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How to cite this manuscript (APA format)

If you make reference to this version of the manuscript, use the following citation format:

Hussain, Mohammed A.M., Anthony, Jennifer L., & Pfromm, Peter H. (2011). Reducing the energy demand of corn based fuel ethanol through salt extractive distillation enabled by electrodialysis. Retrieved from http://krex.ksu.edu

Published Version Information

Citation: Hussain, Mohammed A.M., Anthony, Jennifer L., Pfromm, Peter H. Reducing the energy demand of corn based fuel ethanol through salt extractive distillation enabled by electrodialysis. This is a preprint of an article accepted for publication in AIChE Journal, copyright 2011, American Institute of Chemical Engineers.

Digital Object Identifier (DOI): 10.1002/aic.12577

Publisher's Link: http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1547-5905

Accepted in AICHE Journal on January 17, 2011

Reducing the Energy Demand of Corn Based Fuel Ethanol through Salt Extractive Distillation Enabled by Electrodialysis

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Abstract

The thermal energy demand for producing fuel ethanol from the fermentation broth of a contemporary corn-to-fuel ethanol plant in the U.S. is largely satisfied by combustion of fossil fuels, which impacts the possible economical and environmental advantages of bio-ethanol over fossil fuels. To reduce the thermal energy demand for producing fuel ethanol, a process integrating salt extractive distillation – enabled by a new scheme of electrodialysis and spray drying for salt recovery – in the water-ethanol separation train of a contemporary corn-to-fuel ethanol plant is investigated. Process simulation using Aspen Plus® 2006.5, with the ENRTL-RK property method to model the vapor liquid equilibrium of the water-ethanol-salt system, was carried out. The integrated salt extractive distillation process may provide a thermal energy savings of about 30%, when compared with the contemporary process for separating fuel ethanol from the beer column distillate.

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Topical Heading: Process systems engineering

Keywords: Salt extractive distillation; ethanol distillation; fuel ethanol; electrodialytic concentration; bio-ethanol

Introduction

Currently, the annual production capacity for fuel ethanol, mostly corn-ethanol, in the U.S. is about 55.7 GL, including about 4.5 GL capacity in new construction or expansion.[1] The Renewable Fuels Standard (RFS2), established under the Energy Independence and Security Act (EISA) of 2007, mandates the production of 136.3 GL/year of renewable fuels in 2022: 56.8 GL/year of corn-ethanol, 60.6 GL/year of second-generation bio-fuels such as cellulosic ethanol, and 18.9 GL/year of advanced bio-fuels such as biomass based diesel. Dry milling is currently the most widely used process in the U.S for producing fuel ethanol from corn by fermentation. The energy demand of old dry mill facilities[2-8] was high. Contemporary dry mill facilities have higher energy efficiency, and require about 9.8 MJ (generally from natural gas) of thermal energy and 0.7 MJ (0.19 kWh) of electrical energy to produce 1 liter of non-denatured fuel grade ethanol. The energy demand includes drying of non-fermentables to produce distillers' dried grain with solubles (DDGS).[9-12] The lower heating value of pure ethanol is 21.2 MJ per liter.[13] About 70% of the thermal energy is expended to generate steam which is used for recovering ethanol from fermentation broth, purifying ethanol to fuel grade (99.5 wt%), cooking and liquefying corn mash, and concentrating thin stillage. Recovering and purifying ethanol from fermentation broth is energy intensive and requires about 70 % of the total steam generated in the dry milling plant.[14] Fuel ethanol plants mainly use natural gas boilers to generate steam. Reducing the steam demand for recovering and purifying ethanol is essential to improve the energy balance of bio-ethanol, even if non-fermentable biomass components would be burned instead of natural gas to produce steam. The vast amounts of bio-ethanol produced by fermentation worldwide would similarly benefit from reducing the energy demand of the water (fermentation broth)-ethanol separation.

The ethanol concentration in the fermentation broth may vary from about 10 to 15 wt% for different facilities.[10, 15-18] The fermentation broth contains many components besides water and ethanol: unfermented biomass, microorganisms, proteins, oils, and volatile organics. Recovering ethanol from fermentation broth and purifying to fuel grade is difficult and energy intensive because of the dilute nature of the fermentation broth and the challenging water-ethanol vapor liquid equilibrium (VLE) with an azeotrope at about 96 wt% ethanol and tangential approach of the water-ethanol equilibrium curve to the 45° line at high ethanol concentrations in the familiar y-x VLE diagram representation. Simple distillation cannot be used to distill ethanol above the azeotropic composition. The state of the art technique used in the fuel ethanol industry to produce fuel ethanol is distillation close to the azeotropic composition followed by dehydration in a molecular sieve based adsorption unit[10, 16, 19, 20] or, in some cases, distillation followed by dehydration with membrane vapor permeation.[15, 21] Membrane-assisted vapor stripping was tested at the pilot scale level for producing fuel ethanol from a dilute ethanol feed (5 wt%), representing fermentation broth obtained from lignocellulosic feedstocks.[22, 23] Green field facilities for producing fuel ethanol from lignocellulosic feedstocks are expected to be built to meet the requirements of EISA. Our study focuses on the significant installed capital equipment for corn based fuel ethanol facilities where the ethanol concentration in the fermentation broth is much higher than is expected for the cellulosic case. The technology proposed here would offer retrofit opportunities for existing facilities, while the above mentioned membrane technology would be targeted towards new construction, not making use of the conventional equipment beyond the beer column. Membrane technology will, for example, require specialized ethanol vapor compressors. Heat integrated distillation operations such as multi-effect distillation and vapor recompression can reduce distillation energy demand. In particular, multi-effect distillation can lead to significant energy savings; 45% energy savings has been reported for a heat integrated dry mill process using multi-effect distillation, compared to a heat integrated dry mill process using standard distillation.[24] Nevertheless, multi-effect distillation is not considered in our study, as it requires a complete re-design of the distillation train of the existing dry mill corn-ethanol facilities.

The VLE of the water-ethanol system can be improved by employing a salt dissolved in the liquid phase to raise the equilibrium vapor ethanol content.[25-28] Adding a suitable salt can specifically improve the relative volatility of ethanol ("salting out") as well as break the azeotrope.[25, 27, 29] For example, 99.6 wt % ethanol was distilled using potassium acetate as the salt with only a quarter of the energy required for salt-free distillation to obtain lower quality 93 wt% ethanol directly from a feed containing 70 wt% ethanol.[30] Efficient recovery and reuse of the salt used as the separating agent is, however, crucial.

Potassium acetate[29-37] and calcium chloride[31, 36, 38-40] have been reported for water-ethanol separation utilizing the "salting out" effect. The use of the salt separating agent in a process with tightly closed water cycles such as the state of the art dry mill corn-to-fuel ethanol plant requires that the salt not impact other processing areas negatively. In this study, calcium chloride was selected for the following reasons: low cost, large "salting out" effect of calcium chloride,[31, 36] and process compatibility. Calcium ion stabilizes the α-amylase enzyme,[41, 42] used in the cooking process, and (at low levels) acts as a co-nutrient for yeast used in fermentation.[43]

In a salt extractive distillation column, the salt is usually dissolved in the reflux stream and introduced at the top of the column. Unlike the liquid extractive agents such as ethylene glycol, salt is non volatile and always remains in the liquid phase; thereby, enabling the production of a high purity distillate free of salt. The salt moves downward in the column and is recovered and purified from the distillation column bottoms for re-use in the top of the column. Hence, there are two distinct steps involved: salt extractive distillation and salt recovery/purification. Corrosion due to aqueous ethanolic salt solutions is an issue and special construction materials may be necessary or increased corrosion rates may be planned for.[38, 44] Other issues are related to solids handling, feeding and dissolving salt in the reflux stream, potential decrease in plate efficiency, and foaming inside the column.[25, 27, 29] In the study presented here, the possible benefit in terms of energy demand is established, which will determine if the concept is attractive enough to deal with the possible complications.

There are many experimental and theoretical studies[29-40] on producing fuel ethanol by utilizing the "salting out" effect, but most of them focus only on the salt extractive distillation step. Moreover, the studies[25, 27, 32-35, 37, 38] which include both steps of salt extractive distillation and salt recovery do not consider techniques other than evaporation and drying for salt recovery. Evaporative salt concentration/crystallization and solids drying techniques are energy intensive. Reducing the energy demand for the salt recovery step becomes essential to reap the benefit of salt-induced VLE improvement. In this study, a combination of electrodialysis and spray drying is investigated. The salt extractive column bottoms stream is pre-concentrated by electrodialysis and dried to an anhydrous state by spray drying. In electrodialysis, the dilute salt solution is concentrated by selectively separating the salt ions from the solution[45, 46] rather than evaporating water; therefore, requiring less energy than that of an evaporative process. Moreover, electrodialysis is rugged and can be operated at high ionic strengths.[47] Final recovery of dry salt is achieved in a spray dryer. This approach is widely used to convert a liquid feed containing salt into dry solid particles in a single step.[48, 49] Integrating salt extractive distillation, with salt recovery enabled by electrodialysis and spray drying, in the water-ethanol separation train of a state of the art corn-to-fuel ethanol plant was found to yield significant energy savings through process simulation using Aspen Plus® 2006.5.

Design Cases

Benchmark process: Case I

The target fuel ethanol production rate was set at 151.4 ML ($1.17*10^5$ tonne) per year with an ethanol concentration of 99.5 wt%. In a standard U.S. corn-to-fuel ethanol plant based on fermentation using yeast, recovery of ethanol from the fermentation broth and further purification to fuel grade is achieved by three distillation columns (beer column, rectifier, and side stripper) and final water removal by molecular sieve based adsorption[10, 20] as shown in Figure 1. Beer from the fermentation process is fed to the beer column operated as a stripper (no reflux) to produce a vapor distillate with an ethanol concentration of about 55 wt% and a bottom aqueous stream, termed whole stillage, consisting of water, dissolved matter, unfermented solids, oils, and trace amounts of ethanol. Then, the vapor distillate from the beer column is enriched to about 92 wt% ethanol in the rectifier. In the adsorption cycle of the molecular sieve unit, superheated moist ethanol vapor from the rectifier overhead is dehydrated to fuel grade ethanol by the selective adsorption of water, while in the desorption cycle, the adsorbent bed is depressurized and purged with dry product ethanol vapors for regeneration. The regeneration stream from the adsorbers is recycled to the rectifier. The side stripper strips residual ethanol from the rectifier bottoms stream and the stripped ethanol vapor stream is returned to the rectifier bottoms while the water from the side stripper bottoms is available for recycling to mash preparation and fermentation.

The rectifier and the side stripper essentially operate as a single column, but they are physically separated to minimize capital cost through the opportunity to have the side stripper with a reduced column diameter compared to the rectifier. In this study, a separation train consisting of a beer column, a rectifier (representing both the rectifier and the side stripper in the state of art installations), and a molecular sieve unit is considered as the benchmark process (Figure 2). Further, the beer column and rectifier are assumed to operate under sub atmospheric pressure conditions, enhancing the relative volatility of ethanol at high ethanol concentration.[50] Since the molecular sieve unit requires a superheated vapor feed under pressure (172kPa) in the adsorption cycle, the rectifier overhead condenser is operated as a total condenser producing a liquid distillate which is pressurized with a pump, and then evaporated and superheated for dehydration in the molecular sieve unit.

Salt extractive process: salt in rectifier only, Case II

The efficient recovery and re-use of salt in salt extractive distillation is of paramount importance in regard to the energy demand, capital cost and process requirements. Since separation and recovery of salt from the highly complex beer column bottoms stream would be a formidable challenge, no salt should be added to the beer column. The rectifier deals with a relatively clean feed stream (the beer column distillate) without solids which facilitates salt recovery from the rectifier bottoms stream. Due to the above reason we opted to purify the beer column distillate in a salt extractive rectifier to fuel grade ethanol, eliminating the need for the molecular sieve unit (Figure 3). The salt extractive rectifier bottoms stream is divided into diluate and concentrate for the electrodialysis process. After receiving the salt from the diluate, the salt enriched in the concentrate stream is recovered by evaporating the remaining water with hot natural gas combustion gases in a co-current spray dryer before recycling to the salt extractive rectifier reflux.

Summary of energy demand comparison approach

Comparing energy demands for different processing schemes is complex. Heat integration interconnects unit operations, and different qualities of energy (2nd law of thermodynamics based balance, for example, thermal vs. electrical) besides the simple quantity of energy (1st law of thermodynamics based balance) impact both economics and environmental issues such as green house gas emissions.

The input data and specified parameters for the system boundaries for Case I (benchmark process, Figure 2) and Case II (salt extractive process, Figure 3) are given, respectively, in Table 1 and Table 2. Input in Case I and Case II is an identical stream of 26.2 tonne/h (vapor distillate containing 56 wt% ethanol and balance water) from a beer column operating as a stripping column at a pressure of 44.8 kPa with 13 stages and a beer feed concentration of 12.5 wt% ethanol, an average of the typical fermentation broth ethanol concentrations (about 10 to 15 wt%) prevalent in contemporary dry mill corn-ethanol facilities. Identical streams of fuel ethanol are produced in Case I and II. As an aside, the liquid water output streams from the design cases are not identical since water vapor is lost in the spray dryer with the moist air stream in Case II.

The comparison of the energy demand of Case I and II is based on calculating natural gas energy equivalents (HHV) for electrical energy or steam that is needed. The thermal energy as steam is converted back to natural gas energy equivalents by using a boiler efficiency of 80%, while for electrical energy, a natural gas-to-electrical energy conversion efficiency of 33% was assumed. The thermal energy demand of the spray dryer is directly calculated from the natural gas usage.

Methods

Thermodynamic modeling of the water-ethanol and water-ethanol-$CaCl_2$ systems

The VLE of the water-ethanol system is described by the following equation[51]:

$$y_i \varphi_i P = x_i \gamma_i P_i^* \varphi_i^* \exp\left[\frac{1}{RT}\int_{p_i^*}^{p} v_i^* dp\right] \quad (1)$$

where y_i and x_i represent, respectively, vapor and liquid phase mole fractions, φ_i and φ_i^* represent, respectively, partial and pure component fugacity coefficients, P and P_i^* represent, respectively, system pressure and pure component vapor pressure in *kPa*, γ_i represents the liquid phase activity coefficient, v_i^* represents the saturated liquid molar volume in $m^3/kmol$ at system temperature T in *K*, and R represents the gas constant in *kJ/K.kmol*. In case of the water-ethanol system, vapor phase fugacity coefficients were calculated using the Redlich-Kwong (RK) equation[52], whereas liquid phase activity coefficients were calculated using the Non-Random Two Liquid (NRTL) model.[53] VLE calculations for water–ethanol were performed using default binary parameters (Table 3) in Aspen Properties® 2006.5 for the NRTL-RK property method. The NRTL-RK VLE data shows good agreement with experimental data (Table 4, Figure 4).

In case of the water-ethanol-$CaCl_2$ system, the VLE relationship for the volatile components was determined using Equation 1. The Redlich-Kwong equation was used to calculate vapor phase fugacity coefficients, and the Electrolyte Non-Random Two Liquid (ENRTL) model[54-56] was used to calculate liquid phase activity coefficients. The ENRTL model assumes that the total excess Gibbs energy (G^{ex}) of the mixed solvent electrolyte system can be represented as a sum of three contributions:

$$G^{ex} = G^{ex}_{PDH} + G^{ex}_{lc} + G^{ex}_{Born} \tag{2}$$

where G^{ex}_{PDH} represents the long range interaction contribution from the Pitzer-Debye Huckel equation, accounting for the electrostatic interactions among the ions. G^{ex}_{lc} represents the short range interactions among the solution species. These interaction forces are described based on the local composition concept, and on the assumptions of local electroneutrality and like-ion repulsion. G^{ex}_{Born} represents the Born contribution, accounting for the change in Gibbs energy due to the transfer of ionic species from the infinite dilution mixed solvent reference state to the infinite dilution aqueous reference state. The adjustable ENRTL parameters required for water-ethanol-$CaCl_2$ are molecule-molecule (water-ethanol) and molecule-electrolyte (water-$CaCl_2$/ethanol-$CaCl_2$) pair interaction parameters. In the absence of electrolyte components, the ENRTL model reduces to the NRTL model; hence, molecule-molecule pair parameters used in the NRTL model were retained in the ENRTL model. The molecule-electrolyte pair parameters were regressed from experimental data covering the entire range of the process conditions studied (least squares method based on the maximum likelihood principle, DRS module of Aspen Properties® 2006.5). The Britt-Luecke algorithm[57] along with the Deming initialization method was used to regress the pair parameters shown along with other parameters in Table 5. The approach described above showed good agreement with experimental data (Table 6, Figure 4).

Simulation procedure

The distillation columns were rigorously simulated using the MESH equations implemented in the RadFrac module of Aspen Plus® 2006.5. For the rectifier and the salt extractive rectifier, the Newton algorithm was used, which solves the MESH equations using the Naphtali-Sandholm procedure. Optimum feed stages for the rectifier and the salt extractive rectifier were determined by sensitivity analyses. In Case II, the $CaCl_2$ concentration profile in the salt extractive rectifier is an important parameter. Increasing the $CaCl_2$ concentration in the salt extractive rectifier can decrease the reboiler duty because of the improvement in the VLE, but can lead to an increase in salt recovery energy demand because of the increased $CaCl_2$ mass flow. The $CaCl_2$ concentration in the salt extractive rectifier was optimized to achieve a minimum of the sum of the energy requirements for the system shown in Figure 3. The mass and energy balance calculations for the molecular sieve unit, electrodialyzer, and the spray dryer were separately performed using Microsoft Excel® 2003 and Mathcad® 13. The results were later incorporated in the overall simulation using the User Model feature of Aspen Plus® 2006.5.

Results and Discussion

The target mass flow of fuel grade ethanol to be produced has been fixed (see above) which essentially determines the bottoms mass flow of water from the salt extractive rectifier (Case II), provided there is a negligible ethanol loss with the bottoms. The main parameters are then the reflux (mass flow) in the salt extractive rectifier and the concentration of salt in this reflux stream.

It is necessary to at least eliminate the azeotrope so that fuel grade ethanol can be produced at all in a single salt extractive rectifier. This already occurs at about 2.9 wt% of $CaCl_2$ in the reflux. Above this concentration, the thermal energy demand of the salt extractive rectifier steeply declines with increasing $CaCl_2$ concentration in the reflux but this benefit levels out above about 5 wt% (Figure 5). The reason is that the distillation pinch point, the point of contact between the operating line and the VLE curve in a McCabe-Thiele diagram, shifts from the location at high ethanol content (tangent pinch) to the feed stage (feed pinch) which is at about 56 wt% of ethanol. This shift yields the principal benefit of the salt extractive approach above and beyond eliminating the azeotrope. Further increase in the $CaCl_2$ concentration in the reflux causes an increase in $CaCl_2$ mass flow (Figure 6) along with increasing energy demand for salt recovery (Figure 7) without significant added benefit. The overall combined energy demand, therefore, shows a minimum at about 5.6 wt% $CaCl_2$ in the reflux due to the competition between energy savings due to facilitated distillation, and energy demand for salt recovery (Figure 8). Since there is already a large amount of installed capital for corn based fuel ethanol facilities, the opportunity to improve the already existing process (rectifier and side stripper) by salt extractive distillation is attractive. Matching the salt extractive distillation column diameter, and the reboiler and condenser heat transfer areas with that of the corresponding process equipments from Case I is necessary for retrofit purposes. Based on the reflux salt concentrations showing potential energy savings, design calculations indicated salt extractive distillation columns operating with salt concentrations greater than about 5.6 wt% $CaCl_2$ in the reflux satisfy the capacity requirements. An economic analysis (see Appendix) shows at about 6.1 wt% $CaCl_2$ in the reflux, maximal cost savings on the order of 500,000$ per year (Figure 9) can be achieved. Case I, requires 1778 kJ/L (6378 Btu/gal) for producing fuel ethanol from the beer column distillate. Retrofitted Case II – salt extractive process, requires 1270 kJ/L (4555 Btu/gal, Figure 10), reducing the thermal energy demand, based on the system boundaries selected here, by

28.5%, which translates to 4.3% thermal energy demand reduction on an overall plant level, considering a fermentation based dry corn mill facility producing both fuel ethanol and DDGS.

Conclusions and Outlook

The approach of fundamentally changing the vapor liquid equilibrium of water-ethanol mixtures by adding a salt was investigated by process simulation towards energy savings for fermentative fuel ethanol production from corn in a dry mill with DDGS production. Salt extractive distillation, with salt recovery enabled by a new scheme of electrodialysis and spray drying, was conceptually integrated in the water-ethanol separation train of a contemporary fermentation based corn-to-fuel ethanol plant for reducing the thermal energy demand. The vapor liquid equilibrium of the water-ethanol-$CaCl_2$ system predicted by the ENRTL-RK property method, with the regressed pair parameters, showed good agreement with experimental data covering the entire range of process conditions. Retrofitted salt extractive distillation resulted in a thermal energy reduction of 28.5% for producing fuel ethanol from an assumed beer column distillate, if the state of the art rectification/adsorption process (Case I) is compared to the salt extractive rectification with salt recovery (Case II). A thermal energy savings potential of $7.7*10^{13}$ J (as natural gas HHV) per year with a total annual cost savings potential on the order of \$500,000 per year can be estimated for producing 151.4 ML of fuel ethanol (99.5 wt%) per year. An overall maximum energy savings potential of $5.8*10^{16}$ J or about 0.06 Quad (as natural gas HHV) per year could be realized for the targeted 117.4 GL of fuel ethanol to be produced in the U.S in 2022, if fermentation is the process of choice. The impact of salt extractive distillation on the relatively low ethanol concentrations expected for fermentative cellulosic ethanol production, and the impact of sub atmospheric pressure distillation will be reported separately along with experimental results.

Acknowledgements

Support by the U.S. Department of Transportation, the U.S. Department of Energy and the U.S. Department of Agriculture through the Sun Grant Initiative is gratefully acknowledged (Sub-Award #AB-5-61770-KSU1.01). Support by the Center for Sustainable Energy at Kansas State University is also gratefully acknowledged.

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Appendix

Aspen Icarus Process Evaluator® 2006.5 was used to estimate all process equipment cost except for molecular sieve units and the electrodialyzer. In this study, the costs (US$ basis) were updated using CEPCI – Chemical Engineering Plant Cost Index, and are reported on 2010 second quarter basis. Molecular sieve equipment cost was estimated using the scaling and installation factors taken from Aden et al.,[58] while the electrodialyzer equipment cost was estimated using the following equations:

$$C_{EDZ} = C_P + C_S \tag{A1}$$

$$C_P = 1.5\ x\, C_S \tag{A2}$$

$$C_S = 1.5\ x\,(2M_A)\ x\, C_M \tag{A3}$$

$$M_A = \frac{ZFn_S}{\eta i_{cd}} \tag{A4}$$

where C_{EDZ} is the electrodialyzer installed equipment cost, C_P and C_S are the peripheral and stack costs, respectively, M_A is the overall membrane area required for each ion exchange membrane type (m^2), Z is the ion valence (*equivalent/mol*), F is the Faraday constant (*96485 A.s/equivalent*), n_s is the salt removal rate (*mol/s*), η is the electrical current efficiency and i_{cd} is the operating current density (A/m^2). The following values were used:

$C_M = 100\$/m^2$

$\eta = 0.9$

$i_{cd} = 300\ A/m^2$

To calculate the annual operating costs (C_O), a plant operation time of 7920 *h/year*, and the following utility costs were used: steam – 17.08*US$/ton*, cooling water – 0.07*US$/ton*, process water – 0.53*US$/ton*, electricity – 0.07*$/kW.h*, and natural gas – *5.7US$/GJ* (*6US$/MM Btu*).

The total annualized cost (*TAC*) was calculated using the following equations:

$$TAC = C_O + ACCR \times TIC \tag{A5}$$

$$ACCR = \frac{i(1+i)^n}{(1+i)^n - 1} \tag{A6}$$

where *ACCR* is the annual capital charge ratio, *TIC* is the total installed equipment cost, *i* is the interest rate, and *n* is the plant life (*years*). The following values were used:

$i = 0.1$

$n = 10$ *years* (general plant life)

$n = 5$ *years* (for membrane replacement cost)

Finally, the total annual cost savings (*TACS*) was calculated using the following equation:

$$TACS = TAC_{Case\text{-}I} - TAC_{Case\text{-}II} \tag{A7}$$

Tables

Table 1. Input data and specified parameters for Case I – benchmark process

Input Data and Specified Parameters	Benchmark Process
Rectifier	
Number of Stages	37
Operating Pressure (kPa)	34.5
Distillate Ethanol Concentration (wt%)	92.5
Bottoms Ethanol Concentration (wt%)	0.05
Molecular Sieve Unit [a]	
Operating Temperature (K)	389.15
Adsorption Pressure (kPa)	172.2
Desorption Pressure (kPa)	14.2
Purge Stream Ethanol Concentration (wt%)	72.3
Fuel Ethanol Concentration(wt%)	99.5

[a] Data taken from Aden et al.[58]

Table 2. Input data and specified parameters for Case II – salt extractive process

Input Data and Specified Parameters	Salt Extractive Process
Salt extractive rectifier	
Number of Stages	37
Operating Pressure (kPa)	34.5
Distillate Ethanol Concentration (wt%)	99.5
Bottoms Ethanol Concentration (wt%)	0.03
Electrodialysis	
Operating Temperature (K)	313.15
Concentration of $CaCl_2$ in Concentrate (wt%)	40
Current Efficiency (%)	90
Spray Dryer	
Hot Gas Temperature (K)	923.15
Moist Gas Temperature (K)	473.15

Table 3. Binary parameters of NRTL-RK property method for water(i)-ethanol(j) system[a]

a_{ij}	3.622
a_{ji}	-0.922
b_{ij}	-636.726
b_{ji}	284.286
α_{ij}	0.3

[a] Molecule-molecule binary parameters were retrieved from Aspen Properties® 2006.5. The energy interaction parameter (τ) was considered as temperature dependent: $\tau_{ij} = a_{ij} + b_{ij}/T$ where T is the system temperature. α_{ij} is the nonrandomness factor.

Table 4. Deviation between experimental data and NRTL-RK property method calculations for system temperature (T) and pressure (P), and vapor phase mole fraction of ethanol (y) in water-ethanol system

Isobaric VLE			
Pressure (kPa)	***ΔT (K)***[a]	***Δy***[a]	***Reference***
287.5	0.89	0.011	[59]
101.3	0.11	0.005	[60]
25.3	- -	0.008	[61]
Isothermal VLE			
Temperature (K)	***ΔP (%)***[b]	***Δy***[a]	***Reference***
343.15	0.43	0.004	[62]
363.15	0.38	0.004	[62]

$$^{a}\,AAD = \sum_{i=1}^{k} \frac{\left| Z_i - ZM_i \right|}{k}$$

$$^{b}\,AADP = \frac{100}{k} \sum_{i=1}^{k} \left| \frac{Z_i - ZM_i}{ZM_i} \right|$$

where AAD is the average absolute deviation, $AADP$ is the average absolute deviation in percentage, Z_i is the regressed property value, ZM_i is the corresponding experimental value, and k is the number of data points.

Table 5. Parameters of ENRTL-RK property method for water(i)-ethanol(j)-$CaCl_2$(k) system

Dielectric Constant of Solvents[a]

Solvent	*A*	*B*	*C*
Ethanol	24.11	12601.63	298.15
Water	78.54	31989.38	298.15

Born Radius of Ionic Species[b]

Ionic Species	*Born Radius (10^{-10} m)*
Ca^{2+}	1.862
Cl^-	1.937

Molecule-Electrolyte Binary Parameters Regressed from Experimental Data

Interaction Pair	*Energy Parameter (τ)*	*Nonrandomness Factor (α)*
i,k	10.262	0.2
k,i	-5.160	0.2
j,k	29.571	0.0396
k,j	-16.093	0.0396

[a] Values were retrieved from Aspen Properties® 2006.5. The temperature dependency of the dielectric constant (ε) is given by:

$\varepsilon = A + B (1/T-1/C)$, where T is the system temperature.

[b] Values were taken from Rashin et al.[63]

Table 6. Deviation between experimental data and ENRTL-RK property method calculations for osmotic coefficient (*Φ*), system temperature (T) and pressure (P), and vapor phase mole fraction of ethanol (y) in water-ethanol-$CaCl_2$ system

Osmotic Coefficients in Water-$CaCl_2$ System

Temperature (K)	*Salt concentration (mol/kg solvent)*	$\Delta\Phi^a$	*Reference*
298.15	0.1 - 4	0.058	[64]

Vapor Pressures of Water-$CaCl_2$ System

Temperature (K)	*Salt Concentration (mol/kg solvent)*	ΔP (%)^b	*Reference*
322.7 - 398.5	0.957 - 4.086	0.27	[65]

Isobaric VLE for Water-Ethanol-$CaCl_2$ System

Pressure (kPa)	*Salt Concentration (mol/kg solvent)*	ΔT (K)^a	Δy^a	*Reference*
101.3	1.505	0.419	0.004	[66]
12.3	0.974	0.508	0.001	[67]

Isothermal VLE for Water-Ethanol-$CaCl_2$ System

Temperature (K)	*Salt Concentration (mol/kg solvent)*	ΔP (%)^b	Δy^a	*Reference*
298.15	0.474	0.16	0.007	[68]

$$^a\ AAD = \sum_{i=1}^{k} \frac{\left|Z_i - ZM_i\right|}{k}$$

$$^b\ AADP = \frac{100}{k} \sum_{i=1}^{k} \left|\frac{Z_i - ZM_i}{ZM_i}\right|$$

where *AAD* is the average absolute deviation, *AADP* is the average absolute deviation in percentage, Z_i is the regressed property value, ZM_i is the corresponding experimental value, and k is the number of data points.

Figure Captions

Figure 1. Process flow scheme for ethanol recovery and purification in a state of the art fermentation based corn-to-fuel ethanol plant.

Figure 2. Process flow scheme for Case I – benchmark process.

Figure 3. Process flow scheme for Case II –salt extractive process.

Figure 4. VLE curves for the water-ethanol-$CaCl_2$ and water-ethanol systems: (□) experimental data[67] with 10.8 wt% $CaCl_2$ liquid phase concentration (salt free basis) at 12.3 kPa, (solid line) calculated using ENRTL-RK property method; (Δ) experimental data[61] without salt at 25.3 kPa, (dotted line) calculated using NRTL-RK property method.

Figure 5. Influence of concentration of $CaCl_2$ in reflux on the thermal energy demand of the salt extractive rectifier.

Figure 6. Influence of concentration of $CaCl_2$ in reflux on the total $CaCl_2$ mass flow to the salt extractive rectifier.

Figure 7. Influence of concentration of $CaCl_2$ in reflux on the thermal energy demand of the salt recovery units: (□) total energy demand; (Δ) spray dryer energy demand; (O) electrodialyzer energy demand.

Figure 8. Influence of concentration of $CaCl_2$ in reflux on the total thermal energy demand of the salt extractive rectifier and salt recovery units.

Figure 9. Influence of concentration of $CaCl_2$ in reflux on the total annual cost savings.

Figure 10. Thermal energy demand distribution of individual process units in retrofitted Case II – salt extractive process (total energy demand: 1270 kJ/L).

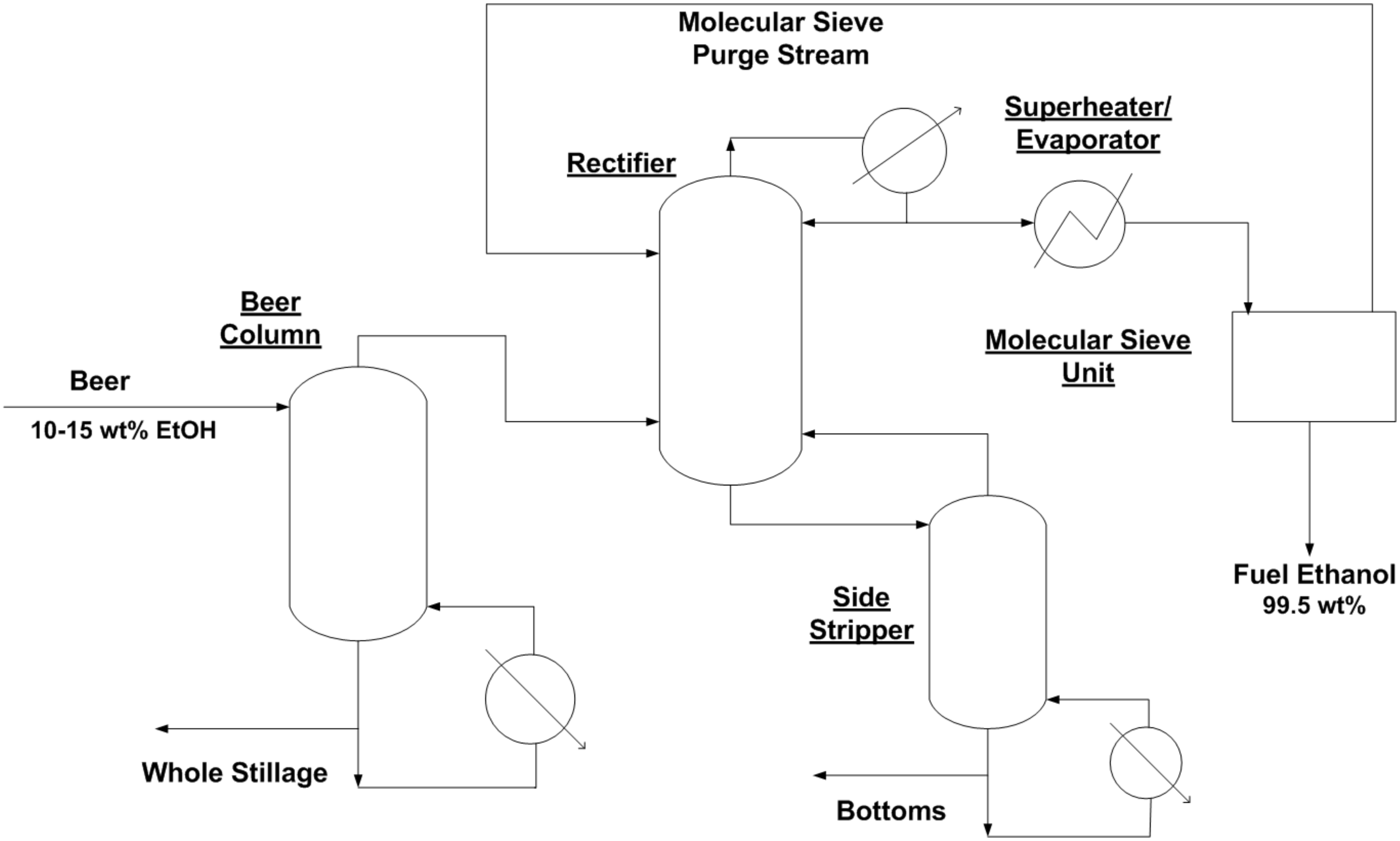

Molecular Sieve
Purge Stream
Superheater/
Evaporator
Rectifier
Beer
Column
Beer
10-15 wt% EtOH
Molecular Sieve
Unit
Fuel Ethanol
99.5 wt%
Side
Stripper
Whole Stillage
Bottoms

Figure 1

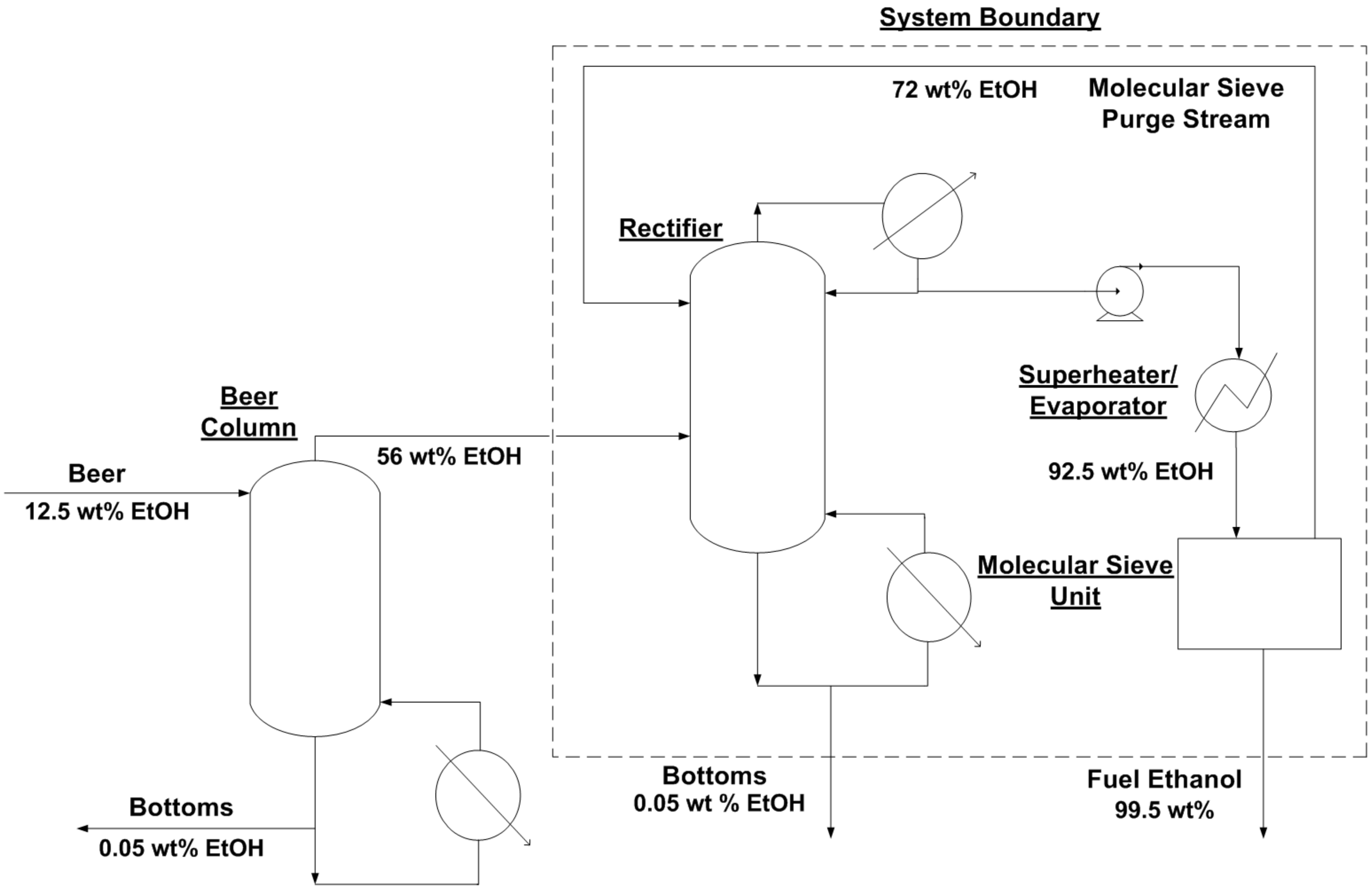

System Boundary
72 wt% EtOH
Molecular Sieve Purge Stream
Rectifier
Superheater/ Evaporator
Beer Column
56 wt% EtOH
92.5 wt% EtOH
Beer
12.5 wt% EtOH
Molecular Sieve Unit
Bottoms
0.05 wt % EtOH
Fuel Ethanol
99.5 wt%
Bottoms
0.05 wt% EtOH

Figure 2

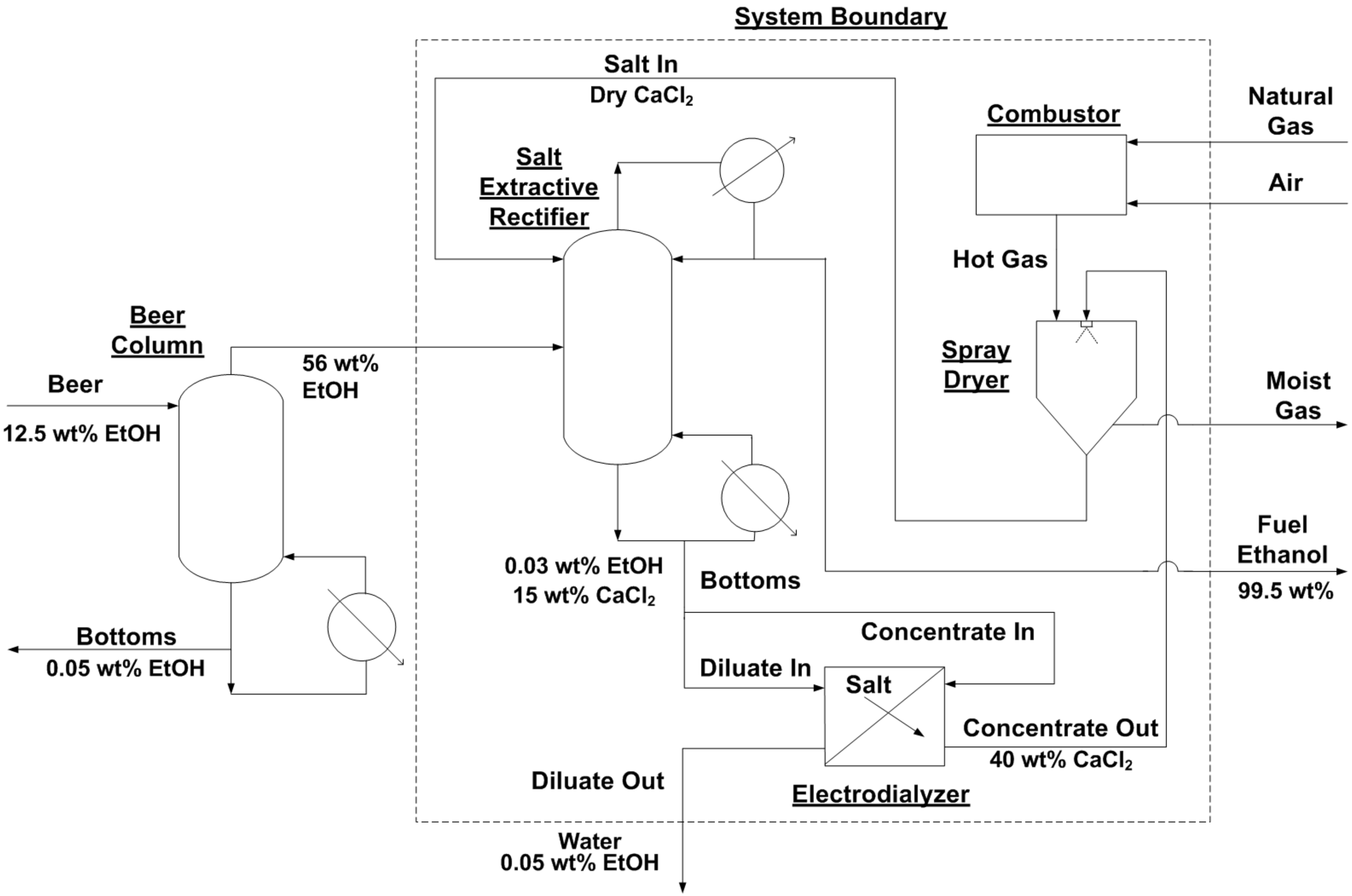
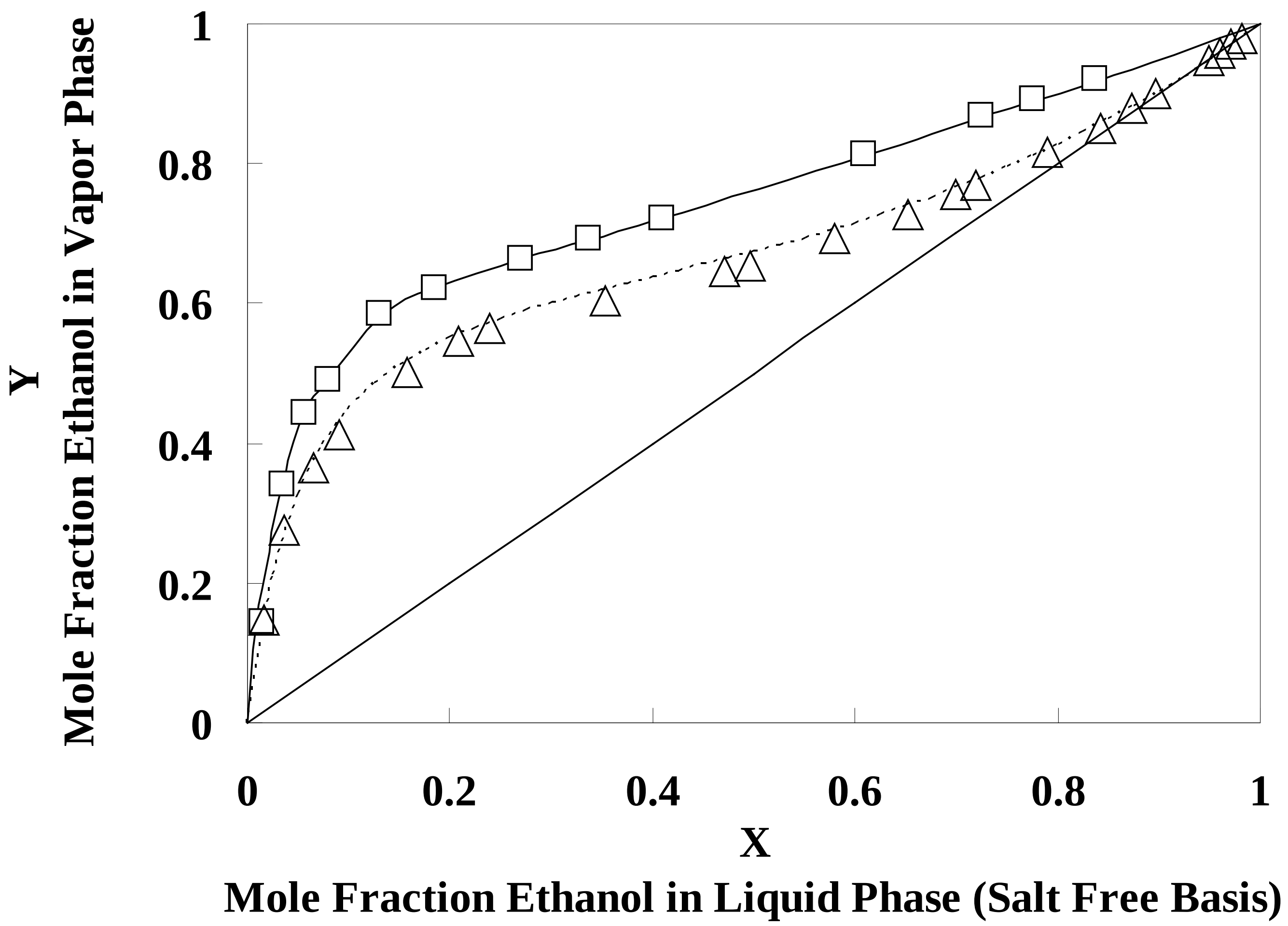
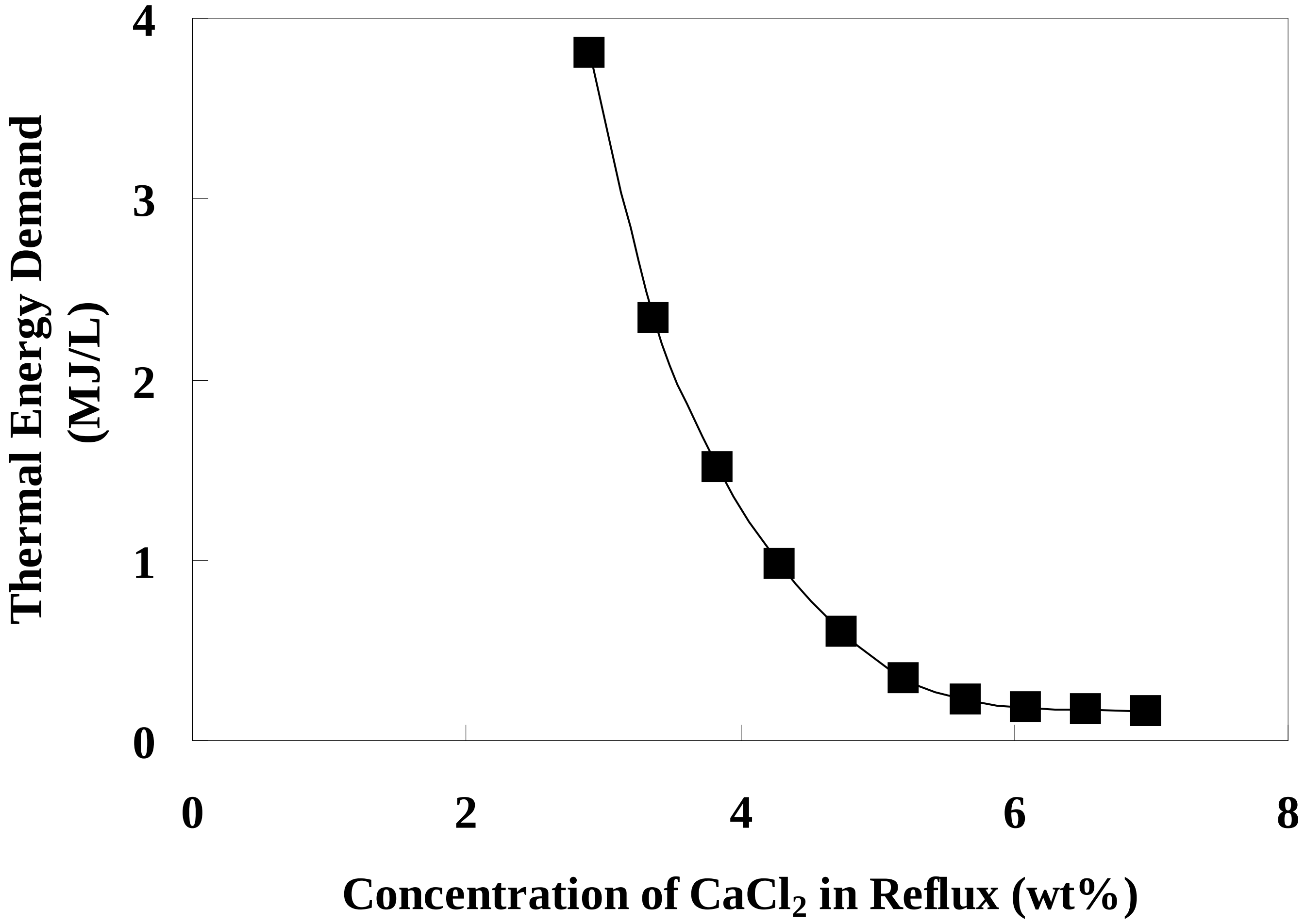

System Boundary
Salt In
Dry $CaCl_2$
Combustor
Natural Gas
Air
Salt Extractive Rectifier
Hot Gas
Beer Column
Beer
12.5 wt% EtOH
56 wt% EtOH
Spray Dryer
Moist Gas
Fuel Ethanol
99.5 wt%
0.03 wt% EtOH
15 wt% $CaCl_2$
Bottoms
Bottoms
0.05 wt% EtOH
Concentrate In
Diluate In
Salt
Concentrate Out
40 wt% $CaCl_2$
Diluate Out
Electrodialyzer
Water
0.05 wt% EtOH

Figure 3



Y
Mole Fraction Ethanol in Vapor Phase
1
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
1
X
Mole Fraction Ethanol in Liquid Phase (Salt Free Basis)

Figure 4



4
3
2
1
0
Thermal Energy Demand (MJ/L)
0
2
4
6
8
Concentration of CaCl$_2$ in Reflux (wt%)

Figure 5

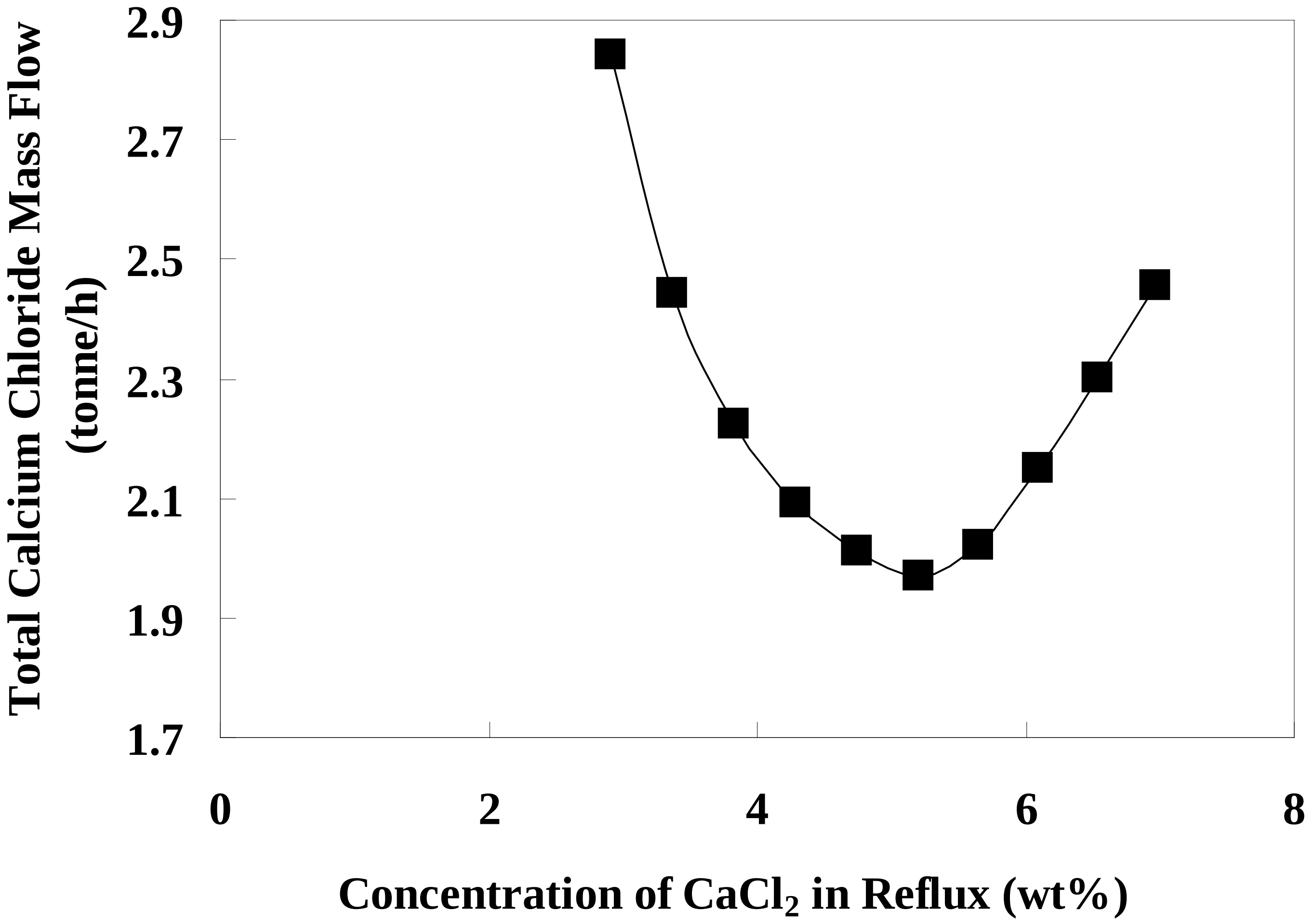

Total Calcium Chloride Mass Flow (tonne/h)
2.9
2.7
2.5
2.3
2.1
1.9
1.7
0
2
4
6
8
Concentration of $CaCl_2$ in Reflux (wt%)

Figure 6

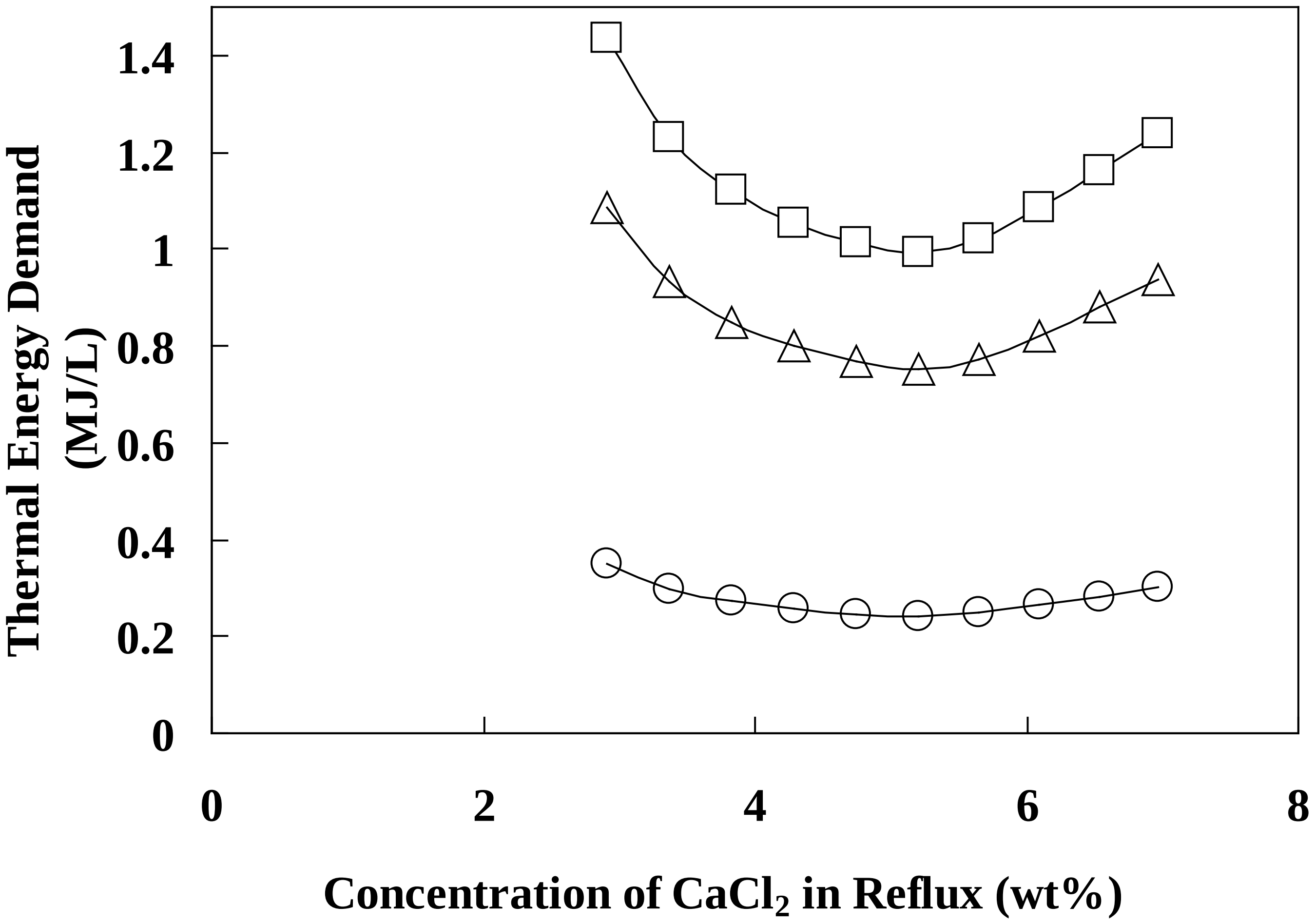

Thermal Energy Demand (MJ/L)
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
2
4
6
8
Concentration of $CaCl_2$ in Reflux (wt%)

Figure 7

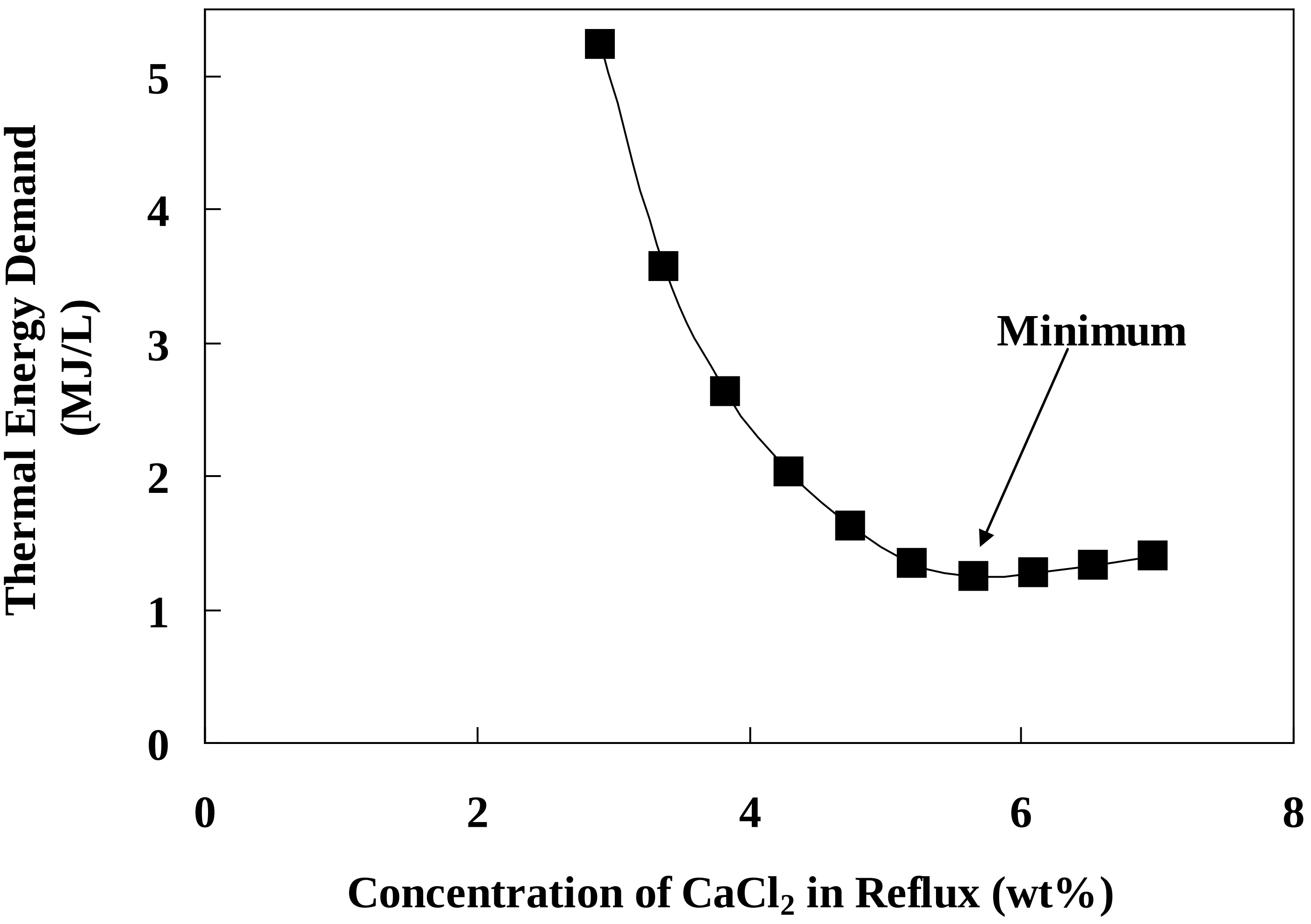

Thermal Energy Demand (MJ/L)
0
1
2
3
4
5
Minimum
0
2
4
6
8
Concentration of CaCl2 in Reflux (wt%)

Figure 8

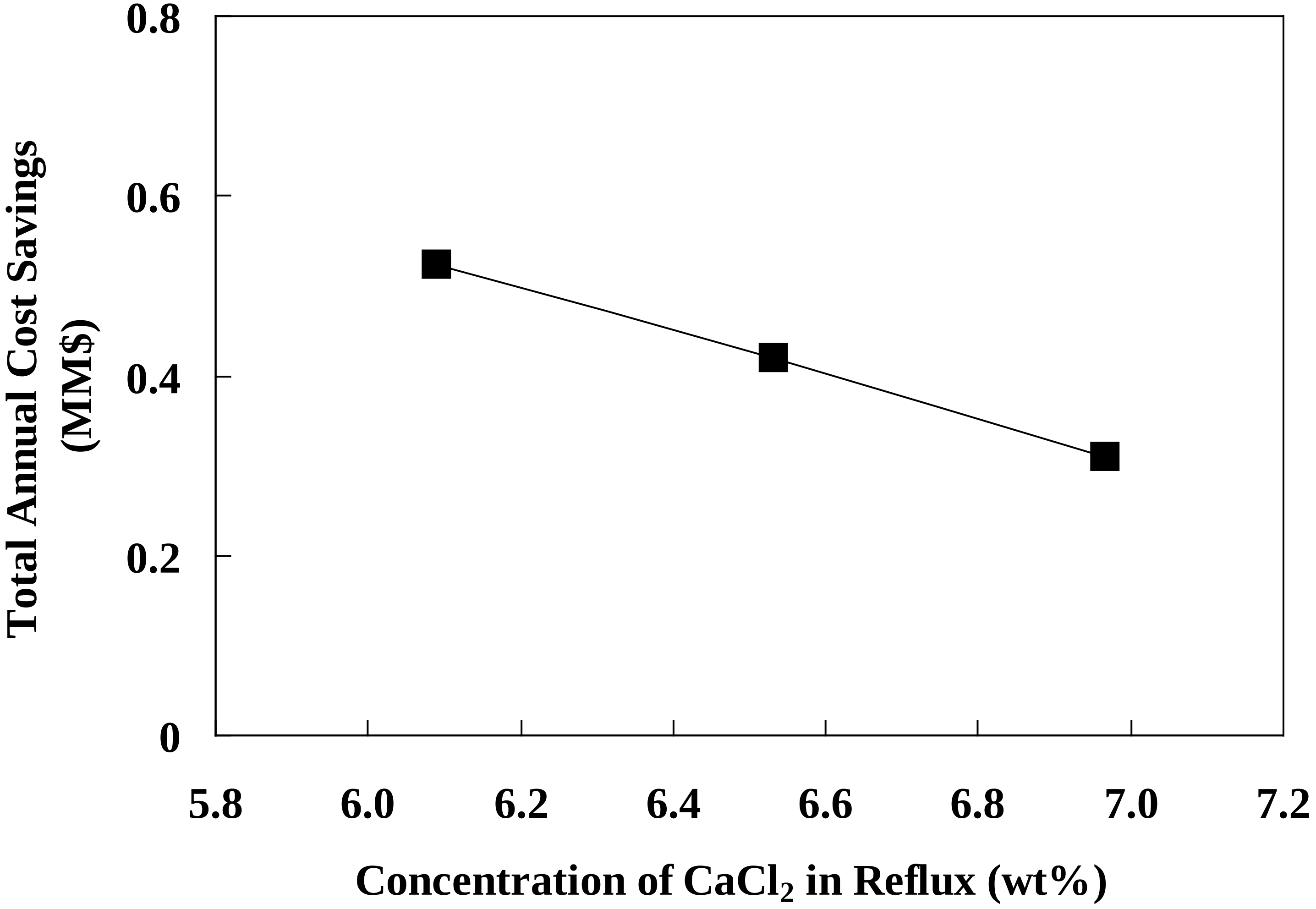

0.8
0.6
0.4
0.2
0
Total Annual Cost Savings (MM$)
5.8
6.0
6.2
6.4
6.6
6.8
7.0
7.2
Concentration of $CaCl_2$ in Reflux (wt%)

Figure 9

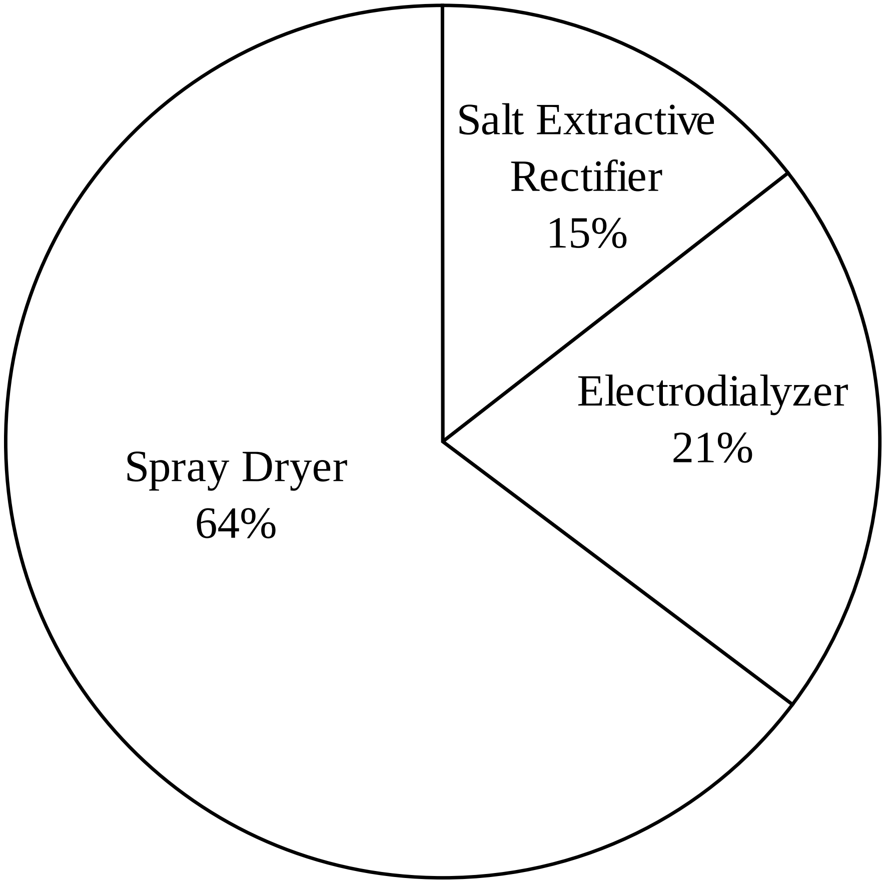

Salt Extractive Rectifier
15%
Electrodialyzer
21%
Spray Dryer
64%

Figure 10