Bioethanol concentration process using solvent extraction

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溶媒抽出を用いたバイオエタノール濃縮プロセス
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　エタノール水溶液を原料とし、キシレンおよびアルデヒド（フルフラールおよびベンズアルデヒド）を溶媒として回分平衡抽出を行った。水に比較してエタノールは選択的に溶媒相側に抽出され，エタノールが濃縮されることを確認した。比較的高いエタノールの分離の選択性を有しかつ分配係数の低い溶媒であるキシレンにアルデヒドを混合することにより、若干の選択性の低下のみで分配係数が向上した。また液液抽出と蒸留を組み合わせたプロセスを想定し、エタノール−水系の共沸点よりも低い範囲におけるエタノール濃縮を計算により検討した。製品中エタノール濃度の増加と共に所要エネルギーは増加し、また製品中エタノール濃度が高い範囲では蒸留のみに比較して液液抽出および蒸留を組み合せた場合の所要エネルギーは小さかった。

1.　Introduction

　Bioethanol is considered to be the most promising fuel of the future since it is obtained from renewable sources, and is environmental friendly. The need of bioethanol is increasing quickly in recent year. However the conventional processes tend to be uneconomic because commodity ethanol is cheap in spite of the great difficulty in the separation of ethanol and water, because the ethanol-water system forms azeotropic mixture at 96 % of ethanol concentration.

　The technology of bioethanol concentration has long been studied. The typical method of purification is distillation, which requires much energy for ethanol recovery and dehydration. Many ethanol recovery methods have been proposed to replace the distillation method, such as membrane separation[4], adsorption[4] and supercritical fluid extraction[5], etc. The solvent extraction technique is regarded as one of the prospective concentration methods.

　In this study, batch equilibrium extraction of ethanol was conducted, and the concentration process using solvent extraction was simulated based on the experimental results.

2.　Batch Extraction

2.1 Solvent Selection

　A large number of organic solvents have been examined to measure the extraction of ethanol [2]. The properties of water and ethanol are quite similar, making solvent selection more complicated. Many factors should be considered to choose favorable solvents for ethanol extraction, such as distribution coefficient of ethanol, separation selectivity of ethanol over water, availability, solvent toxicity, chemical stability

(thermal stability) and rapid phase separation. The first 2 factors are considered as the most important criteria.

　Bioethanol is very cheap and common. Therefore, the solvent should be cheap, common and highly available. These considerations suggested that the favorable solvent would be a hydrocarbon. In the case of the solvent of hydrocarbon, such as, xylene, the distribution coefficient of ethanol was low and the separation selectivity to water was relatively high[1]. Among the xylene isomers, m-xylene was considered to be most favorable because of the poor commercial potential in industry and not expensive, so m-xylene was selected. On the other hand, aldehyde had relatively high solvency for ethanol. In this study, we focus on aldehydes of furfural and benzaldehyde, which are used as an extraction solvent for refining lube oil and as a raw material of chemical synthetic substance, respectively. And the effects of the mixed solvents on the ethanol concentration were also discussed.

2.2 Experimental

　Table 1 shows the experimental conditions for batch extraction. The specified amounts of the feed and solvent phases were contacted and shaken with each other in conical flasks with screw cap in isothermal bath for 24 h at 298 K to equilibrate. After the equilibration, the raffinate and extract were separated by a separating funnel. The respective liquid phases were analyzed by gas chromatography (GC17A, Shimadzu Ltd.) with a 30m× 0.25mm i.d. capillary column and a flame ionization detector, in which the column temperature was maintained at 333K for the initial 5min, and then increased at 5K/min up to 373K. A Karl Fischer titration (758 KFD Titrino Metrohm

Ltd.) was used with dehydrated methanol of HYDRANAL methanol and titration solution of HYDRANAL composite 5, purchased from Sigma-Aldrich Ltd., to measure the water concentration of each solution.

Table 1 Experimental conditions for LLE

Feed system	Aqueous solution of ethanol(50g)
Solvent system	Furfural[2]
	m-Xylene
	Benzaldehyde
	m-Xylene, Benzaldehyde(1:1)
	m-Xylene, Furfural(1:1,7:3,9:1)
$x_{F,EtOH}$	0.1~0.7
S/F ratio	1
Time	24h
Temperature	298±1K

2.3 Results and Discussion

Figure 1 shows the liquid-liquid phase diagram in water-ethanol-solvent system. The heterogeneous region was wider with the solvent of m-xylene than those with the other solvents[1][2]. And it was the smallest in the case of furfural solvent, that is to say, furfural dissolved ethanol most[2].
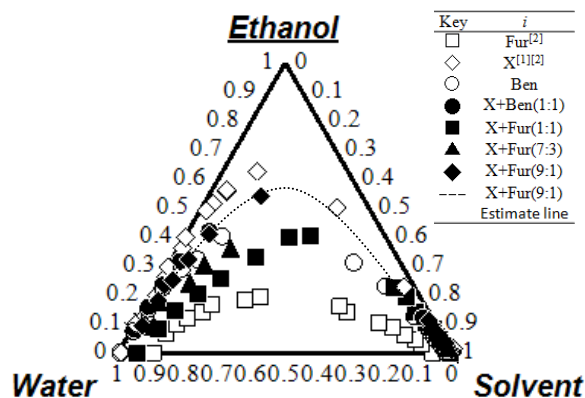

Fig.1 LLE for water-ethanol-solvent system

The ethanol concentrations in the extract phase on solvent-free basis were plotted against the feed ethanol concentrations in **Figure 2**. The concentration of ethanol in the extract phase on solvent-free basis was higher than the ethanol concentration in feed for all runs, namely, ethanol was concentrated by extraction. Although the ethanol was concentrated to relatively high concentration especially in the cases with m-xylene and the mixed solvents of m-xylene-furfural, the concentrations of ethanol in the extract phase based on the solvent-free basis

were lower than that in the azeotropic mixture of ethanol-water system.

The ethanol distribution coefficient and separation selectivity at equilibrium were defined as follows:

$$m_i = y_i/x_i$$

$$\beta_{EtOH,W} = m_{EtOH}/m_W$$

where y_i and x_i are the concentrations of component i in the organic and aqueous phases at liquid-liquid equilibrium.

Figure 3 shows the relation between the ethanol distribution coefficient and separation selectivity. The selectivity decreased with increasing distribution coefficient in all solvents. The m-xylene solvent[1][2] showed a low distribution coefficient, because ethanol has low solubility in m-xylene solvent. However ethanol could be partitioned more easily into the m-xylene phase than the water, so the separation selectivity was very high for m-xylene solvent. The solvent m-xylene-benzaldehyde maintained the separation selectivity and significantly improved the ethanol distribution coefficient. However, benzaldehyde is easily oxidized to benzoic acid, and it is required to care about extraction operation. Comparing with m-xylene-benzaldehyde mixed solvent, the selectivity with m-xylene-furfural mixed solvent was in the same range and the distribution coefficient was higher. Therefore the aldehydes of furfural and benzaldehyde enhanced the ethanol distribution coefficient. And the distribution coefficient increased by greater furfural content, but the heterogeneous region and the ethanol separation selectivity reduced. The addition of only a small amount of furfural significantly improved the distribution coefficient and maintained the separation selectivity.

However, the favorable solvent for concentration process should be selected depending on the process design and specifications.
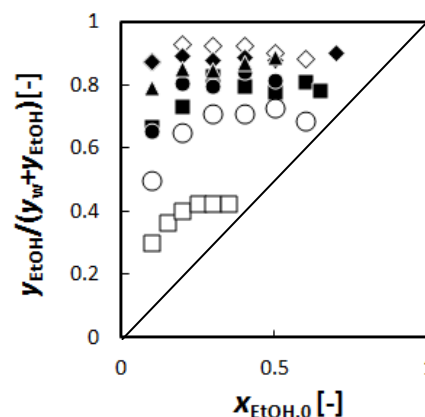

Fig.2 The ethanol concentrations in the extract phase on solvent-free basis at various feed ethanol concentrations.
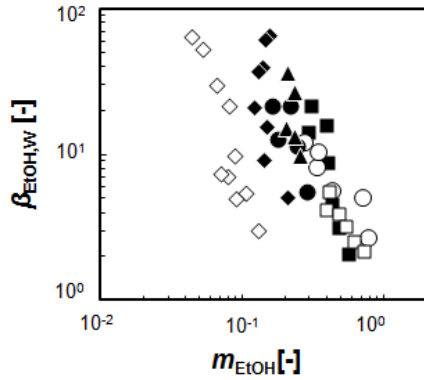
Fig.3 Relation between ethanol distribution coefficient and separation selectivity

Finally the experimental results calculated by the Non-Random Two Liquid (NRTL) model, which is an activity coefficient estimation model can be applied to non-ideal solution.

The NRTL equation and interaction parameters were defined as follows:

$$\ln(\gamma_i) = \frac{\sum_{j=1}^{m} \tau_{ji} G_{ji} x_j}{\sum_{l=1}^{m} G_{li} x_l} + \sum_{l=1}^{m} \frac{x_j G_{ij}}{\sum_{l=1}^{m} G_{lj} x_l} \left(\tau_{ij} - \right.$$

n=1mxnτnjGnjl=1mGljxl

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij})$$

where α_{ij} was the nonrandom parameter, τ_{ij} was the interaction parameter. For all components, α_{ij} was fixed as 0.3. Table3 shows the NRTL parameters obtained by fitting the measured relationship for ethanol+water+m-xylene+furfural system. Calculation result is shown in **Figure 1** as dashed line.

Table2 NRTL Parameters ($\alpha_{ij} = 0.3$)

i	j	τ_{ij}	τ_{ji}
Water	Ethanol	207.8	284.5
Water	m-Xylene	1527.2	3073.6
Water	Furfural	-3565.9	-2915.4
Ethanol	m-Xylene	261.3	808.8
Ethanol	Furfural	1119.6	-355.6
m-Xylene	Furfural	2849.2	456.3

3. Liquid-liquid extraction process

3.1 Process

In this study, the concentration process should be focused to recover ethanol the azeotropic mixture of ethanol-water system.

The combination of extraction and distillation was studied to evaluate the recovery of ethanol. Process flow diagram is shown in **Figure 4**. In this process, bioethanol feed F is supplied into multistage extraction column and contracted with solvent S. The extract phase E is obtained from the top of the extraction column and sent into distillation column 1 to recover solvent. And the distillate D is sent into the distillation column 2 to concentrate ethanol to a high level. The raffinate phase R which comes out at bottom of the extraction column also sent into the distillation column 2 to recover ethanol.
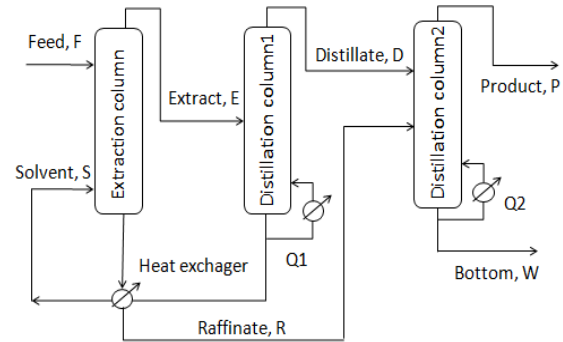

Fig.4 Process flow diagram of ethanol recovery by combination of extraction and distillation

3.2 Process calculation conditions

Aspen Hysys simulator (Aspen Japan, Inc.) was used to simulate extraction process based on the experimental results, which were calculated by the Non-Random Two Liquid (NRTL) model. Table 4 shows calculation conditions of process. The S/F ratio was fixed at 0 to1. If the S/F ratio equal 0, it means that this process consists only of the distillation column2. The feed temperature was 298K, the operation pressure was one atm, and the pressure drop was zero in all runs.

Table4 Calculation conditions of Process

Feed system	Aqueous solution of ethanol
Solvent system	m-Xylene Furfural m-Xylene,Furfural (9:1)
Feed, F	1000 kg/h
$x_{F,EtOH}$	0.1
S/F Ratio	0~1
Extraction Column Stages	3
Distillation Column 1 Stages	10
Distillation Column 2 Stages	20
Total Specification	$x_{p,EtOH}$=0.85~0.95 $Y_{p,Eth}$=0.98
Specification (Distillation Column 1)	$x_{p,EtOH}$=0.6~0.75 $Y_{p,Eth}$=0.99
Specification (Distillation Column 2)	$x_{p,EtOH}$=0.85~0.95 $Y_{p,Eth}$=0.99

3.3 Results and Discussion

Figure 6 and **Figure 7** show the effects of S/F ratio on the energy requirements in different distillation column and in different solvents, respectively. The energy requirements in distillation for Process in **Figure 6** and **Figure 7** were estimated under the same specifications ($x_{p,EtOH}$=0.92, $Y_{p,EtOH}$=0.98).

In **Figure 6**, the calculation results show the increase in S/F ratio resulted in the increase of energy requirements of distillation column1 for all cases. As much as solvents increased, energy requirement for recover solvent became large. On the hand, the energy requirements of distillation column2 decreased with increasing S/F ratio in case of furfural solvent only. In **Figure 7**, the calculation results show that furfural required lower energy requirements than the other solvents. And comparing with the case of S/F=0(Distillation column2 only), the required energy with furfural was also lower, if the S/F ratio was lower than 0.8.
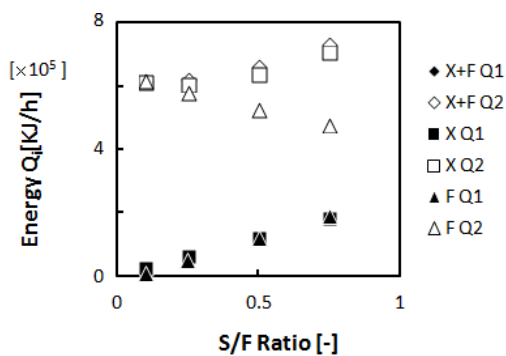

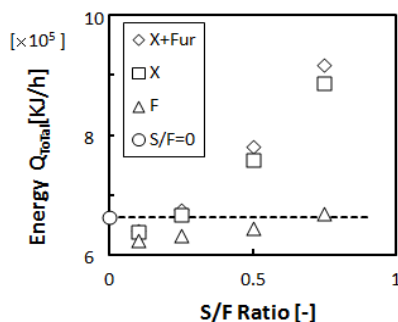Fig.6 Effects of S/F Ratio on energy requirements in different distillation column.

Fig.7 Effects of S/F Ratio on total energy requirements in different solvent.

Figure 8 shows the effects of ethanol concentration in product on energy requirements. The calculation of the energy requirements in Figure 6 was done under same specification ($x_{p,EtOH}$=0.85~0.95,$Y_{p,EtOH}$=0.98).

Energy requirements increases with increasing concentration of ethanol, and it was found that the increase of energy requirements in the case of S/F=0 was particularly noticeable. In the range exceeding 92% of ethanol concentration in product, the solvent extraction process could reduce energy requirements significantly, and could save energy for about 43% to the maximum.
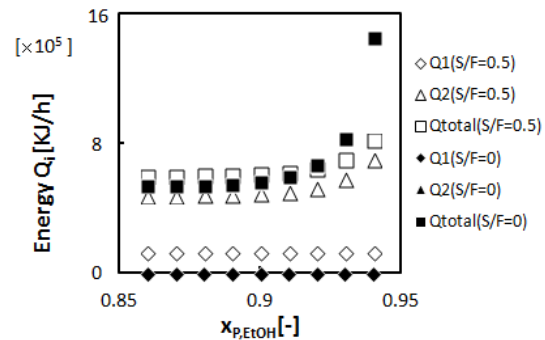

Fig.8 Effects of ethanol concentrations in product on energy requirements

4   Conclusion

Firstly, Ethanol could be concentrated by extraction, and the distribution coefficient of ethanol could be improved by the addition of aldehyde, to the solvent of m-xylene, with little decrease of the selectivity.

Secondly, simulation of the ethanol concentration process shows the extraction process using furfural solvent is required lower energy than distillation process.

The results above confirmed the feasibility of bioethanol concentration process by solvent extraction.

Nomenclatures

m: distribution coefficient, y_i: mass fraction in extract, x_i: mass fraction in raffinate, β: separation selectivity
EtOH: ethanol, W: water, Fur: furfural, X: m-xylene, Ben: Benzaldehyde,
<Subscript>0: initial, R: raffinate, E: extract, D: distillate, P: product, W: bottom,

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