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Sorptive Recovery of Dilute Ethanol from Distillation Column Bottoms Stream

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ABSTRACT

Modern ethanol distillation processes are designed to ensure removal of all ethanol from the column bottoms, i.e., to levels <100 ppm ethanol, and utilize substantial stripping steam to achieve this result. An alternate approach using sorption was attempted as a means to reduce energy requirements in the stripping section, and thereby reduce cost. Adsorbents tested for use in such an application showed that carbonaceous supports, in particular Ambersorb XEN 572, gave alcohol-free water as effluent when a 1% (w/w) starting ethanol concentration was passed downflow at 1 bed vol/h over a fixed-bed adsorber at 70°C. Regeneration was readily achieved at 70–90°C using hot air, vacuum, superheated steam, or hot water to strip the ethanol from the column, and yielded ethanol streams containing a maximum of 5.9% alcohol, with average concentrations of 2.5–3.5% depending on the regeneration method used. These experimentally determined operating conditions combined with distillation energy calculations have enabled development of a process concept for sorptive concentration of dilute ethanol which is more energy efficient than distillation alone. The combination of existing distillation and corn grit drying technologies, with sorptive recovery of dilute ethanol (from the column bottoms) shows promise of recovering a fuel grade, 99.4% ethanol product from a 4.5% ethanol broth with an energy requirement of 23,100 BTU/gal. The potential energy saving of 3600 BTU/gal over distillation alone corresponds to 1.8¢/gal, and provides motivation for further examination of this approach in reducing costs of ethanol production from biomass.

Index Entries: Adsorption; dilute ethanol; Ambersorb; stripping steam; distillation energy.

Abbreviations: C_p, specific heat capacity of water; D, mass flow rate of overhead product; $\dot{m}_c$, mass flow rate of cooling water in overhead condenser; $\dot{m}_s$, mass flow rate of steam in reboiler; R_D, R, reflux ratio for distillation column; R_{Dmin}, R_{min}, minimum reflux ratio; l, latent heat of vaporization of liquid in bottoms; l_s, latent heat of vaporization of steam; ΔT, rise in temperature of cooling water in overhead condenser.

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Table 1
Approximate Cost Ranges for Conversion of Corn to Ethanol (2)

Item	Approximate cost range, ¢/gal
Net corn	40–60
Operating	
Energy fuel (steams)	10–20
Electricity	5–10
Enzymes	3–4.5
Chemicals	1.5–2.5
Other	18.5–38
Capital	30–60
Total	108–195

INTRODUCTION

A modern integrated alcohol plant has energy requirements in the range of 34,000–41,000 BTU/gal, and includes alcohol stripping, rectification and dehydration steps, as well as evaporating water from soluble components and drying fibrous material (1). The energy cost is about 10–20% of the overall cost of ethanol production from corn (Table 1), with a reduction in energy costs often requiring higher capital investment (2). Operating costs are distributed principally among energy, enzyme, chemical, and other costs.

Energy has been a significant operating cost, and therefore, innovations have focused on conserving energy. Although the distillation of ethanol consumed up to 50% of the overall energy used in some types of grain alcohol plants (3,4), process improvements and plant design have significantly reduced this. This area has accounted for most of the savings in the last 5 yr, and further large savings in energy costs are going to be more difficult to achieve (5).

The concentration of fermentation-strength ethanol involves an atmospheric distillation step that removes ethanol from water to obtain an overhead concentration of 90–95.6% (by weight) ethanol. This is followed by adsorption or azeotropic or extractive distillation to obtain fuel-grade ethanol. The energy required to distill fermentation-strength ethanol to its azeotropic composition (95.6% by weight at atmospheric pressure) is a function of ethanol concentration in the feed as well as the reflux ratio (6,7).

Various energy-efficient approaches have been implemented to reduce energy requirements for removing the last 5–10% of water. These include the use of ground corn or molecular sieves in fixed-bed sorption processes, and staged distillation systems that use various organic agents for removing the water in an extractive or azeotropic distillation. Ethanol-water mixtures can be separated by passing the vapors over various biomass materials, such as corn (6,8,9), corn meal (10–14), and corn grits (9,12,15,16); cellulosics (6,11,17); and starch (6,9,11,18,19). The sorption system, which utilizes corn grits as the sorbent currently processes about 50% of the alcohol produced in the United States (750 million gal/yr) (20). Laboratory data show that this process readily accepts 85% ethanol with a minimal energy penalty compared to a 90% ethanol feed (12).

Removing the last traces of alcohol in the bottom or stripping section of the distillation column can also consume a significant fraction of energy, particularly for 4–6% ethanol feed concentrations, which are likely to be typical for cellulose conversion processes. Modern ethanol distillation processes are designed to achieve <100 ppm ethanol in the bottoms composition. Ethanol removal, by use of an adsorbent, has the potential to reduce energy requirements in the stripping section. For example, if the stripping section gives a 1% ethanol stream, the remaining ethanol could be recovered by adsorption. A concentrated aqueous ethanol would be recovered on regeneration of the sorbent and then be reintroduced into the column at or above the feed plate.

This article investigates the potential of achieving significant energy savings using an adsorption step at the bottom of the column, in preference to achieving a comparable concentration by distillation alone, since less water is boiled up to recover the same amount of ethanol. Selection of the sorbent, regeneration conditions, and regeneration media are described.

The energy tradeoffs of a combined distillation/adsorption system, and experimental testing of the process concept, are presented in the context of a first estimate of the material and energy balance for a distillation process with sorptive ethanol recovery.

MATERIALS AND METHODS

Selection of the Sorbent

The sorbents examined in this work were Amberlite XAD-2, XAD-4, Amberchrom CG-71, Ambersorb 563, and Ambersorb XEN 572, corn grits, solka floc, and Avicel (Table 2). The carbonaceous, Ambersorb materials are pyrolyzed, highly sulfonated, styrene/divinyl benzene macroreticular ion exchange resins with surface areas 550 m^2/g (for Ambersorb 563) and 1100 m^2/g (for 572).

Sorption capacities of these materials were measured by adding 4 mL of 1% ethanol to 1 g of each material in a culture tube, capping and sealing the tube, shaking the mixture for 5–30 min at ambient temperature, and then measuring the ethanol removed from the liquid based on a gas chromatography (GC) analysis of the liquid. The ethanol present was measured by GC analysis of 3.5 μL of sample using a Hayes Sep D (Supelco, Bellefonte, PA) column in a Shimadzu GC-14A instrument. This combination of the column and GC instrument gives a baseline separation of water from ethanol with helium as the carrier gas, and detection by a thermal conductivity detector (TDC). The column temperature was 180°C, the injector 120°C, and the detector 135°C for this analysis.

A follow up study at 70°C was conducted with the adsorbent Ambersorb XEN 572, since it was found to have the best properties with respect to removing ethanol from water efficiently. This sorbent has a particle size of 0.3–0.84 mm with a density of 0.49 g/mL, and micro-, meso and macroporosities of 0.41, 0.19, and 0.24, respectively.

Adsorption and Regeneration Methods and Conditions

Apparatus

Testing of adsorption and regeneration conditions was carried out in an experimental apparatus (Fig. 1) consisting of a 25 mm id × 60 cm long, jacketed column

Table 2
Comparison of Ethanol Removed by Different Sorbents at Ambient Temperature

Sorbent	Available from	Chemical structure/ composition	Wt, air-dry, g	Vol 1% EtOH added, mL	Contact time, min	% EtOH removed	Wt EtOH removed, g/g of sorbent
Ambersorb 572	Supelco (Bellefonte, PA) developed by Rohm and Haas	Carbonaceous, produced by pyrolysis of a highly sulfonated styrene-divinyl-benzene macro-reticular ion-exchange resin; surface area = 1100 m^2/g	1	4	30	87	0.0344
			1.0017	4	5	88	0.0347
Ambersorb 563	Supelco	Similar to Ambersorb 572, surface area = 550 m^2/g	1	4	30	87.5	0.0346
			1.0022	4	5	81	0.0319
Amberlite XAD-2	Supelco	Polyaromatic, surface area = 300 m^2/g	1.0008	4	30	0.3	0.0001
Amberlite XAD-4	Supelco	Polyaromatic, surface area = 725 m^2/g	1.0244	4	30	22.1	0.0085
Amberchrom CG-71	Supelco	Highly crosslinked methacrylic resin, surface area = 450–550 m^2/g	1.005	4	30	24.7	0.0097
Corn grits	J. R. Short Milling Co., Kankakee, IL	75% starch, the balance is protein, oil, and fiber	1.0055	8	30	11.9	0.0094
Solka floc	James River Corporation, Berlin, NH	Pulping cellulose	1.0072	8	30	10.5	0.0082
Avicel	FMC Corporation	Microcrystalline cellulose	1.0015	8	30	11.3	0.0089

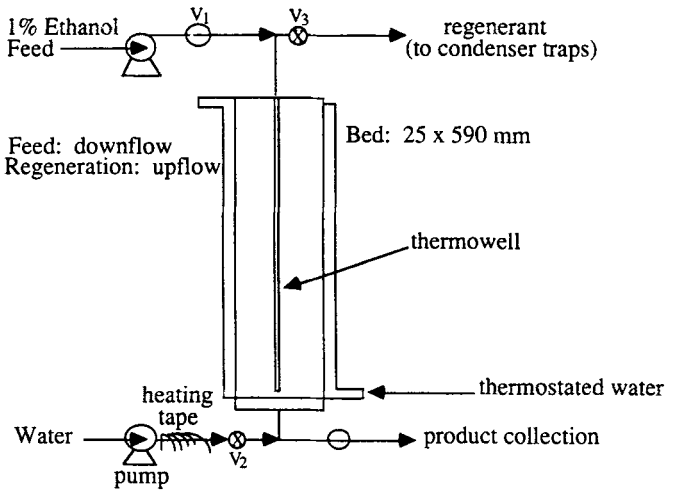

Fig. 1. Schematic representation of adsorption apparatus (not to scale).

containing the Ambersorb XEN 572 adsorbent with a bed height of 59 cm and a bed volume of 288 mL (corrected for the volume displaced by the thermowell). The thermowell (2-mm id) was located in the center of the column, and three thermocouple wires were fitted inside and connected to an automatic signal scanner (Omega Engineering Inc., Stamford, CT) to read the temperature. The wire tips were placed 5, 30, and 55 cm from the bottom of the column. Two circular wire screens were placed on the ends to retain the sorbent. The column (Ace Glass Inc., Vineland, NJ) was inverted and packed with the adsorbent by the tap and fill method. The polypropylene parts were then screwed in. The jacket was heated to the desired temperature using circulating water. Heated 1% aqueous ethanol was passed downflow at 1 bed vol/h.

The connecting tubes of the apparatus were made of steel, except for the tube between valves V_1 and V_3, which was plastic. The tube leading from the preheater to the bottom of the column was covered with insulated electric heating tape. This was connected to a powerstat to control the power and, hence, the temperature of the tape. A setting of 130 was chosen for the powerstat to give a temperature >110°C, to heat the water/ethanol mixture. The pump (Milton Roy Company, Riviera Beach, FL) used was rated at 29–290 mL/h flow rate. Owing to the small size of the apparatus, significant heat losses occurred, thus dropping the temperature to below 100°C.

Operating Procedures

During the adsorption cycle, the valve V_1 was connected to the ethanol feed reservoir, and V_3 was adjusted to make all the ethanol feed enter the column from the top. Samples collected at the column outlet were used to generate breakthrough profiles. The sorbent was regenerated by one of four methods: air, vacuum, steam stripping, and hot water. Each method of regeneration was evaluated with respect to the time of regeneration, percentage of ethanol in the condensate, and the degree of regeneration of the bed. The effectiveness of the regeneration step was assessed by running an adsorption cycle after regeneration and comparing the breakthrough profiles obtained at different regeneration conditions.

During regeneration, valve V_2 was adjusted to allow upward flow, and valve V_3 was switched to collect the stripped vapors. The preheater was kept at 95°C, and the electric heater tape was connected to a powerstat set at 130. The condenser vessel was cooled in a mixture of dry ice and acetone. This facilitated the capture of all condensable vapors for purposes of obtaining accurate mass balances. Regeneration by hot air was carried out with the column jacket maintained at 70°C. Air, heated by the preheater and heating tape to 70°C, was passed upflow at a pressure of 1.5 psig.

Upflow vacuum regeneration was carried out by pulling a vacuum with the jacket at 93°C. During vacuum stripping, the condenser outlet was connected to a vacuum pump, which gave a vacuum of 660 mmHg below atmospheric pressure.

Steam stripping was approximated by pumping water upflow at 5.5 mL/min through a tube covered with heating tape, which vaporized the water. A 660-mmHg vacuum was also applied to prevent condensation of water vapor at the column temperature of 89°C.

The apparatus for runs where regeneration was carried out with pressurized hot liquid water included a 12 mm x 14.5 cm steel column packed with 6.6 g of the Ambersorb XEN 572. Liquid chromatography end fittings with frits were used to retain the sorbent. The column was loaded with 1% ethanol at room temperature at a flow rate of 3.03 mL/min. For regeneration, the entire system, except the condenser, check valve, and pump, was immersed in a sand bath maintained at 120°C. Water was pumped through the column at a back pressure of 350 psig and a flow rate of 3.03 mL/min. In case of water regeneration, a vacuum at 660 mmHg was applied for 10 s between collection of regeneration samples to clear all lines. Vacuum was also applied for 10 min at the end of each run to clear the system of vapors.

Once feasibility was established based on the quick runs with the small column, regeneration with hot water was carried out by pumping at 5.5 mL/min with the larger column at 80°C and atmospheric pressure using the apparatus of Fig. 1. Collection of the effluent was the same as before.

Effect of Glucose on Ethanol Sorption

The dilute fermentation stream that enters a distillation column will have sugars in it. A batch study was conducted with a dilute solution of 4 mg/mL glucose to quantify the adsorption behavior of Ambersorb in the presence of glucose. The procedure consisted of soaking 5.0 g of Ambersorb in 30 mL of water for 60 min. The water was then drained off (9 mL of interstitial water remained) and 50 mL of glucose solution at 3.96 mg/ mL were added. The mixture was allowed to stand with no agitation. The mobile phase glucose concentration at different times was measured by a Beckman Glucose Analyzer (Beckman Instruments Inc., Fullerton, CA).

The effect of glucose on the breakthrough volume for a 1% ethanol feed was also carried out using the column adsorption system shown in Fig. 1. Two runs were carried out with 1% alcohol containing 4 mg/mL glucose. Collection of the sample and analysis of the ethanol content were carried out as described previously. Regeneration was by the hot water method. Vacuum was used between samples to clear the system as previously described.

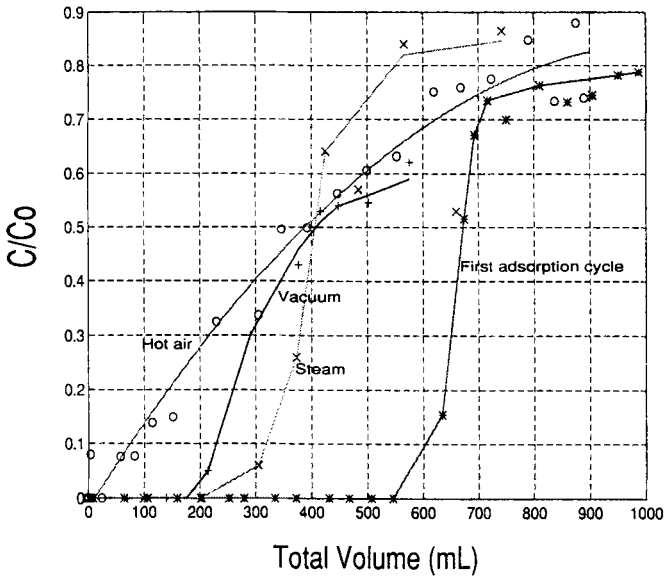

Fig. 2. Ethanol breakthrough profiles for Ambersorb XEN 572 at 70°C for dry, never-used sorbent (first adsorption cycle) and after sorption/regeneration/sorption sequence with regeneration using hot air, steam regeneration, and vacuum.

RESULTS

Sorbent Selection

Ambersorb XEN 572 and 563 removed more than 80% of the ethanol in 30 min of batch contacting. A shorter contact time of 5 min gave similar ethanol uptake, although Ambersorb XEN 572 performed marginally better than 563. The capacities of polymeric, starch (corn grits), and cellulosic (solka floc, Avicel) materials were lower (Table 2). Hence, Ambersorb 572 was selected as the adsorbent to be used in further runs.

Ambersorb 572 had lower capacity at 70°C (81% ethanol uptake) than at room temperature (88% uptake). The difference was small enough, however, that the adsorption step was carried out at 70°C. Sorption at the higher temperature is beneficial since the bottom stream from an ethanol column is hot (typically close to 100°C). Processing of the bottom stream to 70°C (or higher) for the sorption step would leave more of the thermal content of this stream to be used elsewhere in the plant.

Fixed-Bed Adsorption Runs

Dry Ambersorb XEN 572, evaluated in the apparatus shown in Fig. 1, initially gave the sharp breakthrough profile as shown in Fig. 2. Breakthrough occurred at 600 mL. Ethanol uptake, corrected for an estimated column void volume of 115 mL (40%), was 4.85 g of ethanol, or a loading of 16.8 g/L column volume. After several adsorption and regeneration cycles, the breakthrough occurred at 200–220 mL instead of 600 mL. Ethanol uptake, corrected for column void volume, now corresponded to 1 g of ethanol, or 3.4 g/L column volume. Significant, nonreversible

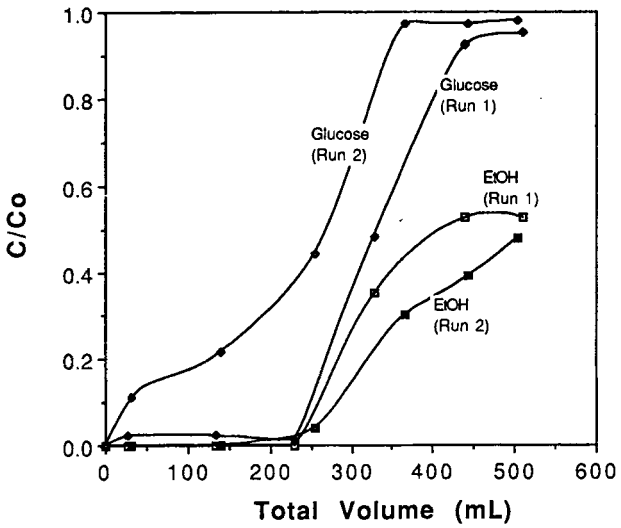

Fig. 3. Ethanol sorption in the presence of glucose—two replicate runs. Glucose breakthrough curves showing lower capacity for glucose uptake after the first run.

ethanol sorption occurs during the initial phases of the adsorption cycles at the regeneration conditions used in this work.

Effect of Glucose on Alcohol Adsorption

The Ambersorb takes up glucose, with 16% of the glucose (at 4 mg/mL) being adsorbed in 40 min. Nearly 70% was removed in 24 h. Since the sorption of glucose is slower than ethanol uptake, a short contact time with a mixture of ethanol and water should favor ethanol sorption.

Ethanol sorption runs with glucose present gave breakthrough volumes for ethanol that were the same as for runs carried out in the absence of glucose (compare Fig. 3 to Fig. 2). The regeneration stream contained 0.1–1.0 mg/mL glucose when regeneration was carried out using hot water at 93°C, with a decrease in glucose uptake occurring after the first adsorption/ regeneration cycle (Fig. 3). This indicates that a background adsorption of glucose occurs. Nonetheless, the adsorbent retains its effectiveness to sorb ethanol in the presence of dilute glucose.

Regeneration

The results of the regeneration run are summarized in Table 3. The degree of regeneration of the bed was measured by loading the column after a regeneration run and recording the breakthrough profile thus obtained. The profiles obtained after regeneration with hot air, steam, and vacuum are shown in Fig. 2. Regeneration with hot air is slow and incomplete, as indicated by the elution profile obtained after regeneration with hot air (Fig. 2). Steam stripping is faster and gives a more complete regeneration of the bed (the breakthrough volume is close to 225 mL). The results for the vacuum regeneration are similar (Fig. 2).

Both methods are relatively expensive and hence a regeneration by hot liquid water was attempted by passing hot water under a 50-psig back pressure through the column. Hot water was found to give a near-complete regeneration of the bed at

Table 3
Results of Regeneration Runs

Method	Temperature, °C	Pump flow rate, mL/min	Volume of condensate, mL	Ethanol in condensate, wt%	Time of regeneration, min	Maximum ethanol concentration obtained wt%
Hot air	70	—	81	4.9	415	6.2
Steam stripping	70	5.50	270	2.6	53	4.1
Vacuum	70	—	120	4.0	75	NA[c]
Hot water column	80	5.50	151	2.3	35	2.6
	93[a]	5.50	83	2.6	30	2.7
	120[b]	3.03	16	2.2	9	2.3
	93[a]	3.06	88	3.2	41	4.7
	93[a]	2.80	70	3.5	41	5.9

[a]Column jacket insulated.
[b]Small column.
[c]Not available.

80°C, but only gave a stripped ethanol concentration of 2.3%. Stripping with hot water at 93°C and 120°C gave almost the same concentration of ethanol in the condensate (2.2%), as expected, since earlier batch studies had indicated only a small temperature dependence for adsorption. When the flow rate of regenerating water was decreased from 5.5 to 3.06 mL/min, the average concentration of ethanol increased to 3.2%. With a still lower flow rate of 2.8 mL/min, an average concentration of 3.5% ethanol was obtained (with a maximum concentration of 5.9%) (Table 3). Sorptive concentration of a 1% ethanol stream using hot water as the regeneration media is thus shown to be possible. This result also indicates that 4% ethanol could be recovered from a hot water regeneration step, if multiple adsorber columns are properly staged for countercurrent flow of hot water. These results justify use of the basis of recovering 3.2% ethanol from a 1% feed for calculating material and energy balances.

Material Balance

The capacity of 3.4 g/L column volume would require a process designed to carry out adsorption/desorption in 5-min cycles. On this basis, the amount of sorbent required for a 50 million gal/yr ethanol plant would be on the order of 250,000 L. Hence, a higher capacity is needed. Significant further research, development, and testing are needed before large-scale use would be achieved. The current work presents the energy consequence of such a process if it were developed and implemented.

A process concept for combined distillation/adsorption was thus developed based on the experimental results, and the material balance generated (Fig. 4). The fermentation broth entering the recovery section is 4.5 wt%. A 90% ethanol overhead product is assumed for the distillation tower. The minimum reflux for such a system is 4.23. A practical operating reflux ratio of 6.35 ($=1.5 \times R_{Dmin}$) is used. The bottoms at 1 wt% alcohol are directed to the adsorber.

DISCUSSION

Description of Distillation/Sorption System

A standard ethanol stripping system splits the feed into an ethanol rich overhead and a dilute bottoms stream. An approach that combines distillation and adsorption would use adsorption processes both overhead and at the bottom of the column as energy-efficient alternatives to remove the remaining small amounts of water and ethanol, respectively. The use of adsorption with stripping entails addition of adsorption columns at the bottom of the distillation tower as illustrated in the simplified diagram of Fig. 5. Energy-efficient integrated distillation systems have been studied and developed, including a staged distillation system using an alkali-extracting agent and distillation with intermediate heat pumps and optimal sidestream return *(21–23)*. The analysis here is for an atmospheric distillation column with recouping of heat from the column bottoms through preheating of the distillation column feed, and condensation of the overhead distillation column vapors to preheat partially the water or gas used to regenerate the sorbent on which the dilute ethanol is captured and concentrated.

Ethanol/Water Vapor-Liquid Equilibrium Data for Energy Calculations

The equilibrium data used for evaluating the energy tradeoffs were obtained from Carey and Lewis *(24)*, and fitted to polynomials by least-squares regression

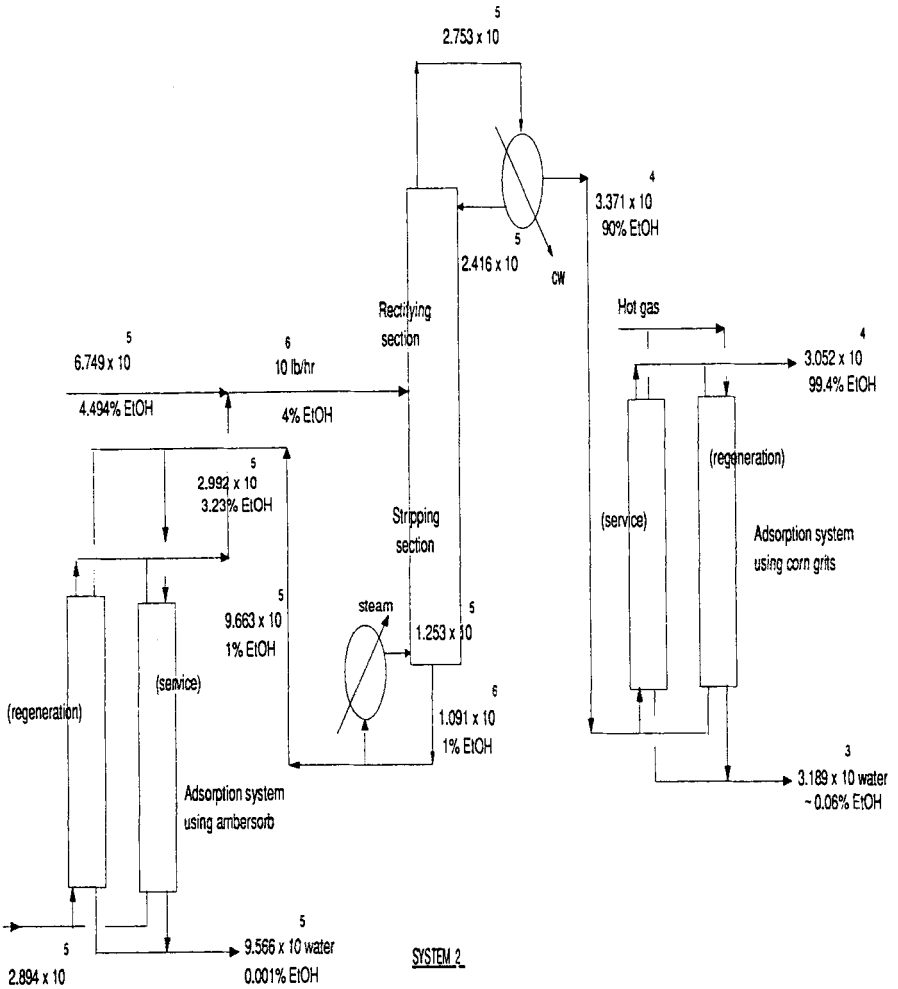

Figure 4. Process schematic with material balance for a combined distillation/adsorption system for ethanol/water, with an ethanol fermentation broth concentration of 4.5%, and a column feed concentration of 4% ethanol. Flows are in lb/h for a 50,000,000 gal/yr plant.

using the statistical package, SAS. The best fit was given by the three polynomials, shown in Table 4. The fit over the ranges of 0.0–0.12, 0.12–0.52, and 0.52–0.9 mol fraction ethanol is shown in the combined plot in Fig. 6. Data from other sources *(25–27)* generally coincided with that of Carey and Lewis as shown in Fig. 6.

Calculation of Energy Requirements

Several cases were calculated with respect to energy requirements. For a thermally saturated liquid feed, the steam required per hour ($\dot{m}_S$) is given by *(28)*:

$$\dot{m}_S = D \times (R_D + 1) \times (\lambda/\lambda_S) \quad (1)$$

The cooling water requirement is given by:

$$\dot{m}_c = D \times (R_D + 1) \times (\lambda/\Delta T) \times C_p \quad (2)$$

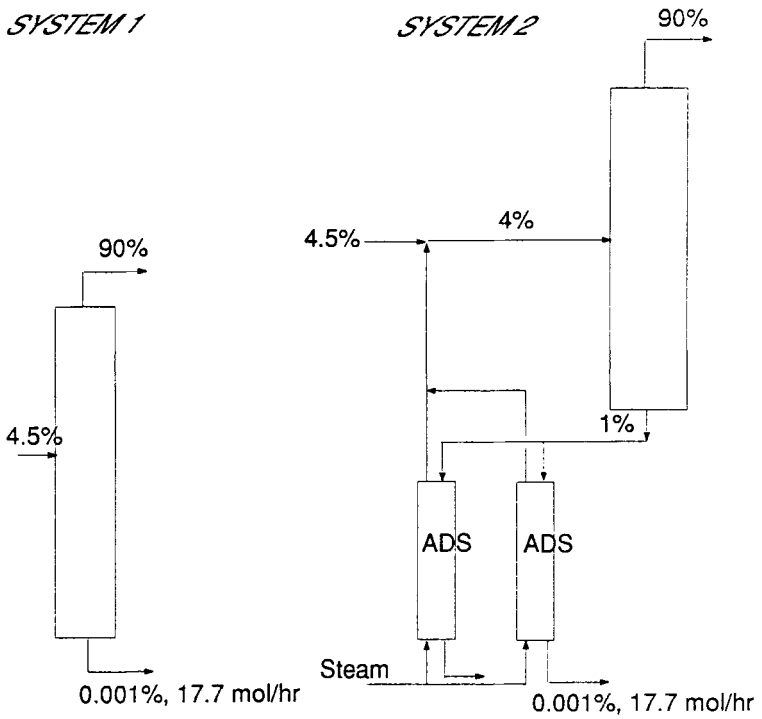

Fig. 5. Simplified schematic: comparing distillation (system 1) vs distillation combined with adsorption (system 2). Overhead condensers, reflux, and reboiler not shown for purposes of this illustration.

The minimum reflux is a function of the wt% ethanol in the feed (Fig. 7). For a 90% (by weight) overhead product, feed compositions of 20% or lower avoid the pinch region between the equilibrium curve and operating line. At 92% ethanol, the pinch region (where the rectifying operating line is tangent to the equilibrium) corresponds to about 17.7 wt% ethanol. Prior calculations have shown that a pinch can occur for 12 wt% ethanol as the azeotrope is approached. The calculation is approximate given the sensitivity of the pinch region (and corresponding feed concentration) to the exact shape of the equilibrium curve. The optimum reflux ratio for the two systems will be 1.2–1.5 times the minimum reflux ratio (R_{Dmin}). We chose $1.5 \times R_{Dmin}$ as the basis of our calculations, together with the assumptions that the feed entering the column is thermally saturated.

The reboiler duty sharply increases for feed concentrations below 3% and under these conditions decreases slightly when the ethanol in the overhead product decreases from 90 to 85%. The energy requirement decreases when the feed concentration increases from 4 to 5% but changes little with respect to changes in the ethanol bottom concentration, assuming that the number of theoretical plates can be adjusted to meet the compositional constraints.

The additional theoretical plates required to increase overhead composition from 85 to 90% is small as long as the reflux ratio is allowed to increase accordingly. However, the number of plates increases dramatically as the reflux ratio decreases (Fig. 8). Figure 8 illustrates the limitations posed: by specifying the bottom composition at 0.001 (rather than 1%) in terms of theoretical plates at reflux ratios of

Table 4
Polynomials Used to Fit Ethanol/Water Vapor/Liquid Equilibria Data from Carey and Lewls *(24)*

Range, mole fraction	Polynomial	R^2
$x \leq 0.1238$	$11.07x - 126.9x^2 + 833.21x^3 - 2279.7x^4$	0.99
$0.1238 \leq x \geq 0.5198$	$0.15 + 4.90x - 27.2x^2 + 86.98x^3 - 159.1x^4 + 162.65x^5 - 74.06x^6$	0.99
$x \geq 0.5198$	$0.98 - 2.72x + 6.82x^2 - 6.67x^3 + 2.61x^4$	0.99

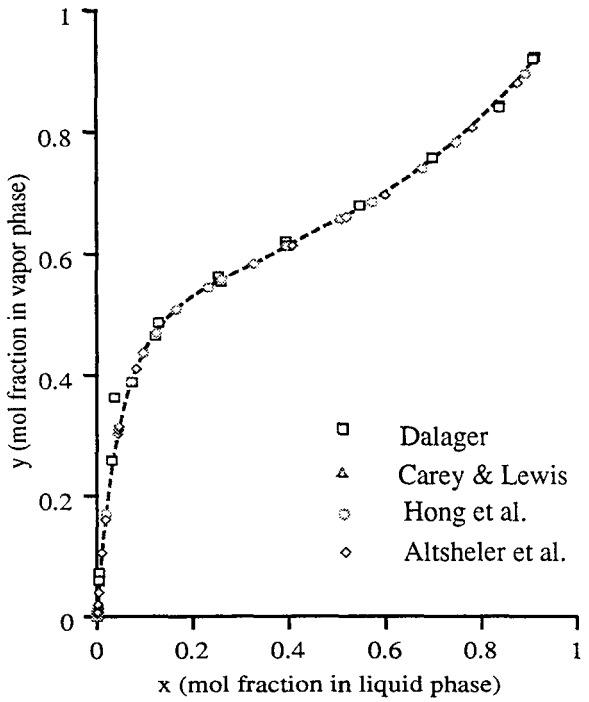

Fig. 6. Comparison of polynomials given in Table 4 to ethanol water equilibrium data atmospheric pressure for ethanol concentrations ranging from 0.0–0.92 mol fraction ethanol. Vapor liquid equilibrium curve based on combined equilibrium data text from several sources *(24–27)*. △, Carey and Lewis *(24)*; ○, Hong et al. *(25)*; □, Dalager *(26)*; ◇, Altsheler *(27)*.

10 or less. A column originally designed for 1% ethanol in the bottoms would be impractical to operate, if 0.01% ethanol were the goal since a very high reflux ratio (much >50) would be needed.

Potential for Energy Savings

The tradeoff between the number of theoretical plates and steam requirements is shown in Fig. 9. An energy usage (as reboiler duty) as low as 20,000 BTU/gal is practical for a 4% feed and 85% overhead product, and about 17,000 BTU/gal for a 5% feed, if the bottoms were to contain 1% ethanol and the overhead product 85% ethanol. The base case of a 90% overhead product with 4% feed shows that a

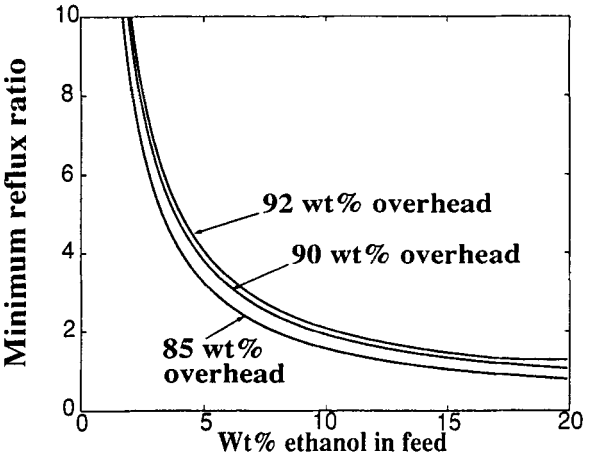

Fig. 7. Minimum reflux as function of ethanol concentration in feed, for 85, 90, and 92% (by weight) ethanol in the overhead.

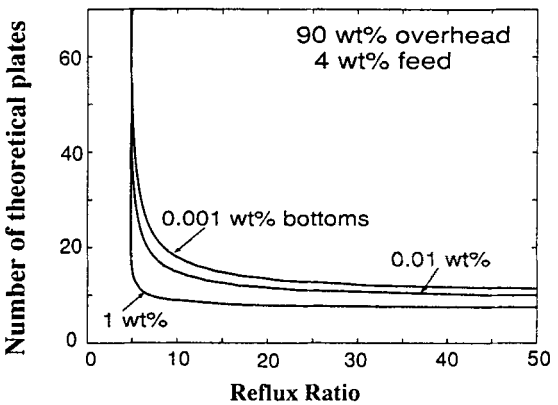

Fig. 8. Theoretical plates as function of reflux ratio for 90% ethanol in overhead product and 4% ethanol in feed.

column with 20 theoretical trays incurs a significant energy penalty as the ethanol in the bottoms decreases from 1 to 0.001 wt% (Figure 9). For a 40-tray column, the difference in energy requirements is <8%. If an overhead product of 90% can be processed by the downstream dehydration system, then the difference in energy required for recovering 0.001% alcohol in the bottoms vs 1% becomes smaller. An additional energy benefit is gained if 5% ethanol feed is available and 85% overhead product can be processed in the dehydration section to give the final fuel grade product. The energy and theoretical plate requirements in Fig. 9 show the potential benefits of stopping distillation at 1% bottoms and then recovering that ethanol by an alternative method.

Energy Requirements

A hypothetical process in which a 4.5% ethanol broth results in a 4% thermally saturated ethanol feed to the distillation column is shown in Fig. 4. A distillation tower

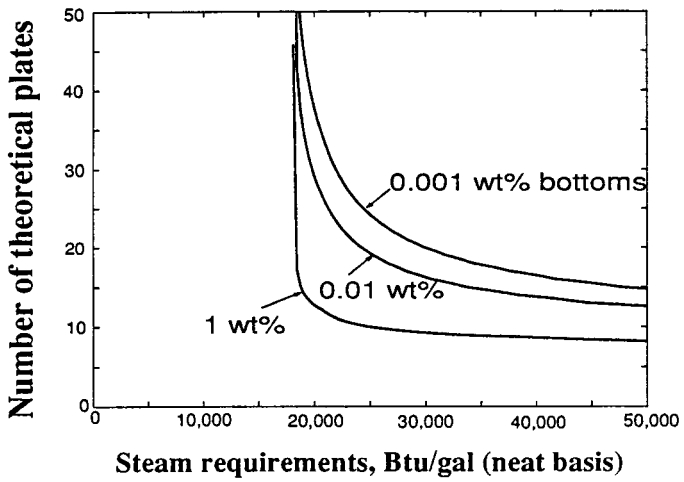

Fig. 9. Comparison of theoretical trays required as a function of steam requirements for 0.001, 0.01, and 1% ethanol (by weight) in the bottom product for 90% ethanol in overhead and 4% feed.

with 23 theoretical trays and a reboiler load of 23,100 BTU/gal ethanol (neat basis) would result. If a feed of 4.5% ethanol, an overhead product of 90%, and a bottom product of 0.001% is specified, the combination of distillation to 1% and adsorption to process the 1% bottom product would result in about 19,500 BTU/gal to obtain a 0.001% bottom stream. Of this energy requirement, about 18,300 BTU/gal are for distillation and about 1200 BTU/gal for regeneration (Fig. 10). The distillation column for such a process could be specifically designed to produce 1% ethanol, thereby offering capital cost savings since only 10 plates would be needed (instead of 21) with a minimal energy penalty. However, once such a column is built, it could not be used to recover 0.01 or 0.001% ethanol directly, since the energy costs would be prohibitive, requiring nearly 127,000 BTU/gal for a 0.01% bottoms and more than 160,000 BTU/gal for a 0.001% bottom.

The energy savings associated with an 90% overhead product are attractive, if the 90% ethanol vapors are dried using a corn grits sorption system. The energy required to obtain a fuel grade, dried ethanol product would be about 2000 BTU/gal for an 90% ethanol vapor stream in a properly designed and integrated unit *(12)*. The data and calculations show that a 4.5% fermentation broth (4% feed to the distillation column) has the potential of yielding a fuel-grade ethanol product using about 21,500 BTU/gal ethanol (as 99.4%). Hence, energy-efficient recovery of an ethanol stream derived from a biomass or cellulose process is shown to be technically feasible if sorptive, liquid-phase, recovery of the ethanol from distillation column bottoms is carried out. A closer study to optimize sorbent characteristics, capacity, and cost is now needed.

CONCLUSIONS

Recovery of ethanol from dilute distillation column bottoms by adsorption is feasible, and benefits can be derived from a reduced distillation tower size or energy savings. Cost savings may be possible if a column is specifically designed for cou-

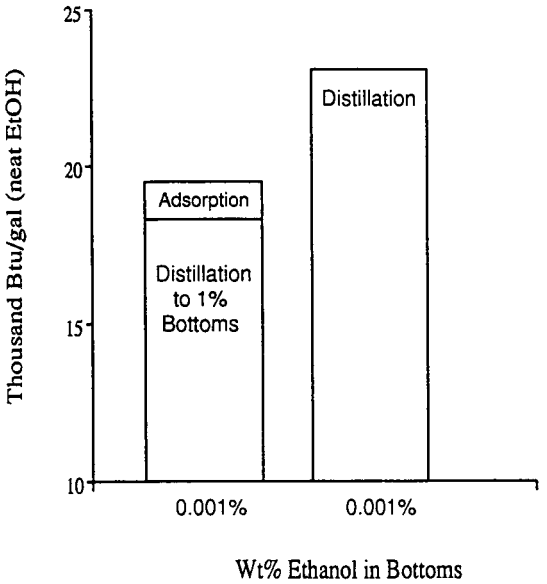

Fig. 10. Comparison of energy requirements of distillation vs distillation/sorption for ethanol recovery for a fermentation broth containing 4.5% ethanol with column designed for 0.001 wt% ethanol in bottom product. 90 wt% overhead; $R = 1.5 \times R$ min; 23 plates.

pling with an adsorptive ethanol recovery system, since the number of theoretical plates is significantly reduced, compared to a process that utilizes only distillation. This could decrease capital cost for a given reflux ratio. The potential energy savings for the case presented in Fig. 10 exceed 3500 BTU/gal. This assumes that a fermentation broth containing 4.5% ethanol (resulting in a distillation column feed containing 4% ethanol) is recovered by a combination of distillation and adsorption, rather than distillation alone, to obtain a 90% overhead product and 0.001% ethanol in the distillation column bottoms. At $5 per million BTU, this corresponds to 1.8¢/gal fuel-grade ethanol product. The benefit of combining distillation with adsorption lies not only in energy savings, but also in the options it offers for designing separation systems that will ultimately be needed for alcohol recovery from biomass conversion processes.

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