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1           **Accepted in AIChE Journal on January 17, 2011**

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

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7           **Abstract**

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

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1   **Topical Heading:** Process systems engineering

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

4   **Introduction**

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

1 instead of natural gas to produce steam. The vast amounts of bio-ethanol produced by  
2 fermentation worldwide would similarly benefit from reducing the energy demand of the water  
3 (fermentation broth)-ethanol separation.

4 The ethanol concentration in the fermentation broth may vary from about 10 to 15 wt% for  
5 different facilities.<sup>10, 15-18</sup> The fermentation broth contains many components besides water and  
6 ethanol: unfermented biomass, microorganisms, proteins, oils, and volatile organics. Recovering  
7 ethanol from fermentation broth and purifying to fuel grade is difficult and energy intensive  
8 because of the dilute nature of the fermentation broth and the challenging water-ethanol vapor  
9 liquid equilibrium (VLE) with an azeotrope at about 96 wt% ethanol and tangential approach of  
10 the water-ethanol equilibrium curve to the 45° line at high ethanol concentrations in the familiar  
11 y-x VLE diagram representation. Simple distillation cannot be used to distill ethanol above the  
12 azeotropic composition. The state of the art technique used in the fuel ethanol industry to  
13 produce fuel ethanol is distillation close to the azeotropic composition followed by dehydration  
14 in a molecular sieve based adsorption unit<sup>10, 16, 19, 20</sup> or, in some cases, distillation followed by  
15 dehydration with membrane vapor permeation.<sup>15, 21</sup> Membrane-assisted vapor stripping was  
16 tested at the pilot scale level for producing fuel ethanol from a dilute ethanol feed (5 wt%),  
17 representing fermentation broth obtained from lignocellulosic feedstocks.<sup>22, 23</sup> Green field  
18 facilities for producing fuel ethanol from lignocellulosic feedstocks are expected to be built to  
19 meet the requirements of EISA. Our study focuses on the significant installed capital equipment  
20 for corn based fuel ethanol facilities where the ethanol concentration in the fermentation broth is  
21 much higher than is expected for the cellulosic case. The technology proposed here would offer  
22 retrofit opportunities for existing facilities, while the above mentioned membrane technology  
23 would be targeted towards new construction, not making use of the conventional equipment

1 beyond the beer column. Membrane technology will, for example, require specialized ethanol  
2 vapor compressors. Heat integrated distillation operations such as multi-effect distillation and  
3 vapor recompression can reduce distillation energy demand. In particular, multi-effect distillation  
4 can lead to significant energy savings; 45% energy savings has been reported for a heat  
5 integrated dry mill process using multi-effect distillation, compared to a heat integrated dry mill  
6 process using standard distillation.<sup>24</sup> Nevertheless, multi-effect distillation is not considered in  
7 our study, as it requires a complete re-design of the distillation train of the existing dry mill corn-  
8 ethanol facilities.

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

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

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

13 There are many experimental and theoretical studies<sup>29-40</sup> on producing fuel ethanol by utilizing  
14 the “salting out” effect, but most of them focus only on the salt extractive distillation step.  
15 Moreover, the studies<sup>25, 27, 32-35, 37, 38</sup> which include both steps of salt extractive distillation and  
16 salt recovery do not consider techniques other than evaporation and drying for salt recovery.  
17 Evaporative salt concentration/crystallization and solids drying techniques are energy intensive.  
18 Reducing the energy demand for the salt recovery step becomes essential to reap the benefit of  
19 salt-induced VLE improvement. In this study, a combination of electrodialysis and spray drying  
20 is investigated. The salt extractive column bottoms stream is pre-concentrated by electrodialysis  
21 and dried to an anhydrous state by spray drying. In electrodialysis, the dilute salt solution is  
22 concentrated by selectively separating the salt ions from the solution<sup>45, 46</sup> rather than evaporating  
23 water; therefore, requiring less energy than that of an evaporative process. Moreover,

1    electrodialysis is rugged and can be operated at high ionic strengths.<sup>47</sup> Final recovery of dry salt  
2    is achieved in a spray dryer. This approach is widely used to convert a liquid feed containing salt  
3    into dry solid particles in a single step.<sup>48, 49</sup> Integrating salt extractive distillation, with salt  
4    recovery enabled by electrodialysis and spray drying, in the water-ethanol separation train of a  
5    state of the art corn-to-fuel ethanol plant was found to yield significant energy savings through  
6    process simulation using Aspen Plus<sup>®</sup> 2006.5.

7    **Design Cases**

8    *Benchmark process: Case I*

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

1 bottoms while the water from the side stripper bottoms is available for recycling to mash  
2 preparation and fermentation.

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

14 *Salt extractive process: salt in rectifier only, Case II*

15 The efficient recovery and re-use of salt in salt extractive distillation is of paramount  
16 importance in regard to the energy demand, capital cost and process requirements. Since  
17 separation and recovery of salt from the highly complex beer column bottoms stream would be a  
18 formidable challenge, no salt should be added to the beer column. The rectifier deals with a  
19 relatively clean feed stream (the beer column distillate) without solids which facilitates salt  
20 recovery from the rectifier bottoms stream. Due to the above reason we opted to purify the beer  
21 column distillate in a salt extractive rectifier to fuel grade ethanol, eliminating the need for the  
22 molecular sieve unit (Figure 3). The salt extractive rectifier bottoms stream is divided into  
23 diluate and concentrate for the electrodialysis process. After receiving the salt from the diluate,

1 the salt enriched in the concentrate stream is recovered by evaporating the remaining water with  
2 hot natural gas combustion gases in a co-current spray dryer before recycling to the salt  
3 extractive rectifier reflux.

4 *Summary of energy demand comparison approach*

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

10 The input data and specified parameters for the system boundaries for Case I (benchmark  
11 process, Figure 2) and Case II (salt extractive process, Figure 3) are given, respectively, in Table  
12 1 and Table 2. Input in Case I and Case II is an identical stream of 26.2 tonne/h (vapor distillate  
13 containing 56 wt% ethanol and balance water) from a beer column operating as a stripping  
14 column at a pressure of 44.8 kPa with 13 stages and a beer feed concentration of 12.5 wt%  
15 ethanol, an average of the typical fermentation broth ethanol concentrations (about 10 to 15  
16 wt%) prevalent in contemporary dry mill corn-ethanol facilities. Identical streams of fuel ethanol  
17 are produced in Case I and II. As an aside, the liquid water output streams from the design cases  
18 are not identical since water vapor is lost in the spray dryer with the moist air stream in Case II.

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

1 assumed. The thermal energy demand of the spray dryer is directly calculated from the natural  
2 gas usage.

3 **Methods**

4 *Thermodynamic modeling of the water-ethanol and water-ethanol-CaCl<sub>2</sub> systems*

5 The VLE of the water-ethanol system is described by the following equation<sup>51</sup>:

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

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

16 In case of the water-ethanol-CaCl<sub>2</sub> system, the VLE relationship for the volatile components  
17 was determined using Equation 1. The Redlich-Kwong equation was used to calculate vapor  
18 phase fugacity coefficients, and the Electrolyte Non-Random Two Liquid (ENRTL) model<sup>54-56</sup>  
19 was used to calculate liquid phase activity coefficients. The ENRTL model assumes that the total

1   excess Gibbs energy ( $G^{ex}$ ) of the mixed solvent electrolyte system can be represented as a sum  
2   of three contributions:

$$G^{ex} = G_{PDH}^{ex} + G_{lc}^{ex} + G_{Born}^{ex} \quad (2)$$

3   where  $G_{PDH}^{ex}$  represents the long range interaction contribution from the Pitzer-Debye Huckel  
4   equation, accounting for the electrostatic interactions among the ions.  $G_{lc}^{ex}$  represents the short  
5   range interactions among the solution species. These interaction forces are described based on  
6   the local composition concept, and on the assumptions of local electroneutrality and like-ion  
7   repulsion.  $G_{Born}^{ex}$  represents the Born contribution, accounting for the change in Gibbs energy  
8   due to the transfer of ionic species from the infinite dilution mixed solvent reference state to the  
9   infinite dilution aqueous reference state. The adjustable ENRTL parameters required for water-  
10   ethanol-CaCl<sub>2</sub> are molecule-molecule (water-ethanol) and molecule-electrolyte (water-  
11   CaCl<sub>2</sub>/ethanol-CaCl<sub>2</sub>) pair interaction parameters. In the absence of electrolyte components, the  
12   ENRTL model reduces to the NRTL model; hence, molecule-molecule pair parameters used in  
13   the NRTL model were retained in the ENRTL model. The molecule-electrolyte pair parameters  
14   were regressed from experimental data covering the entire range of the process conditions  
15   studied (least squares method based on the maximum likelihood principle, DRS module of  
16   Aspen Properties® 2006.5). The Britt-Luecke algorithm<sup>57</sup> along with the Deming initialization  
17   method was used to regress the pair parameters shown along with other parameters in Table 5.  
18   The approach described above showed good agreement with experimental data (Table 6, Figure  
19   4).

1    *Simulation procedure*

2    The distillation columns were rigorously simulated using the MESH equations implemented in  
3    the RadFrac module of Aspen Plus® 2006.5. For the rectifier and the salt extractive rectifier, the  
4    Newton algorithm was used, which solves the MESH equations using the Naphtali-Sandholm  
5    procedure. Optimum feed stages for the rectifier and the salt extractive rectifier were determined  
6    by sensitivity analyses. In Case II, the CaCl<sub>2</sub> concentration profile in the salt extractive rectifier  
7    is an important parameter. Increasing the CaCl<sub>2</sub> concentration in the salt extractive rectifier can  
8    decrease the reboiler duty because of the improvement in the VLE, but can lead to an increase in  
9    salt recovery energy demand because of the increased CaCl<sub>2</sub> mass flow. The CaCl<sub>2</sub> concentration  
10   in the salt extractive rectifier was optimized to achieve a minimum of the sum of the energy  
11   requirements for the system shown in Figure 3. The mass and energy balance calculations for the  
12   molecular sieve unit, electrodialyzer, and the spray dryer were separately performed using  
13   Microsoft Excel® 2003 and Mathcad® 13. The results were later incorporated in the overall  
14   simulation using the User Model feature of Aspen Plus® 2006.5.

15   **Results and Discussion**

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

21   It is necessary to at least eliminate the azeotrope so that fuel grade ethanol can be produced at  
22   all in a single salt extractive rectifier. This already occurs at about 2.9 wt% of CaCl<sub>2</sub> in the  
23   reflux. Above this concentration, the thermal energy demand of the salt extractive rectifier

1 steeply declines with increasing  $\text{CaCl}_2$  concentration in the reflux but this benefit levels out  
2 above about 5 wt% (Figure 5). The reason is that the distillation pinch point, the point of contact  
3 between the operating line and the VLE curve in a McCabe-Thiele diagram, shifts from the  
4 location at high ethanol content (tangent pinch) to the feed stage (feed pinch) which is at about  
5 56 wt% of ethanol. This shift yields the principal benefit of the salt extractive approach above  
6 and beyond eliminating the azeotrope. Further increase in the  $\text{CaCl}_2$  concentration in the reflux  
7 causes an increase in  $\text{CaCl}_2$  mass flow (Figure 6) along with increasing energy demand for salt  
8 recovery (Figure 7) without significant added benefit. The overall combined energy demand,  
9 therefore, shows a minimum at about 5.6 wt%  $\text{CaCl}_2$  in the reflux due to the competition  
10 between energy savings due to facilitated distillation, and energy demand for salt recovery  
11 (Figure 8). Since there is already a large amount of installed capital for corn based fuel ethanol  
12 facilities, the opportunity to improve the already existing process (rectifier and side stripper) by  
13 salt extractive distillation is attractive. Matching the salt extractive distillation column diameter,  
14 and the reboiler and condenser heat transfer areas with that of the corresponding process  
15 equipments from Case I is necessary for retrofit purposes. Based on the reflux salt concentrations  
16 showing potential energy savings, design calculations indicated salt extractive distillation  
17 columns operating with salt concentrations greater than about 5.6 wt%  $\text{CaCl}_2$  in the reflux satisfy  
18 the capacity requirements. An economic analysis (see Appendix) shows at about 6.1 wt%  $\text{CaCl}_2$   
19 in the reflux, maximal cost savings on the order of 500,000\$ per year (Figure 9) can be achieved.  
20 Case I, requires 1778 kJ/L (6378 Btu/gal) for producing fuel ethanol from the beer column  
21 distillate. Retrofitted Case II – salt extractive process, requires 1270 kJ/L (4555 Btu/gal, Figure  
22 10), reducing the thermal energy demand, based on the system boundaries selected here, by

1 28.5%, which translates to 4.3% thermal energy demand reduction on an overall plant level,  
2 considering a fermentation based dry corn mill facility producing both fuel ethanol and DDGS.

3 **Conclusions and Outlook**

4 The approach of fundamentally changing the vapor liquid equilibrium of water-ethanol  
5 mixtures by adding a salt was investigated by process simulation towards energy savings for  
6 fermentative fuel ethanol production from corn in a dry mill with DDGS production. Salt  
7 extractive distillation, with salt recovery enabled by a new scheme of electrodialysis and spray  
8 drying, was conceptually integrated in the water-ethanol separation train of a contemporary  
9 fermentation based corn-to-fuel ethanol plant for reducing the thermal energy demand. The  
10 vapor liquid equilibrium of the water-ethanol-CaCl<sub>2</sub> system predicted by the ENRTL-RK  
11 property method, with the regressed pair parameters, showed good agreement with experimental  
12 data covering the entire range of process conditions. Retrofitted salt extractive distillation  
13 resulted in a thermal energy reduction of 28.5% for producing fuel ethanol from an assumed beer  
14 column distillate, if the state of the art rectification/adsorption process (Case I) is compared to  
15 the salt extractive rectification with salt recovery (Case II). A thermal energy savings potential of  
16  $7.7 \times 10^{13}$  J (as natural gas HHV) per year with a total annual cost savings potential on the order  
17 of \$500,000 per year can be estimated for producing 151.4 ML of fuel ethanol (99.5 wt%) per  
18 year. An overall maximum energy savings potential of  $5.8 \times 10^{16}$  J or about 0.06 Quad (as natural  
19 gas HHV) per year could be realized for the targeted 117.4 GL of fuel ethanol to be produced in  
20 the U.S in 2022, if fermentation is the process of choice. The impact of salt extractive distillation  
21 on the relatively low ethanol concentrations expected for fermentative cellulosic ethanol  
22 production, and the impact of sub atmospheric pressure distillation will be reported separately  
23 along with experimental results.

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6

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25

1      **Appendix**

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

$$C_{EDZ} = C_P + C_S \quad (\text{A1})$$

$$C_P = 1.5 \times C_S \quad (\text{A2})$$

$$C_S = 1.5 \times (2M_A) \times C_M \quad (\text{A3})$$

$$M_A = \frac{ZF n_s}{\eta i_{cd}} \quad (\text{A4})$$

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

13      $C_M = 100\$/m^2$

14      $\eta = 0.9$

15      $i_{cd} = 300 A/m^2$

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

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

$$TAC = C_O + ACCR \times TIC \quad (\text{A5})$$

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

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

7  $i = 0.1$

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

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

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

$$TACS = TAC_{\text{Case-I}} - TAC_{\text{Case-II}} \quad (\text{A7})$$

11

## 1     **Tables**

2

1

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

<b>Input Data and Specified Parameters</b>	<b>Benchmark Process</b>
<b><i>Rectifier</i></b>	
Number of Stages	37
Operating Pressure (kPa)	34.5
Distillate Ethanol Concentration (wt%)	92.5
Bottoms Ethanol Concentration (wt%)	0.05
<b><i>Molecular Sieve Unit <sup>a</sup></i></b>	
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

3 <sup>a</sup> Data taken from Aden et al.<sup>58</sup>

4

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

---

<b>Input Data and Specified Parameters</b>	<b>Salt Extractive Process</b>
<i>Salt extractive rectifier</i>	
Number of Stages	37
Operating Pressure (kPa)	34.5
Distillate Ethanol Concentration (wt%)	99.5
Bottoms Ethanol Concentration (wt%)	0.03
<i>Electrodialysis</i>	
Operating Temperature (K)	313.15
Concentration of CaCl <sub>2</sub> in Concentrate (wt%)	40
Current Efficiency (%)	90
<i>Spray Dryer</i>	
Hot Gas Temperature (K)	923.15
Moist Gas Temperature (K)	473.15

---

1

2 **Table 3. Binary parameters of NRTL-RK property method for water(i)-ethanol(j) system<sup>a</sup>**

a <sub>ij</sub>	3.622
a <sub>ji</sub>	-0.922
b <sub>ij</sub>	-636.726
b <sub>ji</sub>	284.286
α <sub>ij</sub>	0.3

3       <sup>a</sup> Molecule-molecule binary parameters were retrieved from Aspen Properties® 2006.5. The  
4 energy interaction parameter ( $\tau$ ) was considered as temperature dependent:  $\tau_{ij} = a_{ij} + b_{ij}/T$  where  $T$   
5 is the system temperature.  $\alpha_{ij}$  is the nonrandomness factor.

6

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

Isobaric VLE			
Pressure (kPa)	$\Delta T (K)^a$	$\Delta y^a$	Reference
287.5	0.89	0.011	<sup>59</sup>
101.3	0.11	0.005	<sup>60</sup>
25.3	- -	0.008	<sup>61</sup>
Isothermal VLE			
Temperature (K)	$\Delta P (\%)^b$	$\Delta y^a$	Reference
343.15	0.43	0.004	<sup>62</sup>
363.15	0.38	0.004	<sup>62</sup>

4 
$$^a AAD = \sum_{i=1}^k \frac{|Z_i - ZM_i|}{k}$$

5 
$$^b AADP = \frac{100}{k} \sum_{i=1}^k \left| \frac{Z_i - ZM_i}{ZM_i} \right|$$

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

9

1

2   **Table 5. Parameters of ENRTL-RK property method for water(i)-ethanol(j)-CaCl<sub>2</sub>(k)**  
 3   **system**

<b>Dielectric Constant of Solvents<sup>a</sup></b>		
<b>Solvent</b>	<b>A</b>	<b>B</b>
Ethanol	24.11	12601.63
Water	78.54	31989.38
<b>Born Radius of Ionic Species<sup>b</sup></b>		
<i>Ionic Species</i>	<i>Born Radius (10<sup>-10</sup> m)</i>	
Ca <sup>2+</sup>	1.862	
Cl <sup>-</sup>	1.937	
<b>Molecule-Electrolyte Binary Parameters Regressed from Experimental Data</b>		
<i>Interaction Pair</i>	<i>Energy Parameter (<math>\tau</math>)</i>	<i>Nonrandomness Factor (<math>\alpha</math>)</i>
i,k	10.262	0.2
k,i	-5.160	0.2
j,k	29.571	0.0396
k,j	-16.093	0.0396

4   <sup>a</sup> Values were retrieved from Aspen Properties® 2006.5. The temperature dependency of the  
 5   dielectric constant ( $\epsilon$ ) is given by:

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

7   <sup>b</sup> Values were taken from Rashin et al.<sup>63</sup>

8

1

2 **Table 6.** Deviation between experimental data and ENRTL-RK property method  
 3 calculations for osmotic coefficient ( $\Phi$ ), system temperature (T) and pressure (P), and  
 4 vapor phase mole fraction of ethanol (y) in water-ethanol-CaCl<sub>2</sub> system

<b>Osmotic Coefficients in Water-CaCl<sub>2</sub> System</b>				
<i>Temperature (K)</i>	<i>Salt concentration (mol/kg solvent)</i>	$\Delta\Phi^a$	<i>Reference</i>	
298.15	0.1 - 4	0.058		<sup>64</sup>
<b>Vapor Pressures of Water-CaCl<sub>2</sub> System</b>				
<i>Temperature (K)</i>	<i>Salt Concentration (mol/kg solvent)</i>	$\Delta P (\%)^b$	<i>Reference</i>	
322.7 - 398.5	0.957 - 4.086	0.27		<sup>65</sup>
<b>Isobaric VLE for Water-Ethanol-CaCl<sub>2</sub> System</b>				
<i>Pressure (kPa)</i>	<i>Salt Concentration (mol/kg solvent)</i>	$\Delta T (K)^a$	$\Delta y^a$	<i>Reference</i>
101.3	1.505	0.419	0.004	<sup>66</sup>
12.3	0.974	0.508	0.001	<sup>67</sup>
<b>Isothermal VLE for Water-Ethanol-CaCl<sub>2</sub> System</b>				
<i>Temperature (K)</i>	<i>Salt Concentration (mol/kg solvent)</i>	$\Delta P (\%)^b$	$\Delta y^a$	<i>Reference</i>
298.15	0.474	0.16	0.007	<sup>68</sup>

5      
$$^a AAD = \sum_{i=1}^k \frac{|Z_i - ZM_i|}{k}$$

6      
$$^b AADP = \frac{100}{k} \sum_{i=1}^k \left| \frac{Z_i - ZM_i}{ZM_i} \right|$$

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

10

1    **Figure Captions**

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

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

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

6    **Figure 4.** VLE curves for the water-ethanol-CaCl<sub>2</sub> and water-ethanol systems: (□) experimental  
7    data<sup>67</sup> with 10.8 wt% CaCl<sub>2</sub> liquid phase concentration (salt free basis) at 12.3 kPa, (solid line)  
8    calculated using ENRTL-RK property method; (Δ) experimental data<sup>61</sup> without salt at 25.3 kPa,  
9    (dotted line) calculated using NRTL-RK property method.

10    **Figure 5.** Influence of concentration of CaCl<sub>2</sub> in reflux on the thermal energy demand of the salt  
11    extractive rectifier.

12    **Figure 6.** Influence of concentration of CaCl<sub>2</sub> in reflux on the total CaCl<sub>2</sub> mass flow to the salt  
13    extractive rectifier.

14    **Figure 7.** Influence of concentration of CaCl<sub>2</sub> in reflux on the thermal energy demand of the salt  
15    recovery units: (□) total energy demand; (Δ) spray dryer energy demand; (O) electrodialyzer  
16    energy demand.

17    **Figure 8.** Influence of concentration of CaCl<sub>2</sub> in reflux on the total thermal energy demand of  
18    the salt extractive rectifier and salt recovery units.

19    **Figure 9.** Influence of concentration of CaCl<sub>2</sub> in reflux on the total annual cost savings.

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

3

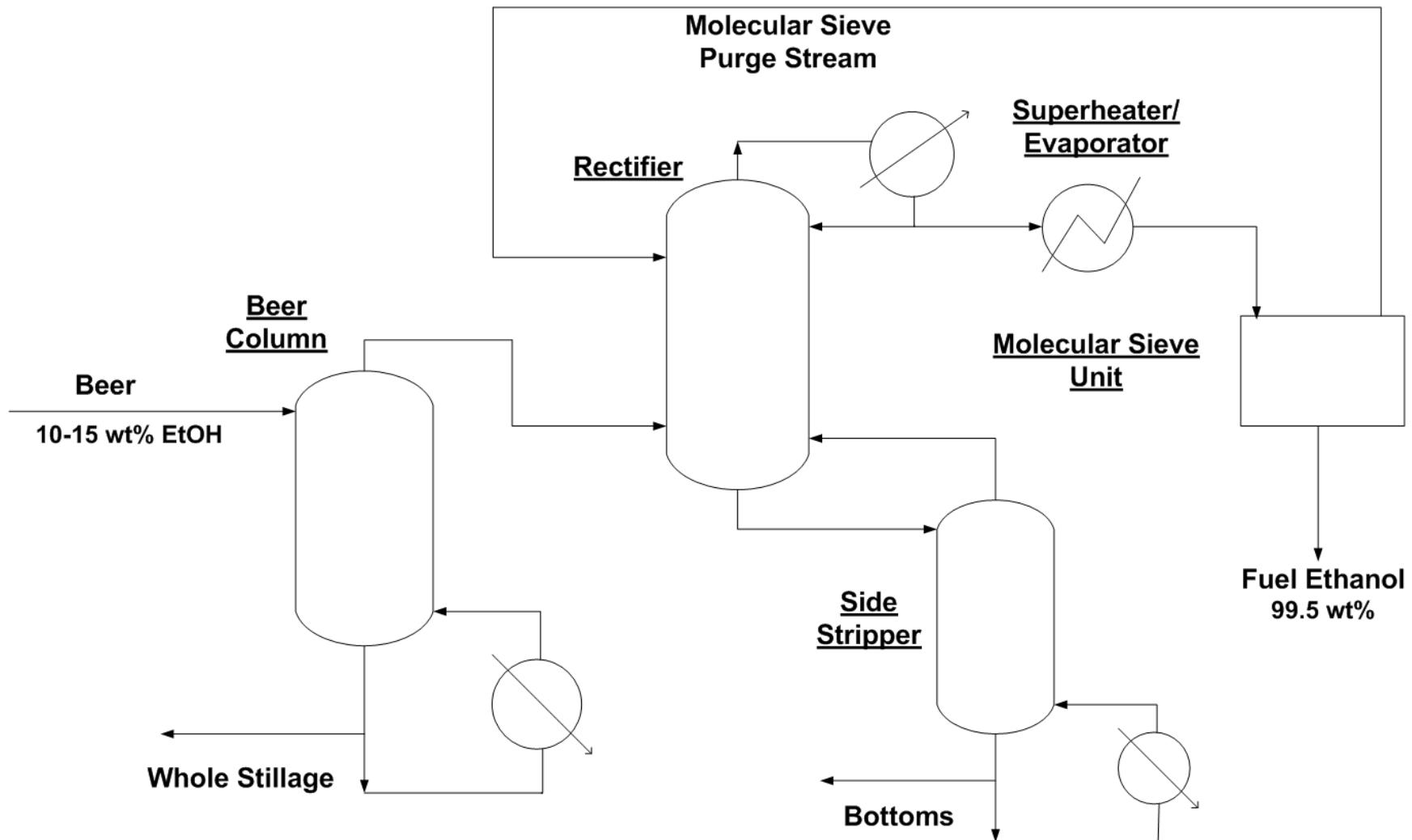
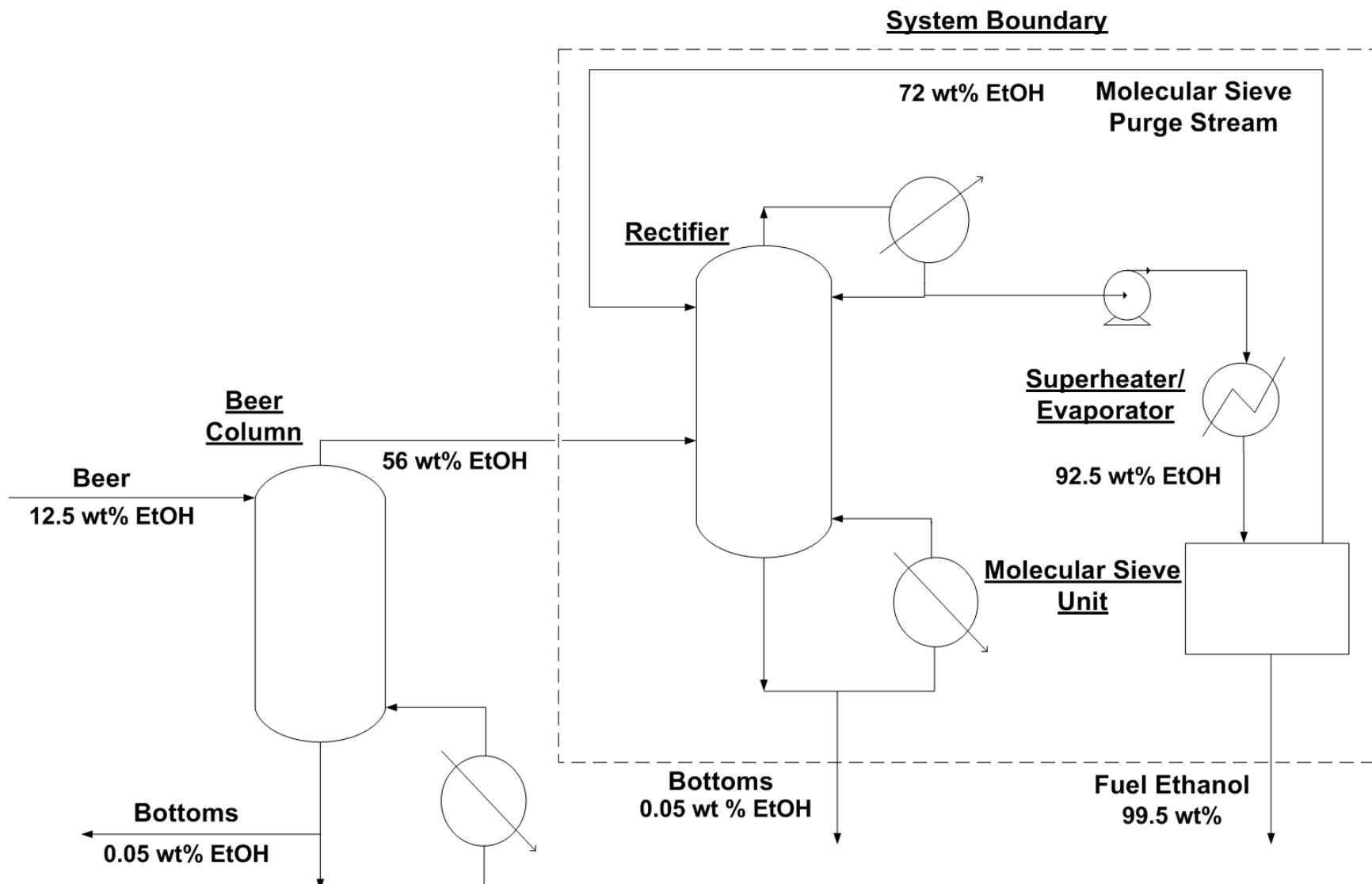


Figure 1

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**Figure 2**

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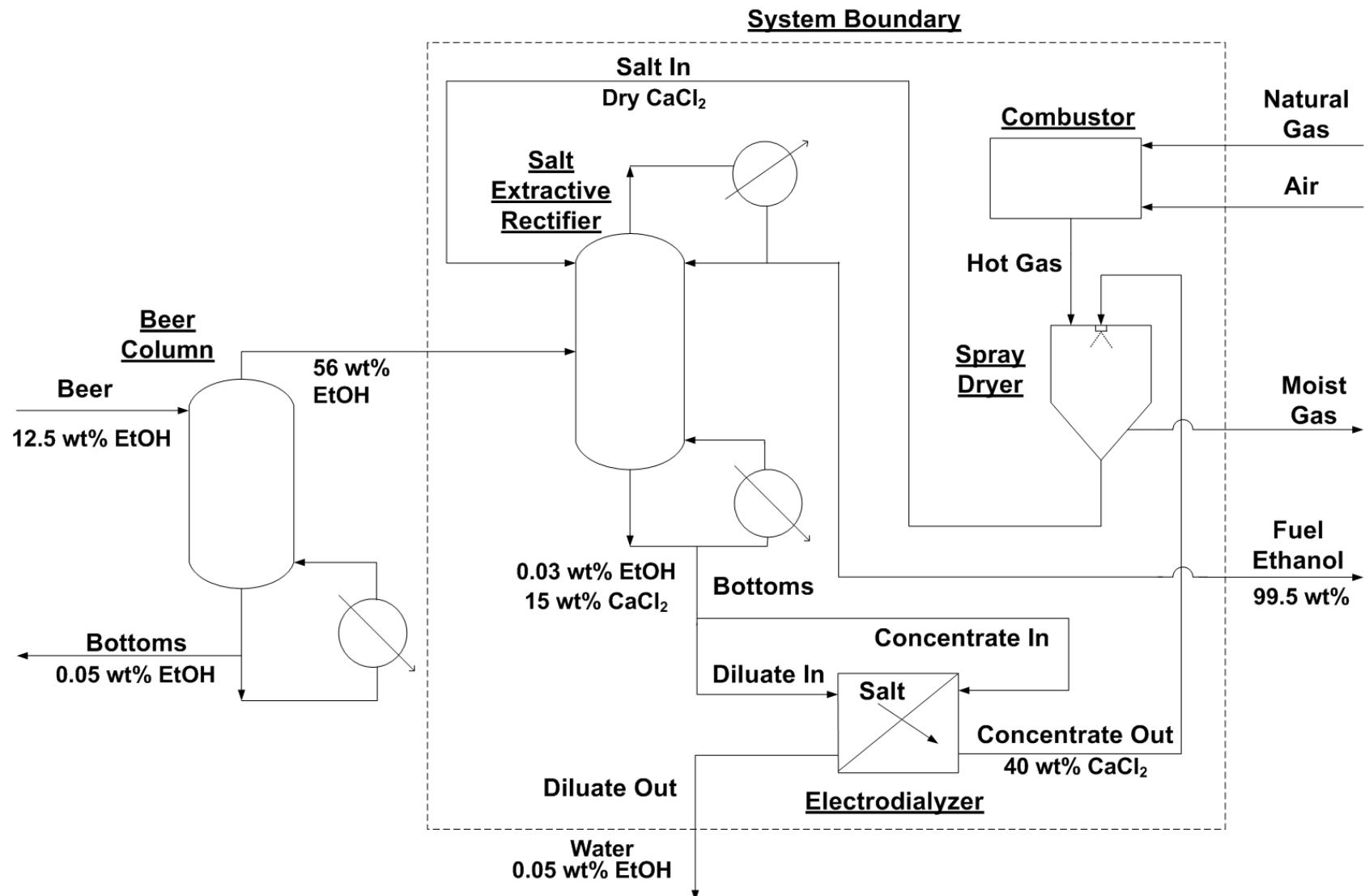


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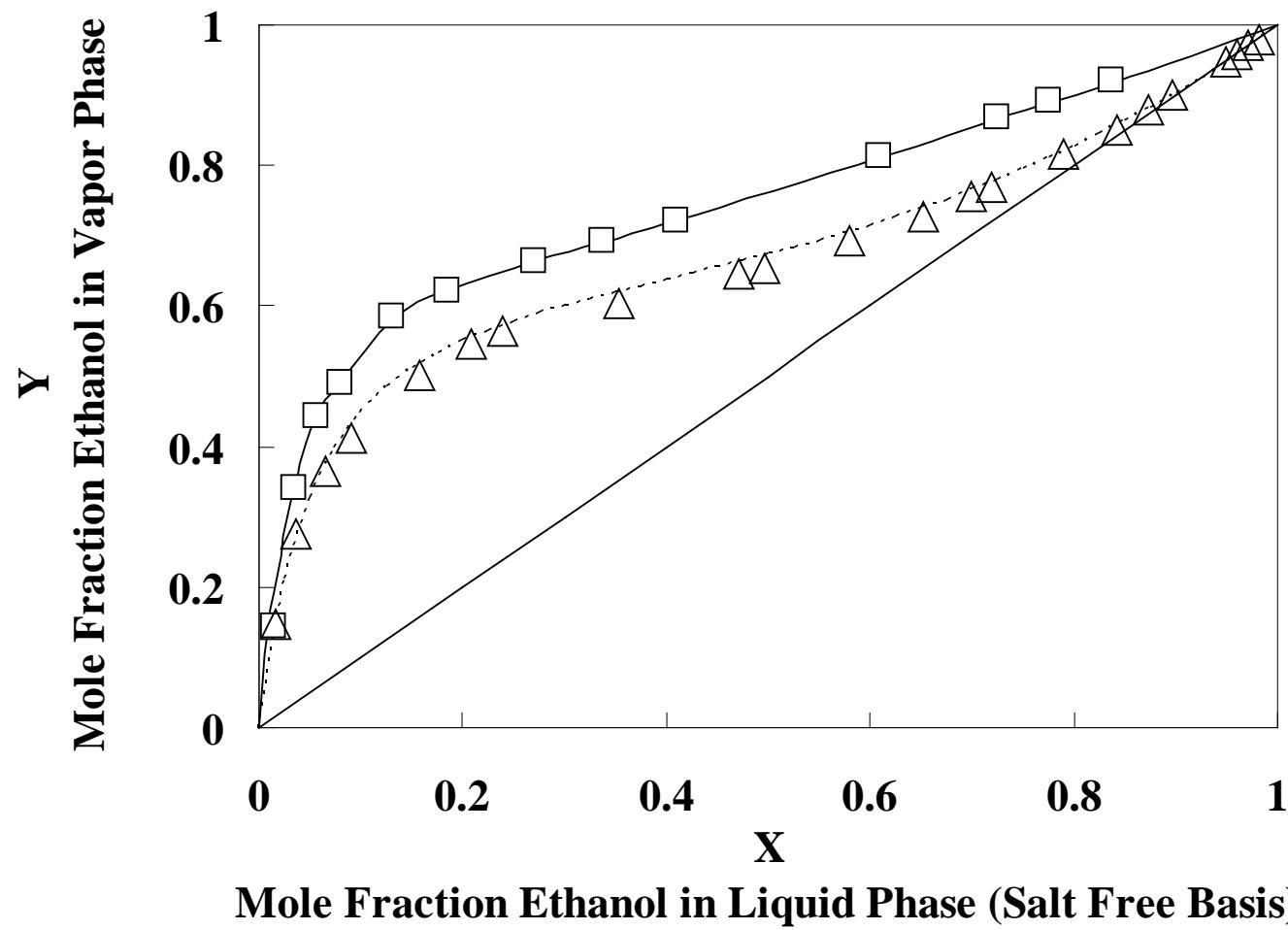


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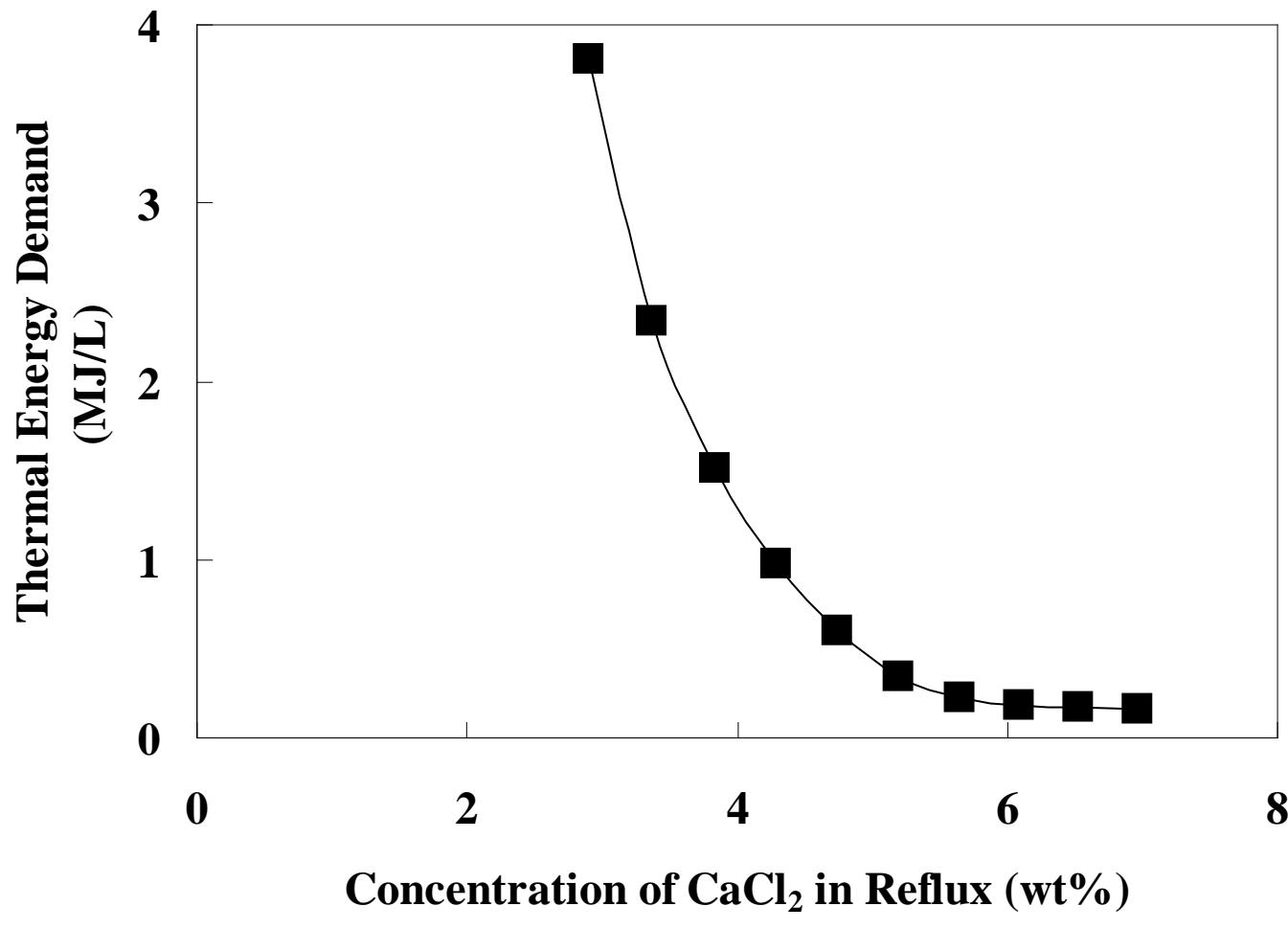


Figure 5

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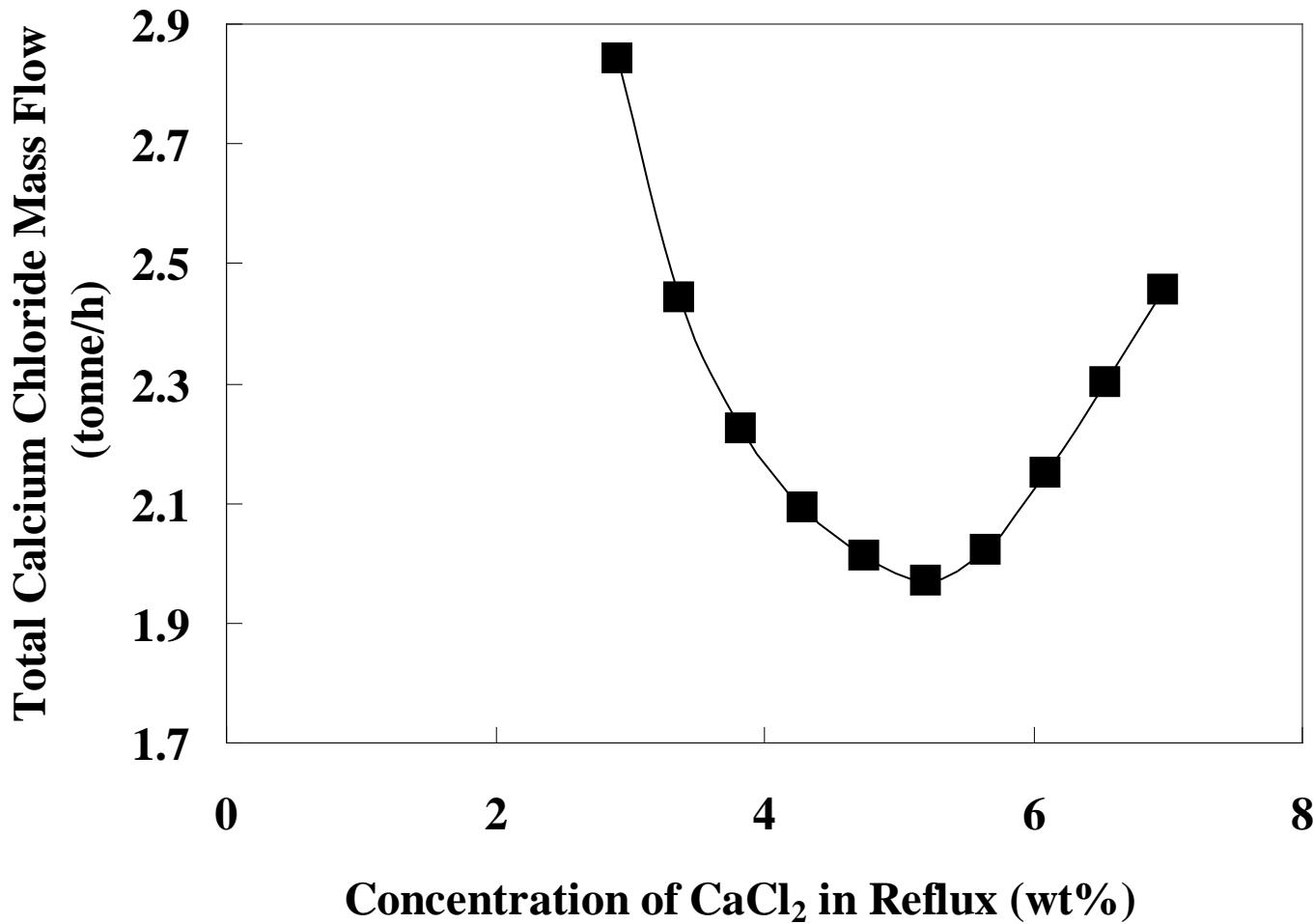


Figure 6

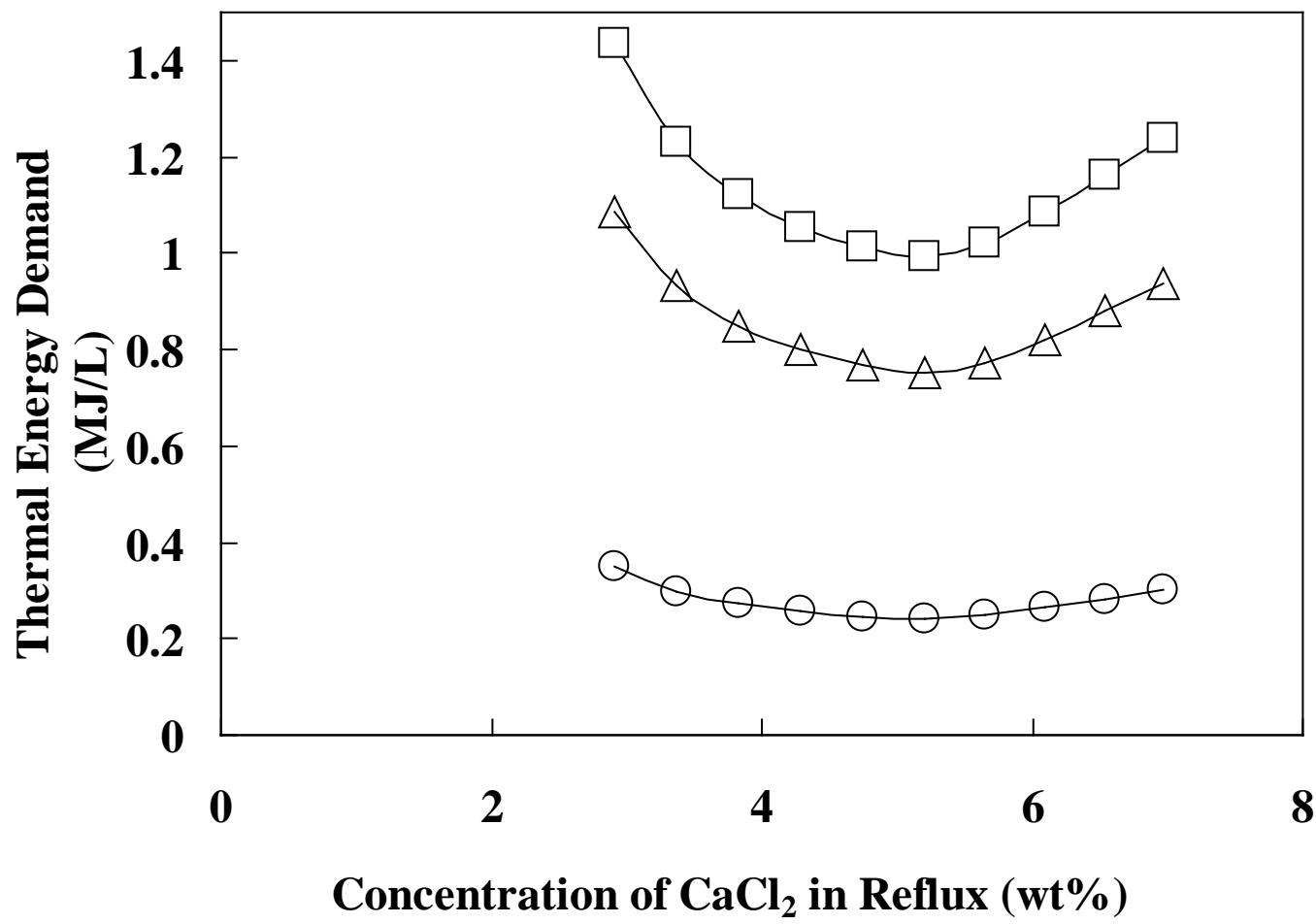


Figure 7

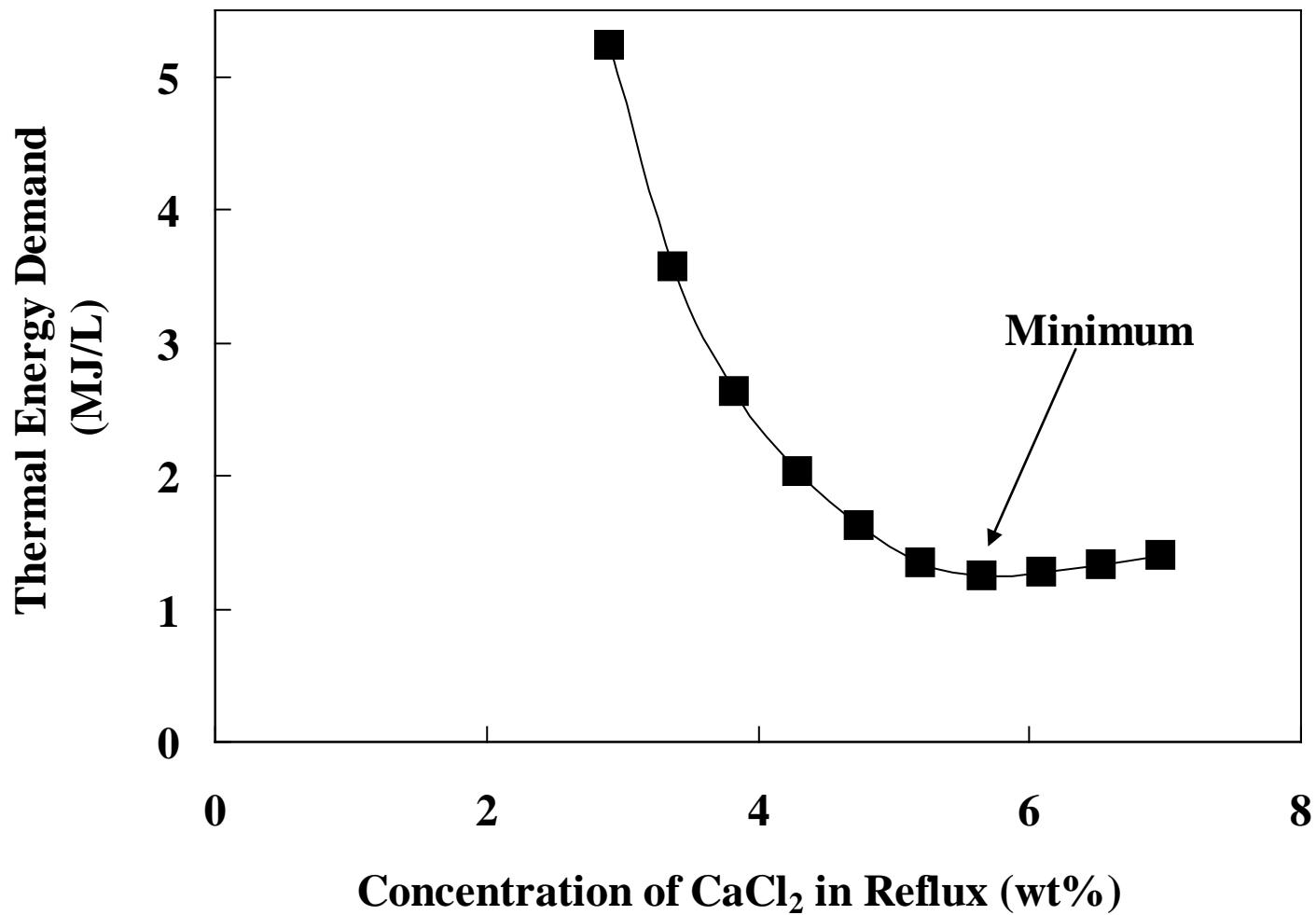


Figure 8

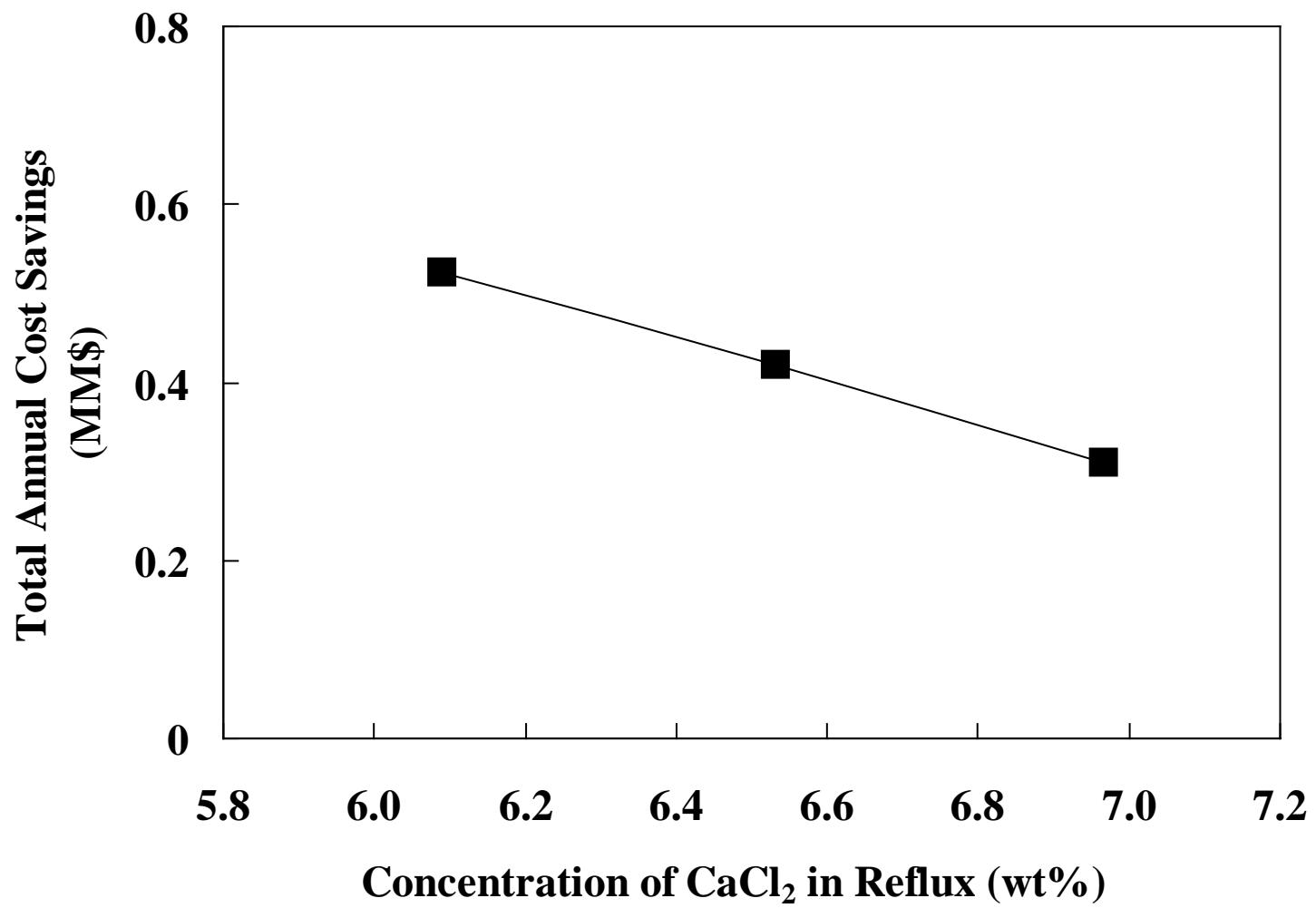
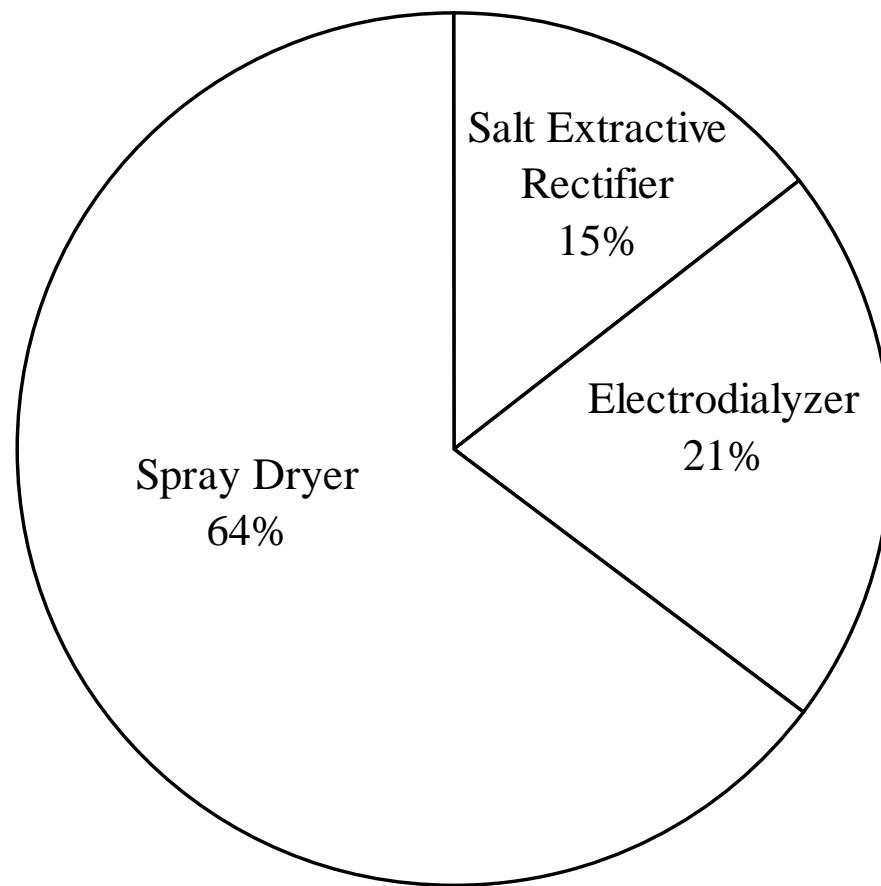


Figure 9



1

2

**Figure 10**