

## 저농도 에탄올 회수공정의 개발

김병철<sup>1</sup>, 우희철<sup>2</sup>, 김영한<sup>2,\*</sup>  
경남정보대학교 신소재화공계열<sup>1</sup>  
부경대학교 화학공학과<sup>2</sup>  
([yhkim2@pknu.ac.kr](mailto:yhkim2@pknu.ac.kr)\*)

### Recovery process development for low content ethanol

Byoung Chul Kim<sup>1</sup>, Hee Chul Woo<sup>2</sup>, and Young Han Kim<sup>2,\*</sup>  
Sub. of Adv. Mater. & Chem. Eng, Kyungnam Coll. of Info. & Tech.<sup>1</sup>  
Department of Chemical Engineering, Pukyong National University<sup>2</sup>  
([yhkim2@pknu.ac.kr](mailto:yhkim2@pknu.ac.kr)\*)

#### 1. Introduction

Extraction is a good recovery process due to its low energy demand. Though recycling its solvent requires energy, an efficient solvent having low solvent to feed ratio and sufficiently large boiling-point difference with product, reduces the energy demand. Note that extraction has high performance at room temperature, no heating necessary, and recycling low-temperature solvent provides heat recovered from high-temperature recycling solvent drawn at solvent recovery column. Process engineers recommend possible extraction solvents, but lack of LLE (liquid-liquid equilibrium) information limits wide application of the extraction. Extraction is an already-developed technique like distillation from long experiences in design and process operation. Therefore, the practical application of newly developed solvent is promising, as long as a potential solvent is found with the thermodynamic information. Moreover, high affinity between ethanol and water leading to an azeotrope makes production of over 95% ethanol difficult. Either extractive or azeotropic distillation can be utilized to produce pure ethanol, but azeotropic distillation needs more energy due to skewed distillation line at the region of high-content ethanol in ternary distillation diagram. Benzene and cyclohexane are solvents for azeotropic extraction, and ethylene glycol, glycerin, and choline/urea are good for extractive distillation. Comparison of energy demands in various ethanol processes indicates that extractive distillation is preferred to azeotropic distillation for concentrated ethanol production.

In this study a solvent, 2-methyl pentanol, is proposed for the extraction of ethanol from 10% ethanol feed, and subsequent distillations of solvent recovery and product purification are developed. Its energy efficiency is compared to existing processes handling the same ethanol feed to demonstrate the performance improvement of the proposed process.

#### 2. Thermodynamic Models

Though the process of extraction and purification is common and easily designed with commercial software Aspen Plus, the necessary thermodynamic information concerning with 2-methyl pentanol is not included in its database. For VLE and LLE computations, the NRTL (non-random two-liquid) model was employed in process design. Because no experimental measurements of VLE and LLE containing the solvent were available, molecular simulation was conducted to get the equilibrium data. The

extraction process was crucial in the proposed process, and several LLE data were experimentally determined to check the molecular simulated LLE results.

The LLE binary parameters were estimated using molecular distribution in two liquid phases, and the distribution was computed with molecular simulation using force computation among constituent molecules in respective liquid phases. The force field of molecular systems consists of intramolecular and intermolecular potentials: the former includes bond stretching, angle bending, and torsion, and the latter includes van der Waals and Coulomb forces.

$$\begin{aligned}
 U(\mathbf{r}) = & \frac{1}{2} \sum_{bonds} k_{ij}^r (r_{ij} - r_{eq})^2 + \frac{1}{2} \sum_{bend\ angles} k_{ijk}^\theta (\theta_{ijk} - \theta_{eq})^2 \\
 & + \frac{1}{2} \sum_{torsion\ angles} \sum_m k_{ijkl}^{\phi,m} [1 + \cos^m(m\phi_{ijkl} - \gamma_m)] \\
 & + \sum_{i=1}^N \sum_{j=i+1}^N \left( 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \right)
 \end{aligned} \tag{1}$$

Molecular simulation determines the molecular distributions in the two liquid phases, which in turn reveal the compositions of the two phases in equilibrium. There are many parameters in the simulation and significantly affect the simulation results. By using measured LLE data in a reference system of different solvent, the tuning parameter was adjusted to its best value for the proposed LLE system. The molecular simulation was conducted with an open software RASPA. In this study, phase transition probability was selected as an adjustable tuning parameter, and all others were set constant during the simulation. The molecular simulation results were partially compared with the experimental results to examine the simulation accuracy. Similarly, molecular distribution in vapor and liquid phases was found from the potential computation, and the VLE data were used in the estimation of VLE binary interaction parameters. The liquid compositions in equilibrium found by the molecular simulation were probed with the results of the experiments conducted in this study.

### 3. Process Design

Bioethanol feed was 10% ethanol, and targets of ethanol purity and recovery were 99% and 98%, respectively. Tray number of the extractor was determined for the ethanol recovery. Distillation columns were optimized for minimum TAC (total annual cost), investment and operating costs. The cost equations are listed in [1], and the cost index of 1638.2, Marshall and Swift equipment cost index in 2018, was used. Payback time of the investment was 7 years, and annual operation day was 300. The optimization was conducted with the response surface method.

### 4. Results and Discussion

Fig. 1 shows the column structures and stream flow rates with energy flows. Because process design software Aspen Plus was utilized in simulation, adjusting reflux flow was only option to find product specification with given tray number and column operating pressure. The tray numbers were

TAC-optimized for the ethanol recovery of 98.1% and purity of 99.2%. Ethanol is fermented from grain, and therefore wastewater can be recycled to fermentation process unless minor amount of solvent is harmful to microorganism. Acute toxicity of 2-methyl pentanol is in category 4. When the wastewater is recycled, no product loss is expected, and the recovery becomes no further problem. In the extraction, 97% of water was removed from feed and separated as wastewater.

The second section of the process was designed to raise ethanol composition from 79%, purity after solvent removed from extraction, to 99.2% of final product. There are many processes in purification, such as azeotropic and extractive distillations with various solvents. Though detailed comparison in energy demand is given in the following section, the design result of a common extractive distillation with ethylene glycol is presented in Fig. 1. For energy recovery, 3 preheaters were installed for feed heating to 3 distillation columns. Because the bottom temperature in the first solvent recovery column is high and more than half of its reboiler duty is recovered at the column, heat supply to the preheaters does not require additional energy. The availability of recovered heat reuse for the feed heaters was examined using heat exchanger network design with pinch technology [2]. With a pinch temperature, sufficient utility was available without additional energy requirement for the feed preheating.

While the investment cost includes column and tray costs in towers and heat exchanger construction cost, operating cost does steam and cooling water. The steam cost was calculated for reboiler duties, because preheaters consumed recovered heat. For 7 year payback period, total annual cost becomes 842,000 in U.S. dollars. Considering 300 days a year operation, bioethanol production cost is 118 US dollars for a ton of ethanol. The cost is comparable to the price of 0.66 USD/L-ethanol [3], 0.84 USD/L [4], and 0.976 USD/kg-ethanol [5]. Like in energy consumption comparison with previous studies, economics can be examined with others, but cost evaluation requires time-dependent cost index. In addition, equipment cost depends on production scale, such that equipment cost increases by scaling-up exponent of 0.68. Utility costs are also determined by solid waste from preprocessing of bio-feed to fermentation. Therefore, economics comparison to other studies bears more uncertainties than that of energy demand.

## **Conclusions**

Bioethanol is known to be energy self-sustainable, but reducing energy demand produces more electricity as byproduct. Conventional distillation for the pre-processing of low-content ethanol is proposed to be replaced with extraction using a newly developed solvent. Due to low boiling point of ethanol, commonly used extraction solvents are not suitable for the ethanol. With the thermodynamic VLE and LLE data obtained in this study, a process of ethanol recovery, a combination of extraction pre-treatment and extractive distillation, is formulated and optimized for an energy-efficient ethanol recovery process. Its energy demand was 28% less than the average of existing processes of distillation-extractive distillation and extraction-extractive distillation. Comparing to current price of bioethanol indicates that the production cost of the proposed process is sufficiently profitable.

## **References**

- [1] L. Domingues, C.I.C. Pinheiro, N.M.C. Oliveira, Economic comparison of a reactive distillation-based process with the conventional process for the production of ethyl tert-butyl ether

(ETBE), Comput. Chem. Eng. 100 (2017) 9-26.

- [2] I.C. Kemp, Pinch Analysis and Process Integration. second ed., Butterworth-Heinemann, Burlington, 2007.
- [3] J.C. Solarte-Toro, J.M. Romero-Garcia, A. Susmozas, E. Ruiz, E. Castro, C.A. Cardona-Alzate, Techno-economic feasibility of bioethanol production via biorefinery of olive tree prunings (OTP): optimization of the pretreatment stage, Holzforschung 73 (2019) 3-13.
- [4] L.W. Ou, T.R. Brown, R. Thilakaratne, G.P. Hu, R.C. Brown, Techno-economic analysis of co-located corn grain and corn stover ethanol plants, Biofuel. Bioprod. Bior. 8 (2014) 412-422.
- [5] C.A. Garcia-Velasquez, C.A. Cardona, Comparison of the biochemical and thermochemical routes for bioenergy production: A techno-economic (TEA), energetic and environmental assessment, Energy 172 (2019) 232-242.

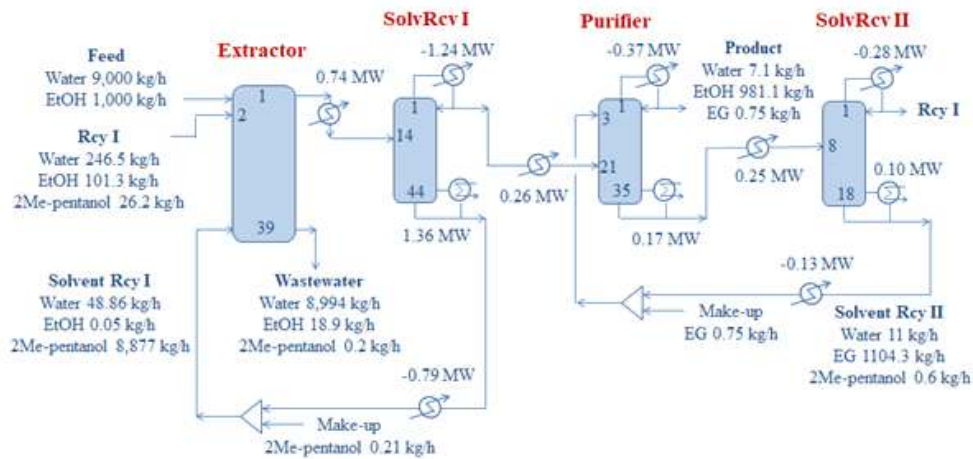


Figure 1. Process flow diagram of the proposed bioethanol recovery process.