

# Phase Equilibrium Measurement of n-Butane/Water/n-Butanol System for Development of an Energy-Saving Biobutanol Extraction Process

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## Abstract

The application of biobutanol as an alternative fuel has numerous advantages compared to bioethanol, such as high heating value, low moisture absorption, and low corrosion, although biobutanol requires a high dehydration energy because of its low initial concentration (approximately 1-3 wt%). To develop energy-saving dehydration process using light hydrocarbon extraction, butane solvent was selected as a suitable solvent because of their properties like no azeotropic point or high butanol solubility. Phase equilibrium data of an n-butane/water/n-butanol system were determined using apparatus for high-pressure phase equilibrium measurements and NRTL model parameters were regressed. The proposed process for butanol dehydration consist the extraction column and distillation column. In the extraction column, butanol is concentrated to 90%, after which butane and butanol are separated in the distillation column. Vapor recompression system was introduced for heat recovery. Anhydrous butanol is recovered from the bottom of the distillation column. Energy consumption of a biobutanol dehydration process was evaluated using the developed model and shows 5 MJ/kg-biobutanol from the initial n-butanol concentration of 2 wt% to the final recovery of 99.9 wt% of biobutanol.

**Keywords:** Biobutanol; Dehydration process; NRTL model; Butane solvent

## Introduction

Biofuel technology has recently attracted a great attention, and first generation of biofuels, such as bioethanol produced from sugarcane or corn, has been already exploited on a commercial scale. The second generation of biofuels, such as ethanol from inedible biomass, represents a highly attractive research field to develop a cost-effective production process. Moreover, the application of biobutanol as an alternative biofuel has many advantages such as high heating value, low moisture absorption, low causticity, and the possibility to be applied to the existing gas stations. Many studies have been conducted on the development of suitable yeast strain for biobutanol production [1-8]. However, a disadvantage of this approach is the low initial concentration of fermented butanol (around 1-3 wt%), which requires a high energy for dehydration [9]. If initial concentration of n-butanol is 1 wt%, a distillation process requires energy of about 30 kJ/kg-butanol for 99.5 wt% recovery, which is close to a lower heating value of n-butanol (Table 1).

Several biobutanol separation processes such as extraction, membrane, adsorption, gas stripping, and pervaporation, have been reported in previous literature [10-20]. For the production of biobutanol on a large scale, the extraction process has a scale up merit. In the case of liquid-liquid extraction processes, a suitable solvent should meet the following requirements:

- High solubility of n-butanol,
- Low solubility of water,
- Ease of separation from n-butanol after extraction (no azeotropic point with n-butanol) and
- Being nontoxic to yeast used for fermentation (Table 2).

In this study, we propose a biobutanol extraction process using n-butane solvent. As a solvent, n-butane has high n-butanol extraction efficiency and an azeotropic point does not exist for it with n-butanol contrary to pentane or hexane. The extraction process used in this study is schematically presented in Figure 1. At first, an n-butanol

fermentation broth (1-3 wt%) is fed to an extraction column and contacted with an n-butane solvent. Butane solvent extracts butanol contained in water by liquid-liquid extraction, and the remaining water is discharged from the bottom of the extraction column. Since the solubility of butane in the water phase is very low, loss of butane solvent can be ignored. Subsequently, the concentrated n-butanol with n-butane solvent is collected from the top of the extraction column. Following the extraction process, the n-butanol and n-butane mixture are separated in a distillation column. Anhydrous n-butanol is collected from the bottom of the distillation column and butane vapor were collected as an overhead products. The vapor is recompressed and the latent heat is recovered as a reboiler heat duty. Butane vapor after heat utilization is liquefied, and water contained in a small amount is excluded by liquid-liquid separation.

In this work, to evaluate the required energy of the proposed system, phase equilibrium data of an n-butane/water/n-butanol system were measured and a model for their presentation was developed. Energy consumption of biobutanol dehydration was evaluated using our developed model.

## Measurement

The n-butane (mass fraction purity of 0.998) was supplied by Toyoko Kagaku Co., Ltd. (Japan) and the n-butanol (mass fraction purity of 0.99) was supplied by Wako Pure Chemical Industries, Ltd. (Japan). Phase equilibrium data of the n-butane/water/n-butanol system were determined using a high-pressure apparatus for the phase equilibrium

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Method	Characteristic
Distillation	Huge energy as same as butanol heating value
Liquid solvent extraction	Suitable solvent has toxicity for yeast
membrane	low scale up merit, low durability
Subcritical butane extraction	Controllable solubility, scale up merit, non-toxic

Table 1: Characteristic of each butanol condensation technology.

Solvent	T <sub>b</sub> (°C)	T <sub>c</sub> (°C)	P <sub>c</sub> (MPa)	Butanol solubility	Azeotropic with butanol
Propane (C <sub>3</sub> H <sub>8</sub> )	-42	96.6	4.24	△	Non
Butane (C <sub>4</sub> H <sub>10</sub> )	-0.5	152	3.8	○	Non
Pentane (C <sub>5</sub> H <sub>12</sub> )	36	223	3.37	○	Exist
Hexane (C <sub>6</sub> H <sub>14</sub> )	69	234	2.97	○	Exist

Table 2: Properties, butanol solubility and azeotropic with butanol of hydrocarbon solvent.

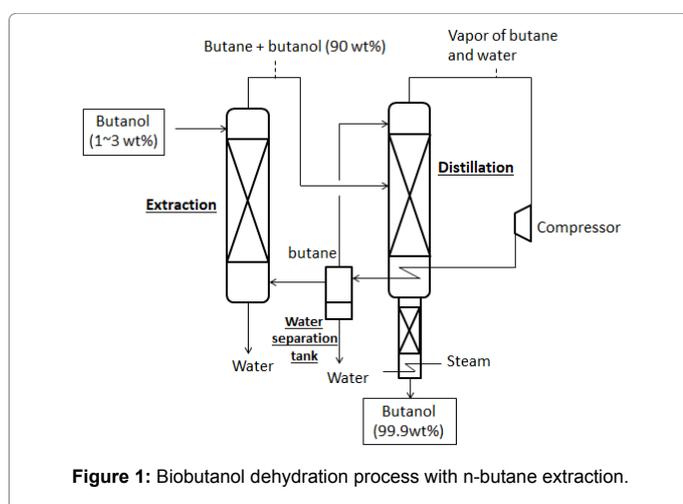


Figure 1: Biobutanol dehydration process with n-butane extraction.

measurements. A detailed description of the measurement apparatus was reported in a previous study [21]. Briefly, the overall procedure can be summarized as follows: a (1-4 wt%) mixture of n-butanol and water was placed in a high-pressure cell; the n-butane solvent was loaded with a diaphragm pump and purged over three times replace the vapor phase. The phase equilibrium was reached by stirring the reaction mixture. The vapor and liquid phases were circulated using a circulation pump. After equilibration, small amounts of the vapor and liquid phases were continuously sampled with the aid of a metering valve and analyzed with a process gas chromatograph (Shimadzu GC-14B, TCD, Column Temp. 190°C, Porapak T+Gaskuropack 54, 4×6 way sampling valve). Each experimental data set was measured at least three times. Reproducibility of the concentrations was accurate up to 0.001 mole fraction.

The initial n-butanol concentration in the water-rich phase was varied from 1-4 wt%. The temperature ranged from 313 to 443 K, and pressure was set to 4 MPa that is higher than vapor pressure of n-butane for all temperature conditions.

## Model

A Non-Random Two Liquid (NRTL) model [22] was used for representing the phase equilibrium data. In this study, the n-butane and water phases are liquids for all investigated points. Therefore, the liquid-liquid equilibrium (LLE) formula was applied.

The LLE equilibrium can be represented by equation (1)

$$(\gamma_i x_i)^W = (\gamma_i x_i)^B \quad (1)$$

where W designates the water phase, and B denotes the n-butane phase; i=1, 2, and 3, stands for n-butane, water, and n-butanol, respectively.

Activity coefficients for the NRTL model with 5 parameters are given as follows:

$$\ln \gamma_i = \sum_j \tau_{ji} G_{ji} x_{ji} + \sum_j \sum_k x_k G_{jk} \left\{ \tau_{ji} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k \tau_{ik} x_k} \right\} \quad (2)$$

$$\tau_{ji} = a_{ij} + \frac{b_{ij}}{T} \quad (3)$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \quad (4)$$

$$a_{ij} \neq a_{ji}, b_{ij} \neq b_{ji}, \alpha_{ij} = \alpha_{ji} \quad (5)$$

Parameters  $a_{ij}$ ,  $a_{ji}$ ,  $b_{ij}$ ,  $b_{ji}$ , and  $\alpha_{ij}$  were determined by minimization of least squares error  $\delta$ , equation (6), along with equilibrium ratio at the experimentally investigated temperatures and pressures at a certain composition, equation (7), given as follows:

$$\delta = \sum \left[ \frac{K_{i,exp} - K_{i,calc}}{K_{i,exp}} \right]^2 \quad (6)$$

$$K_i = \frac{x_i^B}{x_i^W} \quad (7)$$

## Results and Discussion

### Experimental LLE data and regression results

Table 3 shows the experimental data, and Figure 2 depicts the phase equilibrium data of the n-butane/water/n-butanol system at 313 and 383 K. The concentration of n-butanol in the n-butane phase linearly increases with that in the water phase. It means that partitioning of n-butanol between water and n-butane phases does not depend on the concentration of n-butanol in the n-butanol-dilute region. Figure 3 depicts the n-butanol concentration in the n-butane-rich phase. These data were obtained from linear approximation at initial concentration of n-butanol of 1 wt% in water phase at different temperatures. At low temperatures, the n-butanol concentration increased with increasing temperature, attaining a maximum at 373 K. At temperatures higher than 423 K, the n-butane concentration shows a decreasing trend. These trends depend on the temperature dependence of n-butanol vapor pressure and density of the n-butane solvent. The density of butane decreases drastically around its critical point at 425 K. Figure 4 depicts the temperature dependence of the n-butane-free n-butanol concentration, indicating a concentration effect of n-butanol. The concentration of n-butanol in the temperature range of 313-383 K is more than 90 wt% while it shows a decreasing trend at higher temperatures. It depends on water solubility in the n-butane phase,

T/K	P/MPa	$x_1^W$	$x_2^W$	$x_3^W$	$x_1^B$	$x_2^B$	$x_3^B$
313.2	4	N.D.	0.9958	0.0043	0.985	0.004	0.011
313.2	4	N.D.	0.9946	0.0054	0.983	0.003	0.014
363.2	4	N.D.	0.9974	0.0026	0.978	0.005	0.017
383.2	4	N.D.	0.9968	0.0032	0.959	0.011	0.03
383.2	4	N.D.	0.9928	0.0072	0.884	0.027	0.089
383.2	4	N.D.	0.9909	0.0091	0.742	0.064	0.194
393.2	4	N.D.	0.998	0.002	0.97	0.012	0.018
393.2	4	N.D.	0.9965	0.0035	0.953	0.015	0.033
403.2	4	N.D.	0.9966	0.0034	0.948	0.02	0.032
413.2	4	N.D.	0.9966	0.0034	0.942	0.026	0.033
423.2	4	N.D.	0.9959	0.0041	0.916	0.06	0.024
443.2	4	N.D.	0.9945	0.0055	0.82	0.148	0.032

N.D.: not detected;  $u(x_i) = 0.001$ ,  $u(T) = 0.1$  K,  $u(p) = 0.003$  MPa

Table 3: Equilibrium mole fraction data between water and n-butane phases for the n-butane(1)/water(2)/n-butanol(3) system.

i	j	$a_{ij}$	$b_{ij}$	$a_{ji}$	$b_{ji}$	$a_{ij}$
1	2	-7.326	3873	5.961	455.3	0.2
1	3	-6.325	2801	208.7	44650	0.18
2	3	-37.99	16990	-5.135	2512	0.2

Table 4: The NRTL model parameters for the n-butane/water/n-butanol system.

Initial concentration	wt%	1	2
Product concentration	wt%	99.9	99.9
Recovery ratio	%	99.2	99.2
Heat Exchanger	MJ/kg	3.2	1.5
Reboiler	MJ/kg	0.4	0.4
Pump	MJ/kg	2.8	1.3
Compressor	MJ/kg	3.9~5.3	1.8~2.5
Total	MJ/kg	10.3~11.6	5.1~5.7

Table 5: The calculation results of the required energy for the biobutanol extraction process heat to power generating efficiency: 40%; pump efficiency: 60%; adiabatic efficiency of compressor: 60%~80%.

which increases with increasing temperature (Table 3; Figures 2-4).

Comparing Figures 3 and 4, it was found that although the recovery ratio of butanol increased due to temperature increase, at the same time the accompanying amount of water gradually increased. It was decided as the optimal operating condition at 383 K since the recovery ratio of butanol was the maximum and the entrained water content was also small (Table 4).

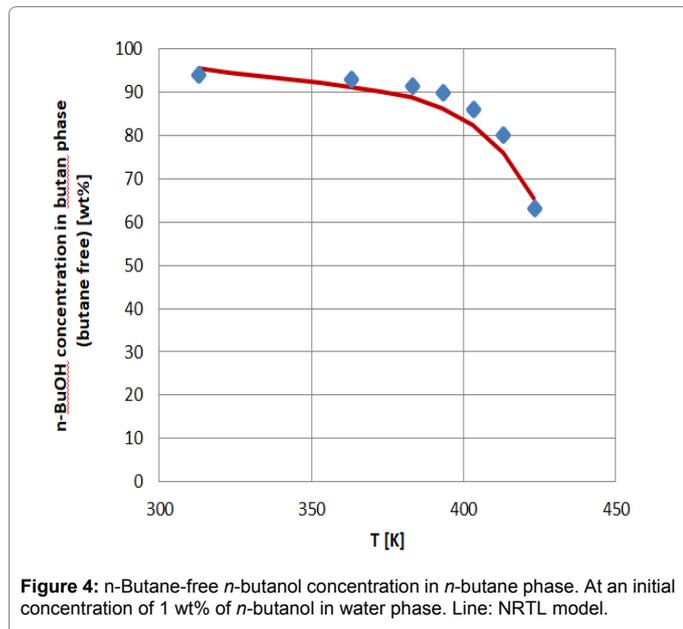
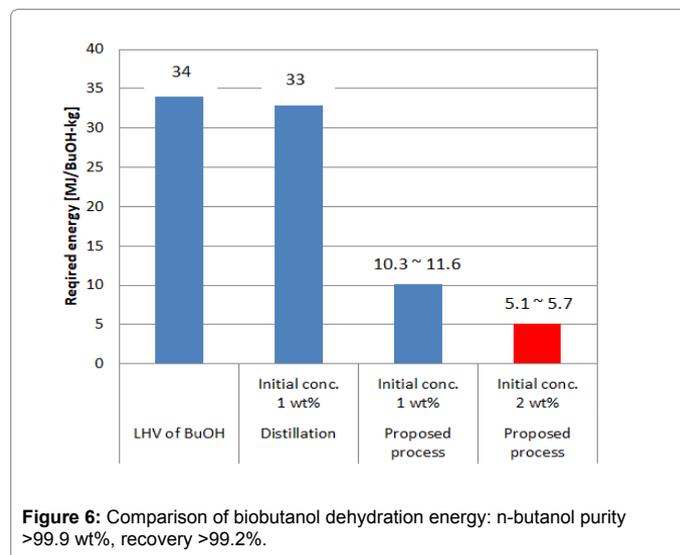
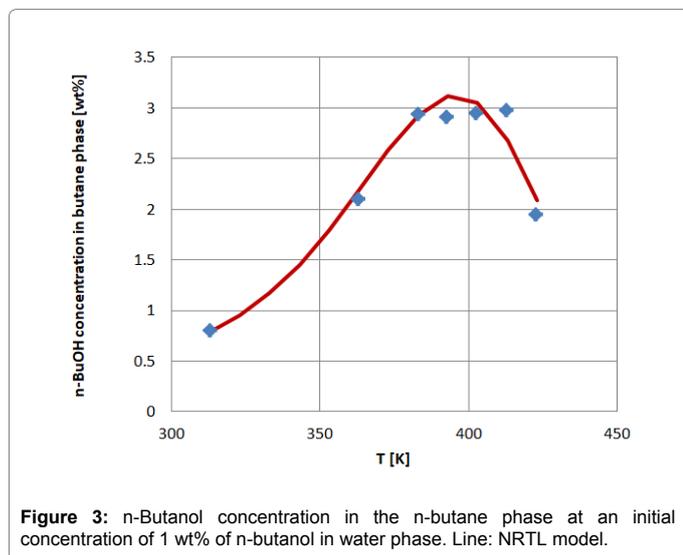
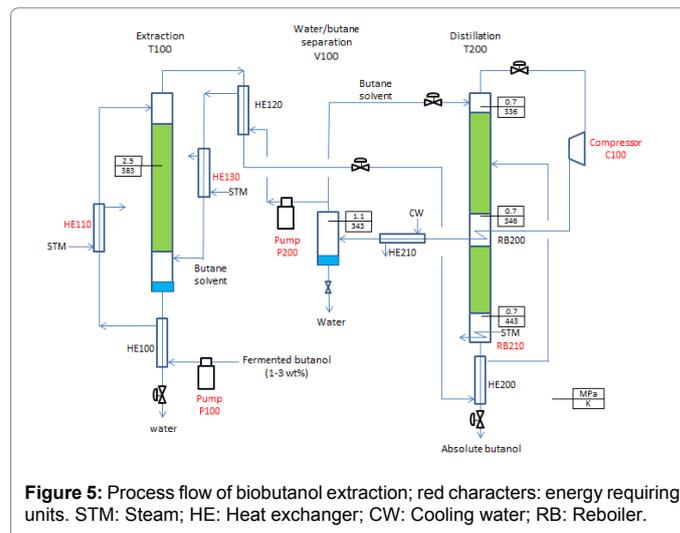
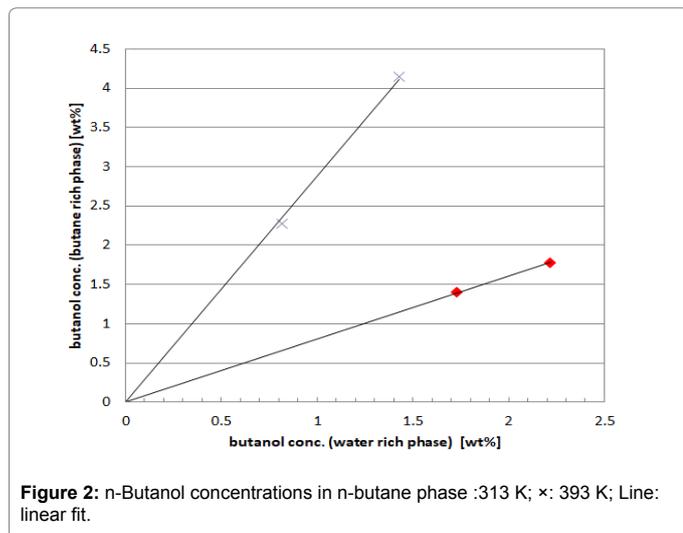
The parameters of the NRTL model were regressed using the experimental data to minimize the absolute average deviation. Only experimental data obtained at temperatures below the n-butane critical temperature (425 K) were used. Table 4 shows the determined parameters, and Figures 2 and 3 show the correlation results. The NRTL model parameters exhibited good correlation with the experimentally obtained data. Although the NRTL model is an empirical model, the parameters at 383 K of n-butane and water ( $\tau_{ij}=2.78$ ,  $\tau_{ji}=7.15$ ) and the those of water and n-butanol ( $\tau_{ij}=6.37$ ,  $\tau_{ji}=1.42$ ) were close, so the affinity of each is found to be close. In Figure 3, since it is the concentration based on weight, butanol is concentrated to three times butane phase, but it is 1.07 times on a molar basis, which is consistent with parameters results.

### Calculation of required energy

Energy requirements for biobutanol recovery of 99.9 wt% from initial n-butanol concentrations of 1 or 2 wt% were calculated by a PRO/II software. Figure 5 depicts a process flow of biobutanol extraction, and

the red characters denote energy-requiring units. This process is almost the same as in Figure 1, but feed and solvent preheating, heat recovery, pump, etc. are added. The NRTL model with previously determined parameters was used for an extraction tower, and a UNIFAC model [23] that uses contributions of present functional groups-to calculate activity coefficients was used for the distillation column. For a compressor calculation, a SRK EoS method [24] was selected. The heat energy was recovered using a heat exchanger, and the reboiler duty of distillation column was recovered using a vapor recompression system. Temperature difference between each heat exchange unit was set to 10 K. The pump efficiency and adiabatic efficiency of the compressor were set to 60% and 60%-80%, respectively. The work of the pump and compressor were translated into primary energy with a heat to power generating efficiency of 40% (Figure 5; Table 5).

Table 5 shows the calculation results, and Figure 6 shows the comparison between the lower heating values (LHVs) of n-butanol, the conventional distillation process, and the n-butane extraction process developed in this study. The exhibited product concentration was over 99.9 wt%, and recovery ratio was 99.2% for each (1 or 2 wt%) initial concentration of n-butanol. Required energy of the heat exchanger, the pump, and the compressor showed inverse proportionality to the initial concentration. The required energy of reboiler was independent on the initial concentration since the ratio of n-butane to n-butanol of the bottom stage was almost the same. The n-butane extraction process presented in this study showed an energy requirement of 5 MJ/kg-biobutanol from the initial concentration of n-butanol of 2 wt% (Figure 6).



## Summary

To develop an energy-saving biobutanol dehydration process with n-butane extraction, the phase equilibrium data of n-butane/water/n-butanol system were measured, and parameters of the thermodynamic NRTL model were regressed. From the calculation results using the model developed in this study, we found that biobutanol recovery over 99.2% can be achieved and the energy required for the n-butane extraction process was 5 MJ/kg-biobutanol from the initial n-butanol concentration of 2 wt% to the final recovery of 99.9 wt% of biobutanol.

## List of Symbols

- $a_{ij}, b_{ij}$  binary parameters of the NRTL model
- $G_{ji}$  interaction energy parameters in the NRTL model
- $K_i$  equilibrium ratio
- $P$  total pressure, MPa
- $P_i^s$  vapor pressure of the pure component I, MPa
- $T$  temperature, K
- $x_i$  liquid phase mole fraction of component I

$y_i$  vapor phase mole fraction of component i

## Greek letters

$\alpha_{ij}$  nonrandomness parameter of the NRTL equation

$\gamma_i$  activity coefficient of component i

$\tau_{ij}$  parameter of the NRTL equation defined by Eq. (3)

$\delta$  sum of the squared relative errors

## Superscript

W water phase

B butane phase

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