

Liquid-liquid equilibrium in concentration and purification of bioethanol by solvent extraction

Student Number: 15M18150 Name: Tomonori MASUDA Supervisor: Ryuichi EGASHIRA

溶媒抽出法によるバイオエタノールの濃縮および精製における液液平衡

増田 知徳

エタノール水溶液を原料、直鎖アルカン又は軽質軽油を溶媒として液液平衡を実測及び活量係数モデルにより推算した。エタノールは水よりも選択的に溶媒相中に抽出された。分子中の炭素原子数(炭素数)の大きい溶媒及び平衡時の温度の低い範囲の条件においてはエタノール-水系の共沸混合物よりもエタノール濃度の高い範囲への濃縮が可能であった。平衡時の温度の上昇又は溶媒の炭素数の減少と共に、エタノールの分配係数は増加し水に対する分離の選択性は低下した。

1. Introduction

Bioethanol is well known as the substitute of motor gasoline and promising fuel since it is obtained from renewable source. Although high purity of ethanol is necessary to blend with motor gasoline, such as more than 99.5vol% [1], the ethanol solution obtained from fermentation process generally contains ethanol lower than 10mass%. Therefore it is necessary to concentrate ethanol up to the specified concentration. Nevertheless it is impossible to attain the specified concentration by the conventional distillation, because of azeotrope mixture at the ethanol mass fraction of 0.96. Other techniques to concentrate ethanol have been studied for a long time. Although a typical method of ethanol concentration is azeotropic distillation, this method should require relatively high energy. Other concentration methods for less energy requirement have been proposed, such as adsorption, membrane separation, solvent extraction and so on. Although the solvent extraction have been studied about various solvents [2][3], for most cases, the ethanol extraction was studied with the solvents giving relatively high ethanol solubility. And generally these solvents formed homogeneous phase with nearly pure ethanol. Accordingly it was difficult to concentrate ethanol up to the specified concentration for fuel use. Therefore it is necessary to study the application of the extraction with the solvents of high separation selectivity of ethanol for the bioethanol production.

This study aimed concentration and purification of bioethanol by solvent extraction based on liquid-liquid equilibrium. The solvents which had potential to concentrate ethanol more than azeotrope composition were selected and the liquid-liquid equilibrium (LLE) of the ethanol-water-solvent was measured. And the effects of conditions on LLE were discussed with experimental results and calculation results using activity coefficient estimation model. The development of bioethanol extraction process with the employed solvent was considered based on the LLE.

2. Liquid-liquid equilibrium measurement

2.1. Experimental

According to previous studies, alkane compounds of higher carbon numbers in molecule were expected to

show higher separation selectivity of ethanol relative to water [2]. Tridecane (C13), tetradecane (C14), and light gas oil (LGO), consisting mainly of alkane compounds, were selected as solvent. The Physical properties of materials are shown in Table 1. The selected solvents are expected to separate from ethanol easily by distillation, because each boiling point of solvents is quite different from that of ethanol.

The experimental conditions of the mutual solubility and LLE measurement are summarized in Table 2. The specified amounts of feed and solvent were put in conical flask and shaken in isothermal bath. After the specified time, raffinate and extract phases were separated into each other by separating funnel. The liquid phases were analyzed by gas chromatograph (GC) with flame ionization detector, and Karl Fischer titrator (KFT) to determine their compositions.

Table 1 Physical properties of materials

Component	Boiling point[K]	Density[kg/L]
Ethanol	351.5	0.789
Tetradecane	526.6	0.764
Tridecane	507.1	0.756
Light gas oil	443~643	0.840

Table 2 Conditions of experiment of liquid-liquid equilibrium

Feed, F	Ethanol aqueous solution
Solvent, S	Tridecane (C13), Tetradecane (C14), Light gas oil (LGO)
Mass of feed	[g] 10~30
Mass fraction of ethanol in feed	[-] 0.00~1.00
Mass ratio of S to F	[-] 1
Temperature, T	[K] 289~333
Time	[h] 48

2.2 Results and discussion

Figure 1 shows the mutual solubility between ethanol and solvent under several temperatures. In the range of lower temperature and larger number of carbon atom in molecules (CN), the solvents formed heterogeneous phase with ethanol. The temperature required to form a

homogeneous phase rose in order of C13 (298K), LGO (303K), and C14 (313K), and this might follow the order of increasing CN. The mutual solubility between ethanol and solvent increased, as temperature was elevated and CN decreased.

The solvent compound in the raffinate phase and water in the extract phase were not detected by GC or KFT analysis, in other words, the mutual solubility between water and C14 or LGO was negligibly small. Then it could be expected that this kind of solvent should give high separation selectivity of ethanol relative to water. Moreover it must be unnecessary to consider the separation between solvent and water.

Figures 2 and 3 show the phase diagrams of ethanol, water, and C14 systems. The solubility of ethanol in extract was clearly larger than that of water. So ethanol was extracted selectively relative to water. The solubility of ethanol and water in the extract phase and that of C14 in the raffinate phase increased with temperature, that is to say, two phase region became smaller with elevating temperature. In this measuring conditions, C14 formed homogeneous phase with some kinds of the feed solutions of higher ethanol concentrations, and the temperature and feed compositions are shown in Table 3. Then, by adjusting temperatures and other conditions appropriately, it is possible to concentrate ethanol up to higher than that specified for the bioethanol production by extraction.

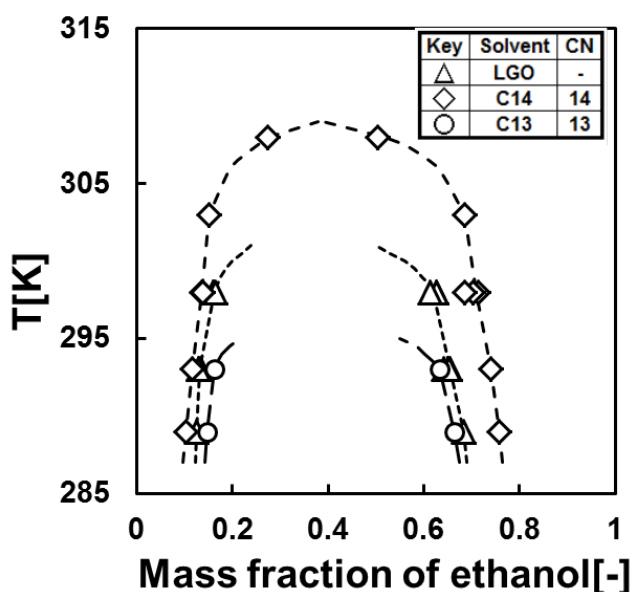


Fig.1 Mutual solubility of ethanol and solvent (dashed lines and dotted lines show the prediction of the mutual solubility in outside of measurement range)

Table 3 Conditions which C14 and feed became homogeneous phase

T[K]	Mass fraction of ethanol in feed
313	1.00
323	0.99, 1.00
333	0.98, 0.99, 1.00

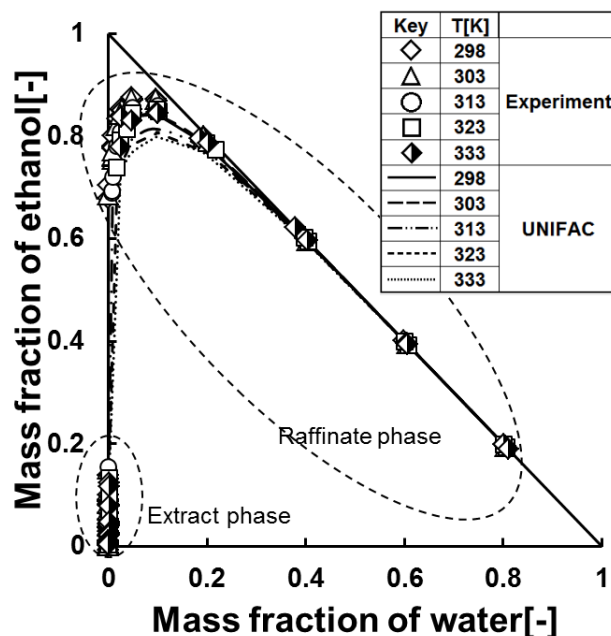


Fig.2 Phase diagram of C14-water-ethanol (experimental results show by points, estimated results show by curves)

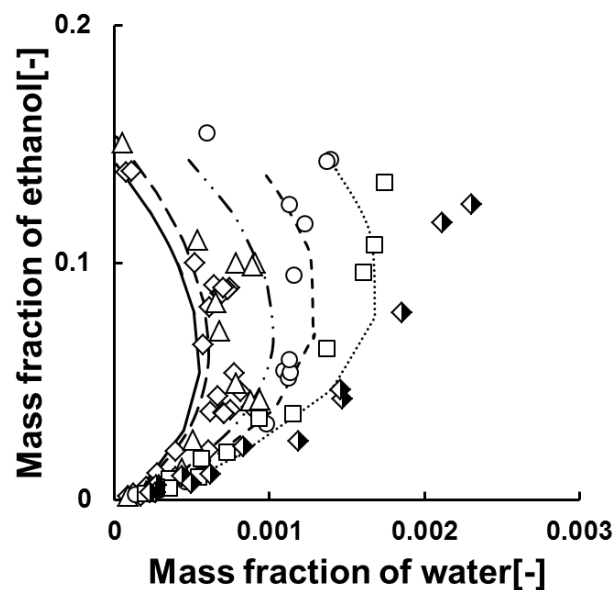


Fig.3 Enlarged view of extract phase on Fig.2 (experimental results show by points, estimated results show by curves)

The LLE of the systems measured in this study were estimated by the UNIFAC method, one of the thermodynamic techniques to estimate activity coefficients with interaction parameters between functional groups composing molecular of component and so on[4]. This model could estimate LLE with many components by a few interaction parameter of functional groups. So, The interaction parameters were determined by fitting the experimental results on estimated results under the respective temperatures. The estimation results in the case of ethanol-water-C14 system are also shown in Figures 2 and 3 by the lines. The UNIFAC method

could favorably estimate the LLE of C14-water-ethanol, especially the compositions in extract phase.

The distribution coefficient of ethanol, m_e , solvent-free mass fraction of ethanol in extract, Z_E , and solvent-free mass fraction of ethanol in raffinate, Z_R were defined as follows:

$$m_e = y_e / x_e \quad (1)$$

$$Z_E = y_e / (y_e + y_w) \quad (2)$$

$$Z_R = x_e / (x_e + x_w) \quad (3)$$

where x_e, x_w were the mass fractions of ethanol and water in extract phase and y_e, y_w were those in raffinate phase.

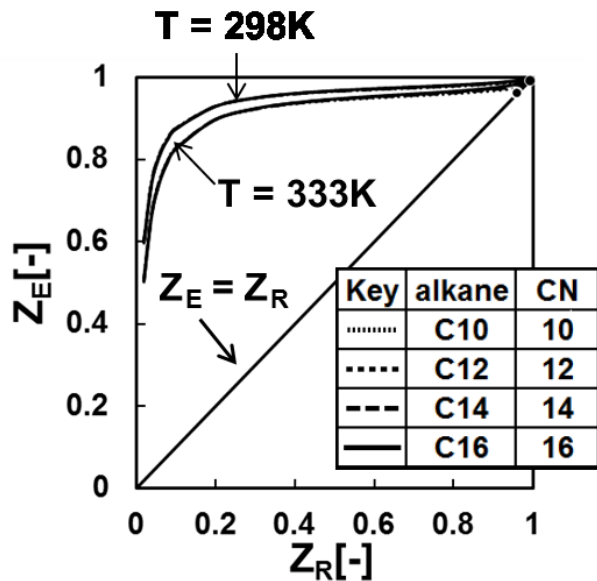


Fig.4 Relation of solvent-free ethanol concentration in each phase

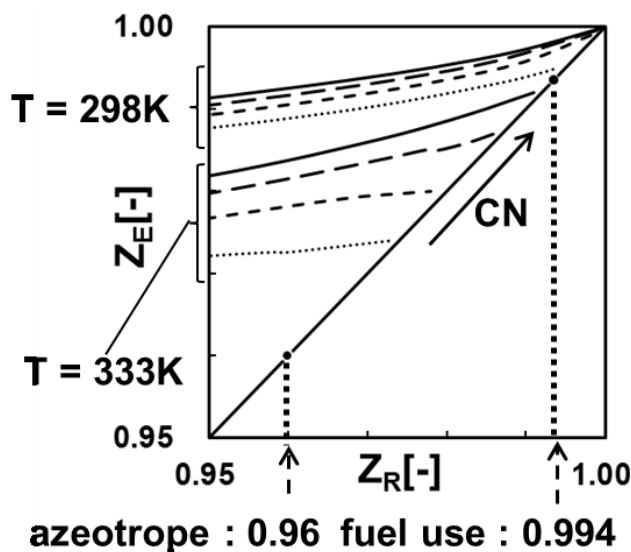


Fig.5 Enlarged view on Fig.4

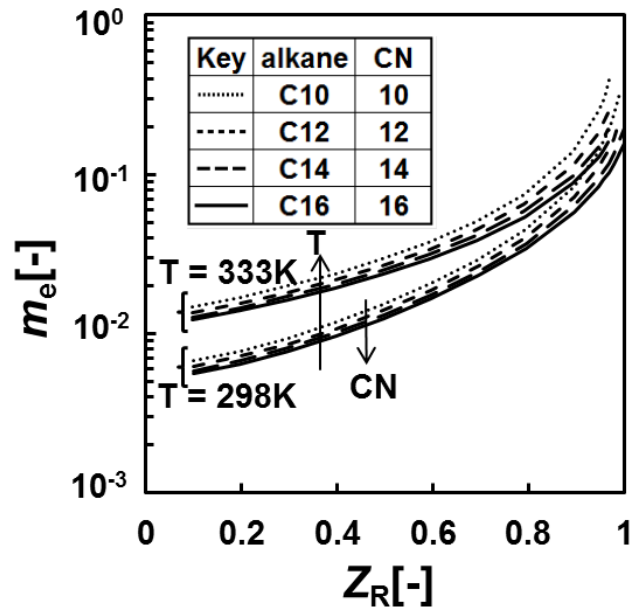


Fig.6 Relation between distribution ratio of ethanol and solvent-free ethanol concentration in the raffinate phase

The LLE of solvent-water-ethanol system was estimated by the UNIFAC method under various temperature and solvents. Figures 4 and 5 show the relation between Z_E and Z_R . The Z_E was always larger than Z_R . The Z_E decreased with elevating temperature and decreasing CN. In the range of lower temperature and larger CN, the Z_E could reach nearly pure. Figure 6 shows the relation between m_e and Z_R . The m_e increased with Z_R , temperature, and decreasing CN. The actual feed solution from the fermentation step generally contained ethanol of 0.1 at most by mass fraction. In this concentration range, m_e was so small. Then the recovery of ethanol from the feed solution must be difficult even though m_e could be improved by temperature elevation.

3. Bioethanol concentration process by solvent extraction

Figure 7 shows the outline of extraction process for bioethanol concentration and purification. The solvent should form heterogeneous two liquid phases with highly pure ethanol in the enriching section between the feed entry point and the top of the extractor, where the ethanol is enriched up to nearly pure with concentration higher than in azeotrope by reflux operation. On the other hand, high solubility of ethanol into the solvent is required in the stripping section lower than the feed entry to reduce ethanol flowing out as a raffinate product. Although these two criteria of the solvent conflict with each other as results of the equilibrium shown in Figures 5 and 6, they can be satisfied at the same time by selecting different operating temperatures for the enriching and stripping sections, for example.

As shown in figure 6, m_e was quite small in the range of lower concentration of ethanol. It is predicted that a large quantity of solvents are necessary for ethanol recovery, even though operating temperature in stripping

section is elevated. The Other method for reduction of ethanol flowing out as a raffinate product is use of distillation before extraction. Mass fraction of ethanol in vapor phase and that of ethanol in liquid phase were defined as Z_V and Z_L . Figure 8 shows Z_E and Z_R on LLE of C14-water-ethanol system and Z_V and Z_L on vapor-liquid equilibrium(VLE) of ethanol-water system. The VLE data was quoted from the literature.[5] Within the range of high concentration of ethanol(around 96wt%), the difference between Z_V and Z_L is much small, so distillation is difficult. On the other hand, in the range of relatively low concentration of ethanol (60-80wt%), the difference between Z_V and Z_L is large enough to distill raw bioethanol feed into 60-80wt% ethanol easily. Figure 9 shows outline of extraction and distillation. The raffinate containing ethanol is introduced into distillation column, then the ethanol in raffinate is distilled into a distillate product. Accordingly it is possible to recover ethanol from raffinate product by using distillation.

The technique which needs lower energy is required of bioethanol purification process. When operating conditions of extraction process are optimized for reduction of energy consumption, these plans such as above are important.

4. Conclusions

The liquid-liquid equilibriums of ethanol-water-solvent were clarified with experiment and calculation. Ethanol was extracted selectively relative to water, and it was possible to concentrate ethanol up to more than ethanol azeotrope composition in the range of lower temperature and larger number of carbon in molecules. The distribution ratio of ethanol increased, with elevating temperature and decreasing number of carbon in molecules.

Based on LLE of experimental results and calculation results by activity coefficient model, the effective operation of bioethanol extraction process was suggested.

Nomenclature

x = mass fraction of component in raffinate phase, y = mass fraction of component in extract phase, Z = solvent-free mass fraction of ethanol, CN = number of carbon in molecule, T = temperature, m = distribution ratio, β = separation selectivity, γ = activity coefficient, a = interaction parameter, C10 = decane, C12 = dodecane, C13 = tridecane, C14 = tetradecane, C16 = hexadecane, LGO = light gas oil, CN = number of carbon atom in molecule, LLE = liquid-liquid equilibrium, VLE = vapor-liquid equilibrium

Subscript

E = extract phase, R = raffinate phase, V = vapor phase, L = liquid phase, w = water, e = ethanol, s = solvent, i = component i, j = component j, p = phase

References

- [1] JIS K 2190:2011 燃料用エタノール
- [2] Roddy, J.W Ind. Eng. Chem. Proc. Des. Dev. p104 (1981)
- [3] S.A.Leeper et al. Ind. Eng. Chem. Proc. Des. Dev. p331-334(1982)
- [4] Fredenslund A AIChE Journal vol.21 p1086-1099(1975)
- [5] 社団法人日本化学工学会 “化学工学基礎編改訂第5版”(2004)

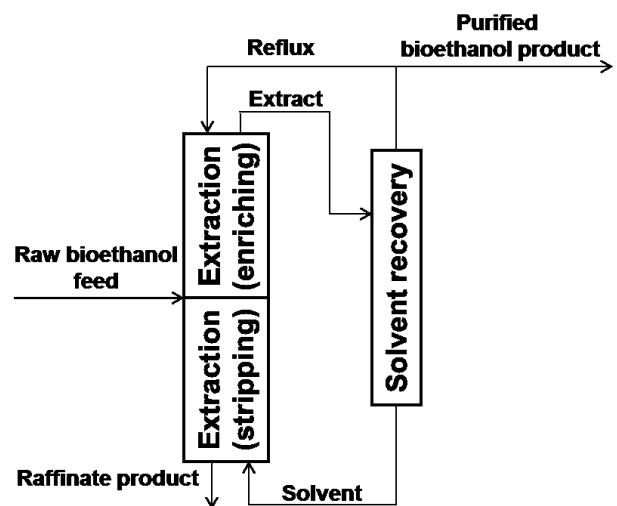


Fig.7 Outline of extraction with product reflux

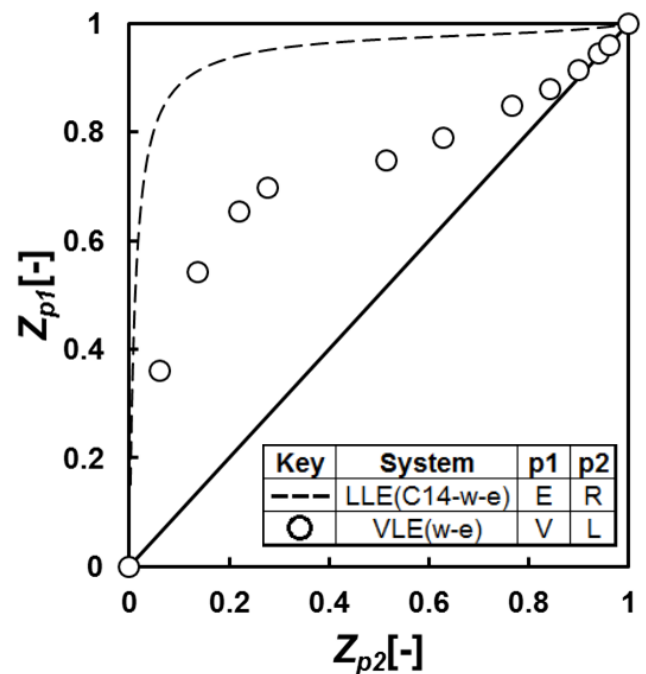


Fig.8 LLE of C14-water- ethanol system and vapor-liquid equilibrium of ethanol-water system

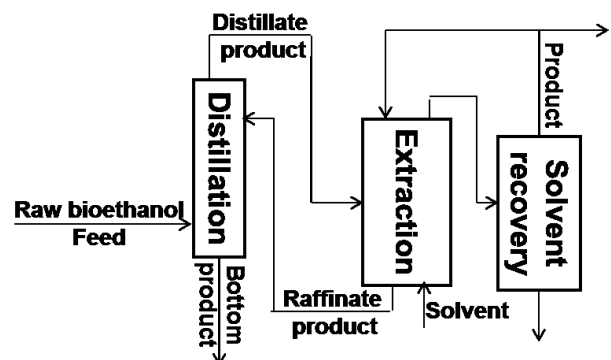


Fig.9 Outline of extraction and distillation