

Design of a Pilot Scale Continuous Stirred Ethanol Reactor Separator with Solvent Absorption and Extractive Distillation

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ABSTRACT

An improved bioreactor has been developed to allow the high speed, continuous, low energy conversion of various substrates to ethanol. The Continuous Stirred Reactor Separator (CSRS) incorporates gas stripping of the ethanol stream between cascading stirred reactors in series to reduce the ethanol concentration within the reactor. A high cell density is maintained on the fermentation stages using a strain of flocculant yeast. The effects of turbulence on floc pellet size was studied. Ethanol recovery from the stripping gas leaving the bioreactor will be by absorption using a hydrophobic solvent. Design of an extractive distillation process to remove the water from the solvent prior to ethanol stripping is discussed. Energy needs for this process have been calculated to be under 8000 BTU/gal steam use for a 25% sugar feed. A 24,000 liter pilot scale version of the bioreactor has been designed, built and installed at an Iowa ethanol plant site. This pilot scale CSRS was started as a cascade reactor using starch dextrins and candy rinse water as a feed in May of '95. The SAED system will be added to the system in the near future.

INTRODUCTION

Ethanol production in the USA can offer a renewable source of liquid fuel produced within the borders of our own nation as well as providing a market for excess grain production capacity of the midwestern states. However, in order for the ethanol fuel industry to be able to expand without state and federal subsidies, ethanol production costs must be reduced closer to the wholesale cost level of refined unleaded gasoline (\$0.55-\$0.75 per gallon). Ethanol production costs can be reduced via: 1) reducing costs of substrate, 2) increasing the efficiency of substrate conversion to ethanol, 3) reducing the energy costs for purifying and dehydrating the ethanol, 4) reducing the amount of effluent 'bottoms' waters which must be treated, 5) reducing the capital costs for the ethanol processing plant, 6) reducing the labor for operating the ethanol plant and 7) increasing the value of the by-products from the ethanol plant. A number of these objectives can be met using a continuous reactor incorporating simultaneous separation of the ethanol from the fermentation broth.

BIO-REACTOR DESIGN

The Continuous Stirred Reactor Separator (CSRS) consists of stirred tank type reactors operated in series, with the liquid streams moving from tank to tank contacted with a stripping gas to remove the ethanol product has been designed and tested. A US patent [1] has been issued to Bio-Process Innovation, Inc

which describes this reactor technology. The CSRS reactor can allow simultaneous saccharification, fermentation, and ethanol separation in a combined process. Combining these reactions allows significant improvements in each operation. Combining reaction with separation allows the fermentation of highly concentrated streams of up to 50% solids [2]. Simultaneous saccharification and fermentation of polysaccharides such as starch [3] and cellulose can be quickly completed in this bio-reactor/separator. Saccharification (of starch or cellulose) is sped by the reduction of sugar concentration as the sugar is fermented to ethanol. Fermentation is sped by the removal of the toxic ethanol product, and ethanol purification and concentration costs are reduced by the enrichment of the ethanol in the vapor phase. The gas stream is co-current to the tank to tank liquid flow in the enriching section, and counter-current in the stripping section. The final effluent from the CSRS should be characterized by complete saccharification of polysaccharides, complete fermentation of sugars to ethanol and complete removal or separation of the ethanol into the gas phase. A schematic of the 4 stage 24,000 liter CSRS pilot plant is shown in Figure 1, with the design flows and concentrations on the various stages.

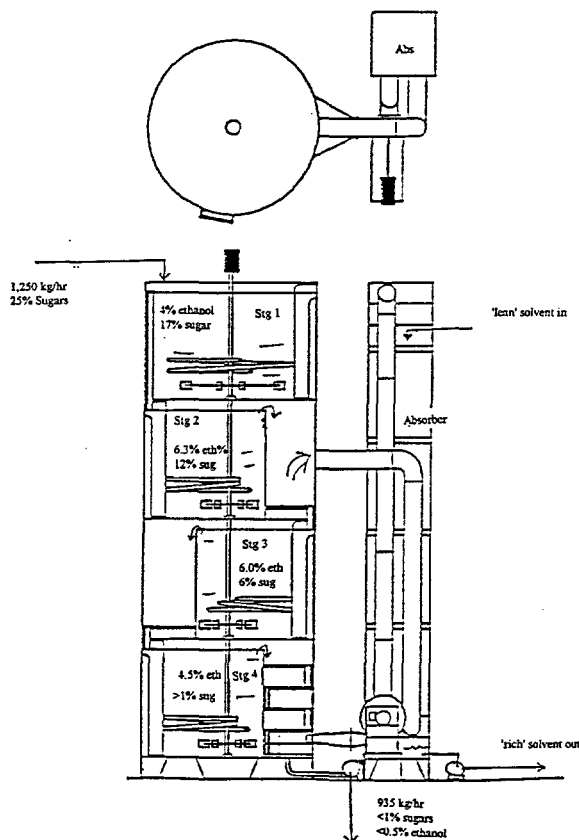


Figure 1. Schematic and design flows and compositions in the 24,000 L CSRS and Solvent Absorber

HIGH DENSITY FLOCCULENT YEAST

Fermentation rates in a bio-reactor are, in general, linearly related to yeast density if 1) the cell viability is maintained, and 2) the cell performance is not limited by local (micro-scale) substrate or product concentration gradients [4]. However, if cells are immobilized in beads or in flocs, there may be a decrease in specific productivity due to diffusion limitations, both of substrate to the cell, and ethanol from the cells. Teixeira and Mota [5] show about a 50% drop in specific sugar uptake in flocculated cells as compared to free cells.

During a normal free cell batch ethanol fermentation of a 15-20% sugar solution, a seed of perhaps 1×10^7 cells (0.5 g/l) increases over the 30 to 60 hour fermentation to a density of 1.5 to 2.0×10^8 (12-18 g/l)[6]. Fermentation rates can be increased if higher cell densities can be maintained during the fermentation. There are three basic ways to maintain a high cell density in a bio-reactor; 1) recycle the yeast after a yeast recovery step such as settling or centrifugation, 2) immobilize the cells within the reactor, in or on a support media (i.e. gel beads), or 3) self-immobilize the yeast by using flocculant yeasts and a settling area before removing the reactor out-flow. Self aggregation of the yeast is perhaps the simplest and cheapest method for achieving a high yeast density in that no additional equipment or support media is required for the process.

Four strains of highly flocculent *S. cerevisiae* and *S. uvarum* type yeast were obtained from various culture collections. Lab scale tests were used to observe the flocculating characteristics of the strains and to compare the settling speeds and fermentation rates. One strain was selected as being slightly more efficient ethanol producer, and adapted for the CSRS application by operating a 1 liter continuous stirred fermenter (New Brunswick Multi-Gen) for 60 days of continuous culture. A 15% sucrose feed was fed to the reactor at a residence time of 15 to 20 hours. Floc pellets of approximately 2 mm to 3 mm diameter developed and were maintained in this bio-reactor. Cell settling was observed to be complete within 15 to 20 sec after stopping the agitation (a stirring speed of 200 RPM- one blade- was required to keep the cells suspended). A cell settling layer of 33% to 40% by volume in the reactor developed and maintained itself at this density over time. Cell density in the supernate was very low, with the supernate broth appearing sparkling clear. Cell density in the settled layer was measured at 60 to 75 g/l at 5 minutes. Average cell density in the reactor for this adapted yeast was 20 to 30 g/l. This adapted floc yeast strain was then used for seeding the 24,000 liter pilot plant.

A short study on the effects of reactor turbulence on the floc pellets of the adapted yeast was performed under continuous fermentation conditions. Different levels of reactor turbulence were maintained by varying the stirring speed in a standard 2 or 4 liter fermenter (New Brunswick and Braun respectively) fitted with either 3 (anaerobic study) or 4 turbines—6 bladed open style—(aerobic study) for 48 hours after which time a sample was taken for microscopic analysis using a Hauser hemocytometer to measure a typical floc pellet dimensions. Under anaerobic conditions, a typical pellet size was observed to fall from 2.4 x 3.0 mm (width x length) at 250 RPM ($Re = 30,000$) to 1.2 x 1.6 mm at 400 RPM ($Re = 50,000$) to 0.2 x 0.4 mm at 700 RPM ($Re = 87,000$) to 0.2 x 0.3 mm at 800 RPM (100,000 Reynolds). A similar experiment run under aerobic conditions (2 VVM) showed pellet size falling from 0.4 x 0.8 mm at 250 RPM ($Re = 40,000$) to 0.4 x 0.4 mm at 500 RPM ($Re = 80,000$), to 0.3 x 0.3 mm at 700 mm ($Re = 115,000$).

Finally, at 750 RPM (Re of 125,000), the flocs were disassociated into free cells. Interestingly, the cells would not re-aggregate when the stirring speed was reduced to 250 RPM, either under aerobic or anaerobic conditions.

ETHANOL RECOVERY VIA SOLVENT ABSORPTION AND EXTRACTIVE DISTILLATION

The CSRS can be coupled with an isothermal solvent ethanol recovery system to give a low energy continuous process for the production of purified ethanol. A solvent is used to absorb the ethanol from the gas stream exiting the CSRS. The solvent should have the following properties: 1) low vapor pressure, 2) high affinity and miscibility with ethanol, 3) non-toxicity of any solvent vapor carry-over to the microbes in CSRS, 4) low affinity/solubility of water in the solvent, and 5) low solubility of solvent in water. The ideal solvent would absorb only ethanol from the vapor stream, allowing an anhydrous ethanol product to be stripped from the rich solvent. However, the close similarity in size and polarity between ethanol and water results in solvents having the ability to solvate ethanol also dissolve some water. Tedder et al. [7] tested for direct solvent extraction of ethanol using solvents with a 3 to 5% water weight fraction in the solvent phase when contacted with an aqueous phase and suggested the re-use of the solvent as an extractive distillation agent (SEED process).

Each solvent can be characterized by an equilibrium distribution coefficient, for ethanol between the water/aqueous phase and the solvent phase ($K_{dc} = x_{e(aq)} / x_{e(sol)}$), where x_e is the mass fraction of ethanol in either phase. There is a similar distribution coefficient for water, K_{dw} between the aqueous and solvent phases. Dividing the ethanol distribution coefficient by the water distribution coefficient (K_{dc} / K_{dw}) gives a separation factor, α , which describes the relative affinity of the solvent for ethanol compared to water. Dodecanol, found by Minier and Goma [8] to be nontoxic in direct solvent extraction in-situ separation, has an ethanol distribution coefficient of .21, and an ethanol/water separation, a factor of 21. Work by Kollerup and Daugulis [9] indicated that dodecanol was somewhat toxic to microbes. Research in our labs has shown that dodecanol in direct contact with immobilized cells was toxic to yeast, but when used as vapor ethanol absorber, the dodecanol vapors carried over to an immobilized cell type reactor were not toxic, with fermentation rates of immobilized cells stable over 4 to 6 days [10]. By not actually contacting the cells with an organic phase, toxicity problems and solvent loss into the water phase are both minimized. Solvents examined for in-situ or post fermentation ethanol extraction include alcohols, esters, ketones, phenols, carboxylic acids, chlorinated hydrocarbons, amines, phosphorals, aromatic hydrocarbons, and oils [11, 12, 13].

An anhydrous ethanol product may be recovered from the solvent using an extractive distillation utilizing the same solvent used for the ethanol absorption leading to a solvent absorption extractive distillation (SAED) process as shown in Figure 2 [14]. The extractive dehydration process uses the principle that the solvent enhances the volatility of water more than ethanol, reversing the relative volatilities of ethanol and water. The activity coefficient for water in the solvent can be determined by the solubility of water in the solvent. For a three phase system (vapor, aqueous, organic) we can write:

$$P_w = \lambda(aq) P_w^o x_w(aq) = \lambda(sol) P_w^o x_w(sol)$$

where P_w is the vapor pressure of water, $\lambda(\text{solv})$ is the activity coefficient for water in the organic solvent phase, $x_w(\text{solv})$ is the mole fraction of water dissolved in the solvent, and P_w° is the vapor pressure of pure water. For pure water in contact with a test solvent, this reduces to:

$$\lambda(\text{solv}) = 1 / x_w(\text{solv})$$

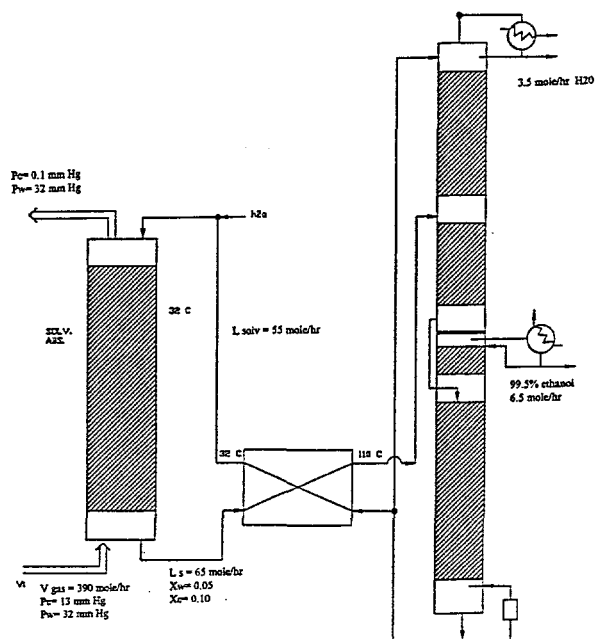


Figure 2. The Solvent Absorption- Extractive Distillation (SAED) process for ethanol recovery from gas streams

The liquid/vapor equilibrium relationship for water (x_w) and ethanol in a test solvent (linoleic acid) as determined by our own solubility studies [15] and as given by the ASPEN 2 model are plotted in Figure 3 on a solvent free basis along with a proprietary second solvent (Solv.2) currently under evaluation for the SAED process. There is good agreement between our calculated equilibrium data for linoleic acid and the equilibrium curve suggested by ASPEN 2. Dehydration of the solvent would involve distillation of the water from the mixture as shown in the McCabe-Theile type analysis of Figure 4 for linoleic acid (equilibrium line from our data). As per Figure 4, approximately 13 stages (7 stripping, and 6 rectifying) with a water reflux ratio of 0.9 will allow a 98% mole percent water product to be recovered as a distillate from the top of the column, and a bottoms product with only 2% mole fraction water remaining in the ethanol. Vapor flow up the column can be provided either with a reboiler, vaporizing ethanol from the solvent, or by introducing an inert gas, CO_2 , to move the vapors upwards. Introducing the inert gas allows the temperature of the column bottom to be held near the temperature of the feed stream, allowing a single regenerative heat exchanger to feed the system as per Figure 2. The effects of temperature and inert gas flow rate in the dehydration column have been modeled using the Aspen II simulation using linoleic acid (11 stages, feed on stage 6) as shown in Figures 5 and 6. Assuming otherwise constant operational parameters (an inert gas to solvent mole ratio of 0.2, a solvent return to the top of the dehydrator at 0.5 F_{solv} and a water reflux ratio of 1.7), the fraction of water recovered in the distillate increases from 95% at 160° F to 99.5% at 200° F as the operating temperature of the column increases, but the fraction of ethanol leaving in the top distillate

also increases, so that a lower fraction of the ethanol leaves with the solvent in the bottoms stream as seen in Figure 5. Figure 6 shows the effect of the inert gas flow in the dehydration column at a feed/bottoms temperature of 170°F. If no inert gas is fed, very little water vapor exits the top of the column, and as the ratio of inert gas to solvent increases, the amount of water removed from the solvent increases, but the amount of ethanol leaving with the distillate also increases. A 98% removal of the water in the distillate, and a 94% recovery of the ethanol in the bottoms is obtained at an inert gas ratio of 0.2. After the water is removed from the solvent, the ethanol is vacuum stripped from the heavy solvent in a solvent stripping column. The hot solvent from the bottom of this solvent stripper is then taken back to the regenerative heat exchanger, cooled and recycled to absorb ethanol in the absorber again (Figure 2).

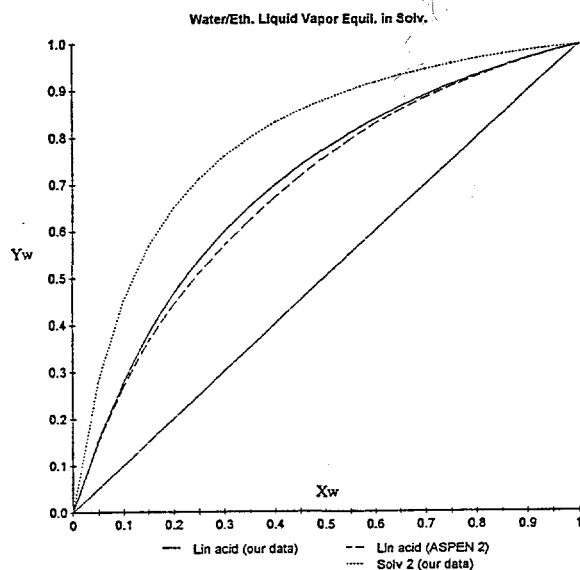


Figure 3. Water/Ethanol liquid vapor equilibrium in a hydrophobic solvent on a solvent free basis.

EXPERIMENTAL PERFORMANCE OF SAED SYSTEM

A six inch diameter column packed with Goodloe type net packing was built to test the performance of the SAED system. The extractive distillation column was 48" tall with approximately 18" of packing in the stripping portion of the column and 18" in the rectifying portion. Solvent with about 0.2-0.4% water, and 0.2-0.3% ethanol was fed to the system through a small plate and frame regenerative heat exchanger. Temperatures of 190-230 F were maintained using steam coils in the bottom of the dehydrator and vacuum stripper columns. Reflux ratios, temperatures, and flow rates were varied to test the ability of the dehydrator to distill water from the solvent, and the stripper to remove ethanol from the solvent. Table 1 gives our data on two runs. The results verify that the conditions identified in our hand and computer model can give good separations, with water taken as an overhead product, and ethanol as a bottoms. Ethanol levels in the distillate are higher than desired in Run 54 (20% vs. 5% w/v), but we feel that if there were more equilibrium stages in the dehydrator and vacuum stripper, results comparable to the model would be easily attained.

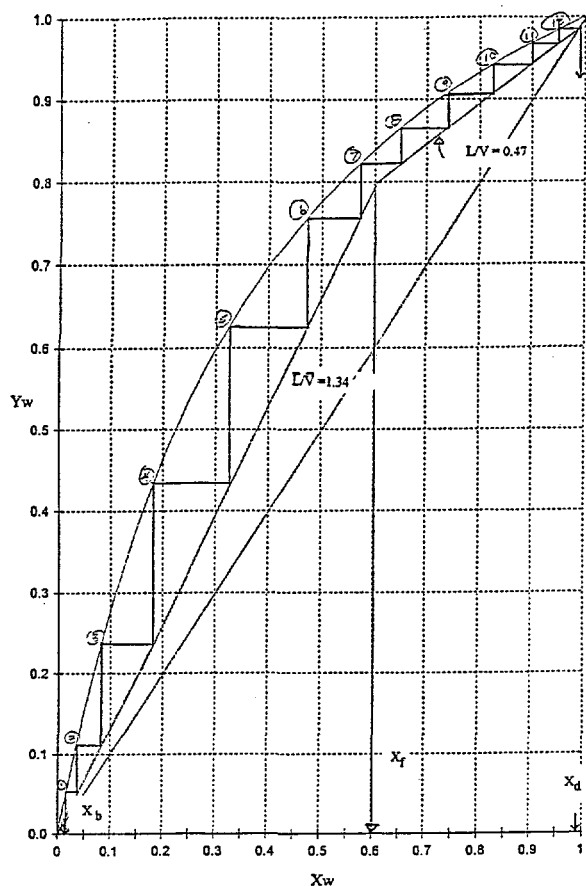


Figure 4. A McCabe-Thiele analysis of the extractive distillation of water from the solvent (solvent free basis)

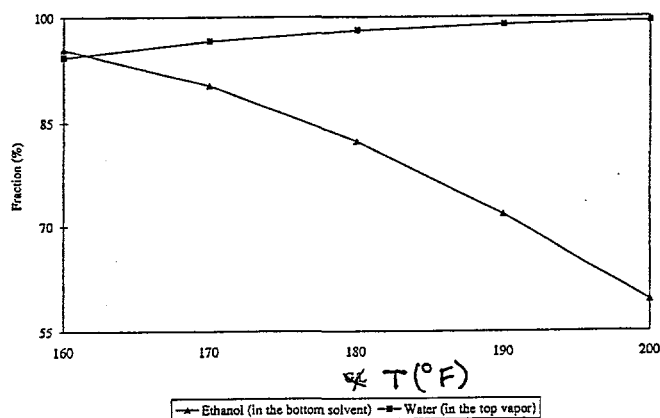


Figure 5. The effect of operating temperature on the extractive distillation column based on ASPEN 2 analysis (11 stages).

NON-ISOTHERMAL OPERATION OF THE CSRS AND SOLVENT ABSORBER

Stripping efficiency of ethanol from the fermentation broth improves at higher temperatures due to the increased vapor pressure of ethanol, similarly absorption efficiency improves at lower temperatures due to the decreased vapor pressure of ethanol. Thus, if the stripping gas introduced to the CSRS is run warmer than the absorber the amount of gas recalcitrated can be reduced, leading to a reduced flow of solvent in the SAED system. For example, if the inlet gas to the CSRS is warmed to 42

Table 1
Experimental data from a 6" OD pilot scale SAED system.

Extractive Distillation (Dehydration Column)	Run 54	Run 29
Solv. Feed Rate	500 ml/min	750 ml/min
Feed Solv. Composition		
ethanol	2.1 g/l	1.8 g/l
water	3.7 g/l	6.2 g/l
Feed Inlet Temp	215F	183F
Bottoms Temp	231F	220F
Headspace Temp	202F	182F
Solvent Reflux Rate	250 ml/min	75 ml/min
Water Reflux Rate	0.8 ml/min	0
Inert Gas Rate	12.7 l/min	6 l/min
Distillate Composition		
ethanol	200 g/l	67 g/l
water	933 g/l	
rate	3.1 ml/min	n/m
Bottoms Composition		
ethanol	1.8 g/l	1.5 g/l
water	1.0 g/l	3.0 g/l
Vacuum Ethanol Stripper		
Feed Temp	226F	170F
Column Temp below Feed	219F	205F
Column midpt Temp	213F	205F
Bottoms Temp	230F	220F
Cond. Temp	44F	37F
Inert Gas Rate	3.4 l/min	6 l/min
Vacuum	24.2" Hg	23.5 in Hg
Distillate Composition		
ethanol	93% ethanol	45% ethanol
water	743 g/l	
rate	60 g/l	
rate	0.43 ml/min	n/m
Bottoms Composition		
ethanol	0.32 g/l	1.3 g/l
water	0.47 g/l	0.5 g/l

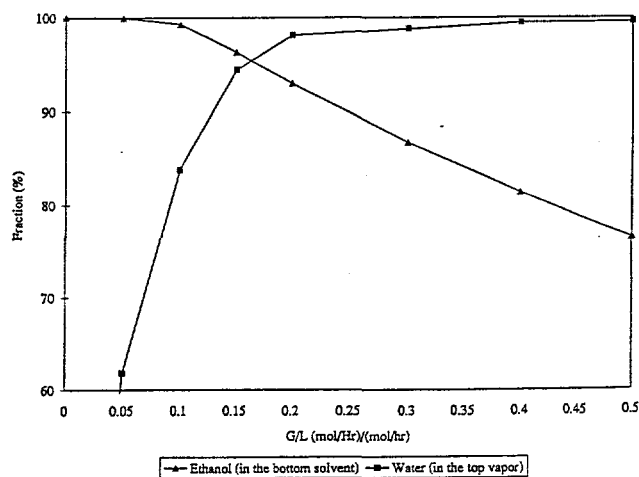


Figure 6. The effect of inert gas flow on extractive distillation performance at 170°F based on ASPEN 2 analysis.

Energy Use as Function of Feed Sugar

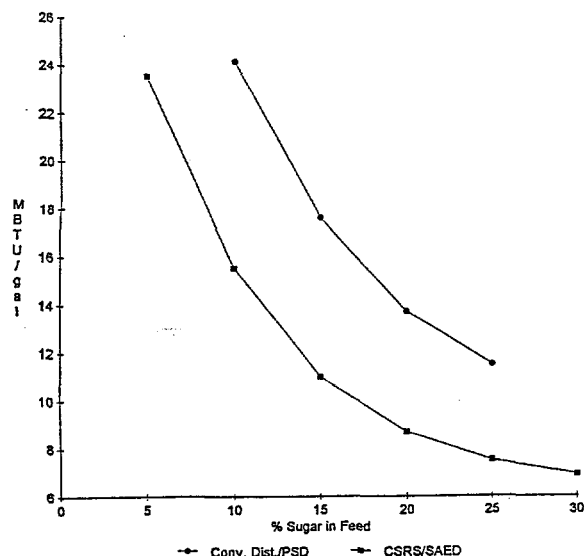


Figure 7. Steam energy requirements for SAED compared to a conventional distillation for fermentation broths with different initial sugar concentrations.

C, (with heat added by the blower and some steam) while the absorber is operated at 25 C, the gas flow rate can be reduced by 33% in the CSRS, and the solvent flow through the SAED system can be reduced by 55% as compared to an isothermal system running at 32 C. These reductions in solvent flow also give a concomitant reduction in energy requirements.

ENERGY REQUIREMENTS FOR THE SAED PROCESS

The energy use for recovery of an anhydrous ethanol product from vapors in contact with various concentrations of ethanol was estimated. These energy calculations were done with the following assumptions: 1) an approach temperature of 5° C is maintained in the solvent regenerative heat exchanger. The inlet temperature of the rich cool solvent is 32° C, with an outlet temperature of 94° C, inlet temperature of hot lean solvent is 100°, and outlet temperature is 37°, 2) the rich solvent is heated a further 6° C with steam to 100°, 3) the lean solvent is cooled from 100° to 37° C regeneratively, and then cooled 60 to 31 C. with cooling water, 4) a molar reflux water ratio (L/D) of 1.0 is used in the dehydrator, 5) a reflux ethanol ratio (L/D) of 0.05 is used in the vacuum stripper, 6) an inert (CO₂) mole ratio of 0.1 (mole CO₂/mole solvent) is used in both the vacuum stripper and dehydration columns, 7) there is a 50 difference in operating temperature between the absorber (30°) and the gas to the bottom of the CSRS (35° C), 8) the vapor-liquid equilibrium for ethanol and water in the solvent is based on Figure 4, and 9) the inlet water concentration in the solvent is 0.4% by weight.

The calculated energy usages (based only on steam requirements) to recover an anhydrous product from feeds at various sugar concentrations are shown in Figure 7. These energy uses are approximately 55 to 66% of the energy costs associated with conventional distillation [16] combined with pressure swing dehydration (PSD) using molecular sieves. PSD was assumed to use about 1000 BTU/gal [17,18]. Energy requirements drop more or less linearly as sugar concentrations rise and higher ethanol concentrations are reached in the beer (an ethanol yield of 0.46 Y p/s was used in these calculations) However, once beer concentrations reach 10% (21% sugar) the

energy savings decrease slowly. Conventional brewing is generally limited to 10-12% ethanol to keep the length of brewing time low, while the CSRS can handle higher level sugars due to the gas stripping of ethanol.

THE PILOT SCALE CSRS

A 24,000 liter, four stage lab scale CSRS was constructed by Lamont Fabrication Co, Lamont IA. under the supervision of R.L. Lehman of PRI. The diameter of the column is 8 ft. and the total height is 22 ft. with the schematic in Figure 2. The ethanol vapors in the CO₂ stream leaving the CSRS are taken to the solvent absorber column. The absorber is rectangular in design and packed with a structured type packing to minimize gas phase pressure drop. A 10HP regenerative pressure blower from the New York Blower Company is used to recirculate CO₂ in the CSRS and absorber system.

The reactor was installed at the Iowa test site in March of 1995. The reactor was seeded and fermentation tests began in May. Nutrients (corn steep liquor and minerals) were metered using a peristaltic type lab pump. Problems were encountered with the seals leaking around the stirring shaft, which is of a single shaft design, going down the center of the CSRS. These seals were initially a block of Teflon with a close tolerance to the shaft dimension (2" diameter). This shaft leakage allowed the fermentation broth to drain from the top 3 stages without overflowing onto the gas-liquid contacting plates. Three different strategies for replacement of these seals with other type seals were tried in succession, until we moved to a 3" ID shaft sleeve/weir which was installed in August. The reactor was then reseeded and feed started on Sept. 8th. The reactor has been running continuously since this start-up through the current time (Dec. 1995), with no further difficulties with shaft leakage. Feed rates to the reactor range from 2 to 4 GPM at 20-23% sucrose, and flocculant settled cell densities (5 min) have been measured at between 5 and 30% v/v. Outlet sugar concentrations have been between 0 and 1% with ethanol concentrations of 9 to 11% ethanol determined.

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