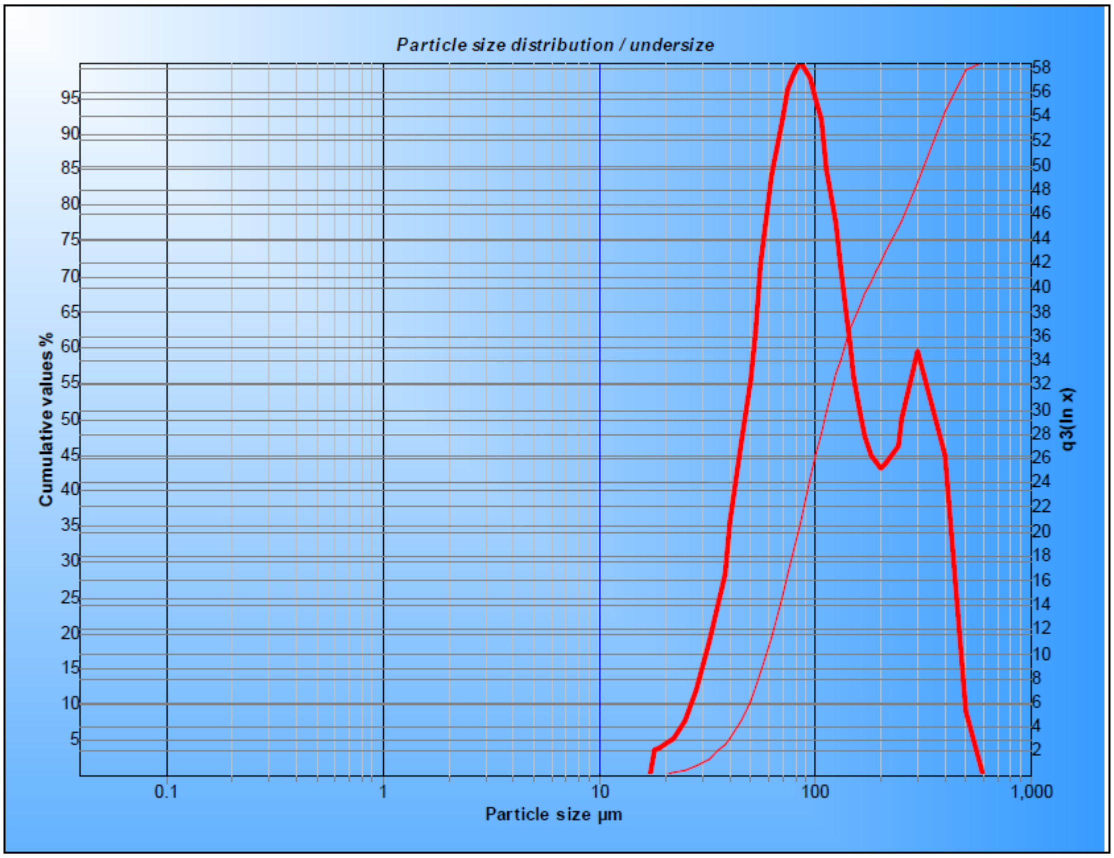

Figure 28 Bubble size distribution from DAF saturator at 60 psi.

Median bubble size was 107 µm, substantially larger than the 40 µm value reported by Edzwald (1995). The distribution of bubble sizes was also broader than the range of 10-100 µm commonly reported. However, 75% of bubbles were in the range of 10-200 µm, which is a suitable size for flotation processes. Due to the nature of analysis and mixing provided by the circulation pump of the analyzer, the bubble sizes would be overestimated due to bubble coalescence during the measurement. The generation of these larger bubbles likely led to the double peak in the distribution in Figure 28.

4.8.2 Effect of Air-to-Solids and Recycle Ratios

Batch DAF experiments were performed to select parameters (air-to-solids and recycle ratios) for scale-up to continuous flotation. The recycle ratios and corresponding air-to-solids ratios tested are presented in Table 12.

Table 12 Recycle ratios and corresponding air-to-solids ratios.

Recycle Ratio (%)	Air-to-Solids Ratio
100.0	0.0090
112.5	0.0100
125.0	0.0110
137.5	0.0125
150.0	0.0140

Typically DAF is applied for feed streams with solids concentrations up to 5,000 mg/l. Due to higher solids concentration in the feed material in this study (10,000-12,000 mg/l), recycle ratios were in the upper range and the air-to-solids ratios were on the lower side of values found in industrial applications. The separation efficiencies (defined as percentage of solids recovered) of the batch flotation process at increasing recycle ratios are presented in Figure 29. Three polymers (7282, 7302, and 7303) at 5ppm were evaluated.

Separation efficiencies improved as the recycle ratio was increased, due to more available air for flotation. A sharp increase was measured for recycle ratios from 100-125% for each polymer. From this point, additional air did not result in marked increase in flotation performance for polymer 7303. A recycle ratio of 150% resulted in a separation efficiency of 48% and 46% for polymers 7282 and 7303 respectively.

DAF is most efficient for separating particles from 10-200 μm. Particle size measurements of the flocculated slurry showed between 50% and 60% of solids were in this range. With an efficient DAF process, separation efficiencies in the range of 50-60% could reasonably be expected.

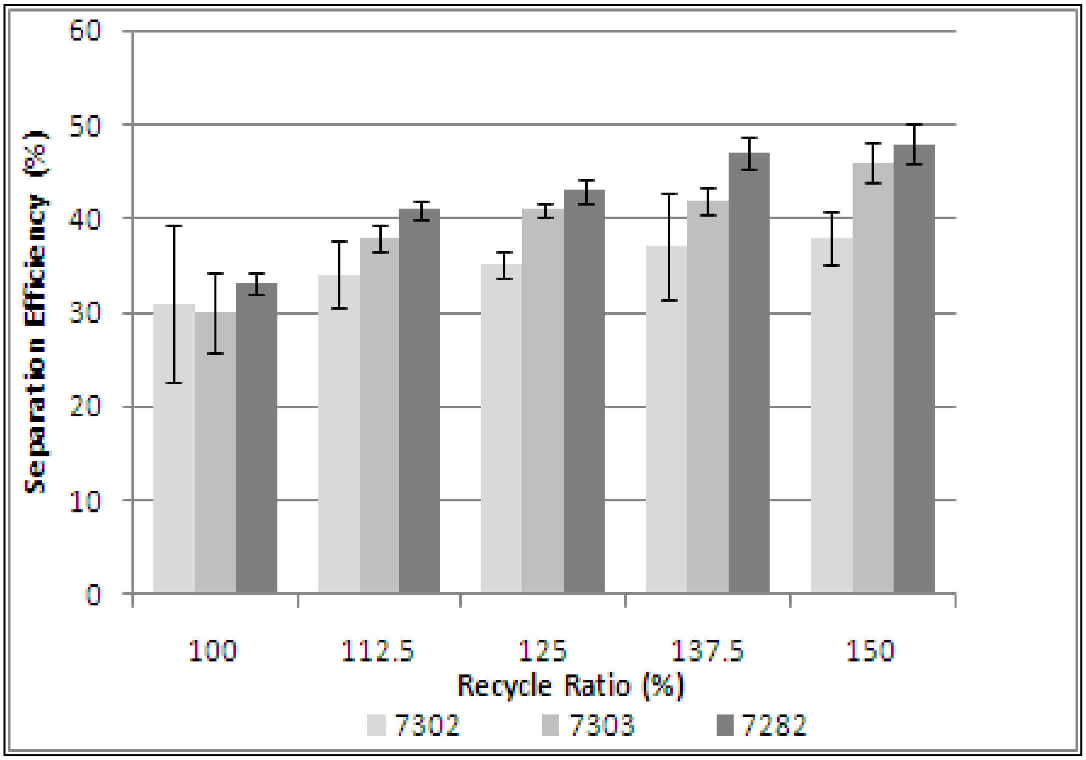

Figure 29 Effect of recycle ratio and polymer addition on separation efficiency of batch DAF.

4.9 Continuous Flotation

Experiments on continuous DAF were considered an important step in generating data for future scale-up. The DAF process was evaluated for solids recovery and concentration of floated solids fraction. Two polymers were selected from batch testing for comparison in the continuous unit. The DAF process was evaluated at various hydraulic loadings.

4.9.1 Polymer Evaluation with DAF

Based on results from polymer screening in the preliminary batch tests, two flocculants were selected for use in continuous flotation process (7282 and 7302). Recycle ratio of 150% was applied based on the previous tests. With a conservative retention time of 30 minutes it was expected that flotation in the continuous DAF unit would result in higher separation efficiencies and float solids concentrations than batch testing. Mean results from duplicate continuous flotation tests with polymers 7282 and 7303 are presented in Table 13.

Table 13 Separation efficiency of continuous DAF process.

Polymer	Influent SS (g/l)	Floated Solids (g)	Moisture Content of Floated Solids (%)	Separation Efficiency (%)
7282	10.6	260.2	91.02	55.6
7303	10.6	275.5	92.13	51.2

Float solids concentrations were substantially higher in continuous flotation, ranging from 8-9% compared to less than 1% in the batch testing. A photograph of the flotation tank showing the solid-liquid interface formed during continuous flotation is presented in Figure 30.

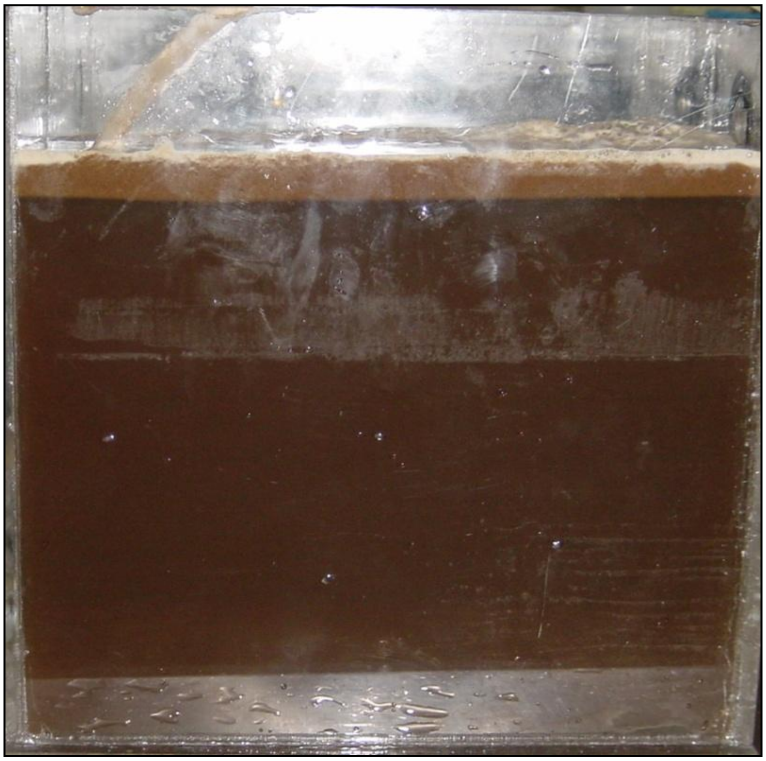

Figure 30 Solid-liquid interface formed in flotation tank during continuous operation.

Continuous flotation with 150% recycle ratio resulted in improved separation efficiency for both polymers tested (15.8% and 10.8% increases for polymers 7282 and 7302 respectively). Flotation with both polymers successfully thickened solids from approximately 0.1% to 8-9% solids. Float solids concentrations were equivalent to those found in efficient industrial thickening applications. Figure 31 is a picture of the floated solids in the tank (A) and after being scooped off (B).

Figure 31 A-floated solids in flotation tank B-Portion of skimmed solids.

4.9.2 Hydraulic Loading

Hydraulic loading rates which correspond to retention times representative of full-scale flotation processes were tested (Table 14). The following hydraulic loading rates were evaluated—10, 11.5, 14.5, and 19.3 $m^3 m^{-2} day^{-1}$. All tests were performed at 150% recycle ratio. The flow rates of influent and recycle are presented in Table 14.

Table 14 Flow rates for hydraulic loading rates tested in continuous flotation

Hydraulic Loading Rate ($m^3 m^{-2} day^{-1}$)	**Influent Flow Rate (ml/min)**	**Recycle Flow Rate (ml/min)**	**Retention Time (minutes)**
10	38	57	30
11.5	45	67	25
14.5	56	84	20
19.3	75	112	15

Continuous flotation tests were performed in duplicate at each hydraulic loading. The results in Figure 32 represent averages of the duplicates. Polymer 7282 was used for testing, as it was found to produce substantially higher separation efficiencies in the continuous flotation unit.

Separation efficiencies were negatively affected by higher hydraulic loading rates. With shorter retention times in the flotation tank, more dense solids, which have a slower rise rate, may not have adequate time to reach the solid-liquid interface above the subnatant draw-off point. These solids are thereby entrained in the subnatant and not recovered with the floated fraction.

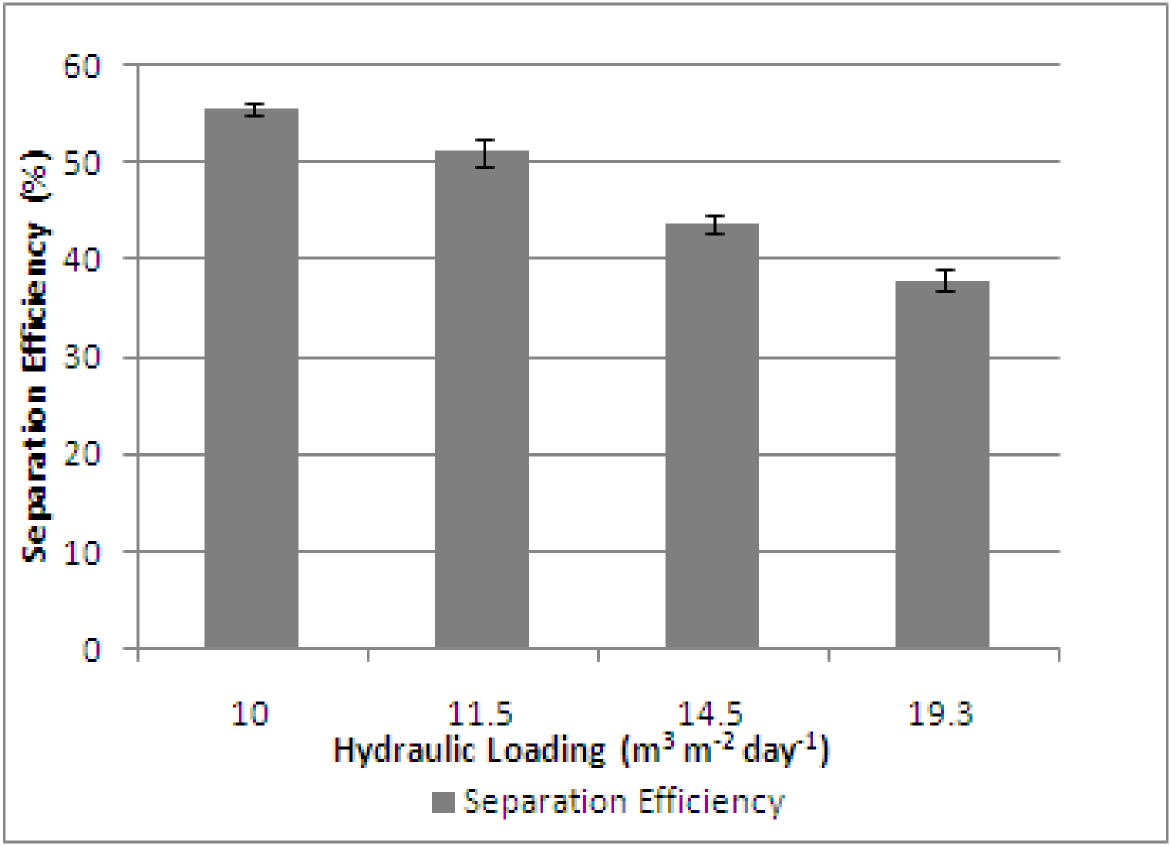

Figure 32 Separation efficiencies of continuous flotation at various hydraulic loading rates.

The concentrations of floated solids were measured for each test. Solids concentration in the floated fraction was not found to be affected by the hydraulic loading rates. The values are reported in Table 15.

Hydraulic loading is a measure of the flow rate per unit surface area of the flotation tank. Retention time, however, is a relation between the volume of the flotation tank and the flow rate. If flow rate to the flotation tank is increased, maintaining a constant hydraulic loading rate requires larger surface area. On the other hand to keep retention time unchanged at higher flow rates, a larger tank height would be required.

Table 15 Solids concentrations in supernatant at various hydraulic loading rates.

Hydraulic Loading Rate (m^3 m^{-2} day^{-1})	**Float Solids Concentration (%)**
10	8.98
	9.14
11.5	8.73
	9.21
14.5	9.31
	8.68
19.3	8.85
	9.01

Increasing height may not be beneficial for flotation tanks. The tank should be of sufficient depth to allow bubble-particle complex to rise to the solid-liquid interface before traversing the length of the unit. Beyond this point, a deeper tank increases the likelihood that solids will be entrained with the underflow. Large tank height could also be detrimental to the efficiency of the process by creating potential areas for turbulence, leading to detachment of bubbles from particles. As flow rate through the flotation tank increases, employing a tank with a higher length-to-height ratio, improves solids recovery in DAF processes (Ta, Beckley and Eades, 2001).

4.10 Summary

Fine particles, smaller than 10μm, cannot be effectively separated using a flotation process. Because of this, a treatment was established, following a method similar to phosphatation procedure common in sugar refining processes, to agglomerate the solids in a dilute-ammonia pretreated bagasse stream and reduce the fraction of particles smaller than 10μm. Addition of phosphoric acid and calcium hydroxide, followed by a small dose (5ppm) of anionic polyacrylamide flocculant were found to effectively agglomerate suspended solids. To select the best performing polymers for use in DAF, floatability of flocculated solids in the feed material was initially evaluated using a batch dispersed air flotation process.

Batch DAF tests were carried out to select air-to-solid and recycle ratios for scale-up to continuous operation. Testing was limited to a range typically employed in industrial DAF applications. In this range, air-to-solids and recycle ratios of 0.014 and 150% respectively were found to be most efficient. These parameters were used in all continuous DAF tests.

Initial continuous DAF experiments were performed to compare two different polymers which performed well in batch testing. Results indicated a dose of 5 ppm of polymer 7282 was the most effective. The effect of hydraulic loading rates on the efficiency of the DAF was investigated. Increasing hydraulic loading rates was found to be detrimental to separation efficiency of the DAF. Of the hydraulic loading rates tested flotation at 10 m^3 m^{-2} day^{-1}resulted in the highest separation efficiency (55.6%). Floated solids concentration was consistently measured at 8-9% for each hydraulic loading rate evaluated. It was concluded that the geometry of the tank should be reevaluated if increased hydraulic loading rates are applied upon scale-up. Surface area of the flotation cell should be increased by lengthening the sides.

Chapter 5 Conclusions

5.1 Project Summary

A methodology for material balance calculations specific to solid-liquid separation technologies was established and applied to two cellulosic ethanol processes which utilize alkaline-based pretreatments. The input parameters were determined experimentally by analyzing process solutions obtained from pilot installations. Analytical procedures and experimental techniques, which allowed for quick application in alternative process configurations, were evaluated and summarized.

Efficiency parameters of each separation were varied to evaluate the sensitivity of the overall process yields to solid-liquid separations. This allowed for quantification of critical efficiency targets for solid-liquid separations and assisted in selection of suitable technologies to maximize ethanol yield in conversion of sugar cane bagasse. Various solid-liquid separation methods were evaluated on the bench and pilot scales to meet the identified target efficiencies. Scale-up constraints of these technologies were identified. It was found that losses of biomass due to inefficient separations can reduce ethanol yields by as much as 10%. Traditional methods of separation, e.g. filtration and sedimentation, were found to be inefficient for recovering suspended solids from liquid streams. Though centrifugation provided high-efficiency solid-liquid separation in the bench tests, it is economically advantageous to avoid this technology where possible due to high capital and operating costs. Thus, a new approach has been proposed to concentrate suspended solids from pretreated biomass streams.

Based on characteristics of the process stream, it was expected that flotation could be effective for thickening suspended solids in a dilute-ammonia pretreated bagasse stream. A bench-scale continuous DAF was developed and the effects of process parameters on separation efficiency were identified experimentally.

. The DAF process improved recovery of suspended solids 27% over sedimentation. This enhanced separation efficiency was also coupled with a substantial improvement in concentration of the solid phase. With a retention time in the flotation tank of 30 minutes, the DAF process separated 57% of the solids and concentrated solids from 0.1% in the feed material to 8-9% in the floated fraction.

5.2 Future Considerations

Several possibilities exist for future research to continue progress in development of the ASI cellulosic ethanol processes. The present research identified target solid-liquid separation efficiencies and can aid in selection of appropriate techniques which can provide the efficiencies required. Future studies could build on this information by developing economic models for the processes and comparing process configurations. This would be beneficial for selection of the most appropriate solid-liquid separation technologies for economic feasibility.

Further research to refine the DAF process could also be explored. It was understood that using DAF exclusively for separating solids and liquids in the feed material in this study would not be highly efficient (>90% separation) due to presence of particles larger than 200μm. These solids will not be easily floated in a DAF process. Most commercial DAF units employ a bottoms scraper which removes those particles which settle. In the current study, only solids recovered in the floated fraction were included in the separation efficiency calculations. Therefore, improved efficiencies would be expected if a means of capturing the settled solids was devised. A beneficial future study could investigate the efficiency of a process combining settling and DAF processes. One alternative configuration could involve a DAF and with a sedimentation clarifier in series. Recycle-stream pressurization effectively dilutes the subnatant from DAF; therefore a larger settling basin may be required. However, it has been shown that settling of the feed material prior to DAF is inefficient due to the large fraction of small particles

(<100 μm). It is recommended that the configuration be such that the smaller particles are removed using DAF first.

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Appendix A: Dilute-Ammonia Pretreatment Procedures

General Information:

- To operate reactor discharge valve using the provided fob, the air supply hose must be connected, air valve open, power cord connected, and power switch to the reactor must be in ON position. If these conditions are met, pressing red button on fob will open/close the valve.
- Power switch must be in ON position when steam supply hoses are connected to the reactor. Toggle switches behind the reactor operate pneumatic control valves for the steam supply.

Procedures:

1. Sample bagasse for moisture content.
2. Weight supplies listed below:
    a. Bagasse before pretreatment
    b. Buckets
    c. Screen (including retaining ring and connection for reactor)
    d. Rubber bin
    e. Pressure vessel
3. Calculate the amount of dry bagasse.
    a. Based on moisture analysis, calculate the amount of water contained in the raw bagasse.
4. Calculated amount of water to be added to reactor
    a. Subtract water contained in the bagasse from moisture.
5. Calculate amount of ammonium hydroxide and water to be added.

    a. Ratio (Dry Bagasse : Ammonia : Water)
        i. 1 : 0.5 : 8

6. Add 1 kg water to pressure vessel
7. Add remainder of water to bagasse in bucket.
8. Ensure the valves on the reactor are all in the closed position.
9. Place bagasse/water into the reactor.
    a. Close top of reactor and tighten all bolts.
    b. Rotate reactor to ensure there are no leaks.
10. Add required mass of ammonium hydroxide into pressure vessel.
    a. Close top of pressure vessel securely.
    b. Ensure all valves on pressure vessel are closed.
    c. Connect air line.
    d. Supply air until pressure is approximately 30 psi.
11. Connect line from pressure vessel to reactor.
    a. Slowly open valves to allow ammonia to enter the reactor.
    b. After pressure equalizes, shake to ensure all contents of pressure vessel have been transferred into reactor.
        i. If there are still contents in the pressure vessel, add more pressure, repeat steps 10b-11a.
12. Close all valves and disconnect pressure vessel from reactor.
13. Ensure steam valves on reactor are closed and attach steam lines (high and low pressure) to the reactor.
14. Open steam supply valves.
15. Connect air supply line to control panel on reactor frame.

    a. Ensure both toggle switches (for pneumatic control valve) are in the ON position.

16. Open steam valves on reactor.
    a. Place the back condensate hose in drain. Be sure that the hose is anchored securely.
17. Start rotating the reactor.
18. Wait until Pressure reaches 160psi (temperature approximately 320^{o}F)
    a. Start timer for 1 hour.
19. After 1 hour, close steam supply valves, close steam valves on reactor, turn control valve switches off, and disconnect air hose.
20. Once the reactor cools, stop reactor in upright position and connect screen (placed in rubber bin) to bottom of reactor.
21. Reconnect air hoses to reactor and valve.
22. Stand a distance from the reactor and with fob, open valve to discharge contents of reactor into the basket.

After pressure is released from pretreatment reactor, the solids are retained in the basket and the liquid is collected in the rubber bin. The weights of each fraction can then be determined, knowing the weights of the containers.

Appendix B: Calcium Hydroxide Pretreatment Procedures

General Information:

- Equipment required: 500-ml Erlenmeyer flask, vacuum funnel apparatus, filter screen, aluminum foil, 250-ml vacuum flask.

Procedures:

1. Sample bagasse for moisture content.
2. Weigh the following supplies:
    a. 500-ml Erlenmeyer flask
    b. Bagasse before pretreatment
    c. Filter screen
3. Calculate the dry mass of bagasse.
4. Weigh and place bagasse to be pretreated into 500-ml flask.
5. Weigh the required amount of calcium hydroxide ($Ca(OH)_2$). (Ratio required is 0.2 g $Ca(OH)_2$ per dry gram of bagasse.)
6. Measure 8g distilled water per gram of dry bagasse.
7. Mix the $Ca(OH)_2$ with water.
8. Pour lime and water mixture into flask with bagasse
9. Stir to saturate the bagasse
10. Cover flask tightly with aluminum foil.
11. Place into autoclave at 121^{o}C for 1 hour.
12. Assemble vacuum filtration apparatus.
13. After autoclave is complete, pour contents of Erlenmeyer flask onto the filter screen.
    a. Connect vacuum line and filter for 5 minutes.
    b. Collect filtrate for further analysis.

c. Collect sample of pretreated bagasse for moisture analysis.

Vita

Keith Miller was born in Eunice, Louisiana, in February 1986 to Frederick and Bertha Miller. He was raised in rural Basile, Louisiana. After graduating high school from the Louisiana School for Math, Science, and the Arts in Natchitoches, Louisiana, in 2004, he enrolled at Louisiana State University as a first-generation Tiger. In May 2008, Keith graduated with a Bachelor of Science degree in biological engineering and continued with graduate studies in the same department in August 2008. He is a candidate for the degree of Master of Science in Biological and Agricultural Engineering to be awarded in May 2010.