Full Length Research Paper

Ethanol heterogeneous azeotropic distillation design and construction

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This study examines the design and installation of a continuous ethanol distillation unit based on the heterogeneous azeotropic approach using *n*-heptane as the entrainer. This technique entails the dehydration of ethanol, by which, technically, bioethanol can be produced. An ethanol distillation unit was designed, using mainly stainless steel. Bubble caps were constructed for a column which consisted of 11 stages of bubble caps. The decanter design was used for organic reflux. A reboiler with an electric heater was used in the dehydrating column. The prototype design restricted the feed flow rates to 0.2 kg·mol/h of ethanol 95.0 mol%, using the mixed reflux between *n*-heptane and ethanol during distillation process. The experimental product gave an approximate maximum of 99.2 mol% of absolute ethanol.

Key words: Heterogeneous azeotropic distillation, ethanol dehydration, feed flow rate, entrainer flow rate, reflux flow rate.

INTRODUCTION

An azeotropic distillation is a widely practiced process to split one needed component from its heterogeneous system where the third component, known as an "entrainer", is incorporated. Depending on the proper entrainer selected, a high purity of distillate can be manufactured either from the binary or from the ternary azeotropic mixture. Moreover, the entrainer can be recovered. At the Industrial scale, this technique can successfully remove water from 95.0% ethanol to produce 99.5% ethanol, which is aimed at gasoline substitution. Alcohol increases octant level and also promotes more complete fuel burning that can reduce harmful exhaust pipe emissions.

Heterogeneous azeotropic distillation columns are commonly used in industry to separate mixtures of close relative volatility and for breaking azeotropes (Chien et al., 2004). A nice review paper by Widagdo and Seider (1996) showed that parametric sensitivity, multiple steady states, and long transient and nonlinear dynamics were found by many authors using theoretical models and computer simulation. These heterogeneous azeotropic distillation columns are known to be difficult to operate and control. One of the systems commonly using heterogeneous azeotropic distillation for the separation of azeotropes is the system of alcohol dehydration. Kovach and

Seider (1987) performed step tests on feed rate and operating variables for an industrial column for dehydrating ethanol using di-*sec*-butyl ether as an entrainer and found erratic behavior which was attributed to parametric sensitivity. Bozenhardt (1998) proposed a control strategy involving an average temperature control, on-line breakpoint position control, and five feed forward control loops for the ethanol, ether and the water system. Rovaglio et al. (1992, 1993, 1995) proposed an average temperature control and two feed forward control loops for the ethanol, benzene and the water system. Muller et al. (1997) were able to fit data obtained by a laboratory tray column with an equilibrium stage model for an ethanol, cyclohexane and water system, and reported evidence of multiple steady states for this system. But these entrainers (ether, bezene and cyclohexane) are volatile chemicals and some of these entrainer (such as ether and bezene) are carcinogenic compounds. The *n*-heptane is one of the usual hydrocarbons in the gasoline that could be used. Different researchers (Prikhodko et al., 1997; Peng and Tu, 2004) have paid attention to the determination of liquid-liquid equilibrium (LLE) and vapor-liquid equilibrium (VLE) of the water, ethanol and *n*- heptane system. How-ever, it is not possible to find a complete experimental study of the isobaric LLE and VLE equilibrium of this sys-tem that is required for the design of an azeotropic sepa-ration process.

Design of a column sequence, suitable for the dehydra-

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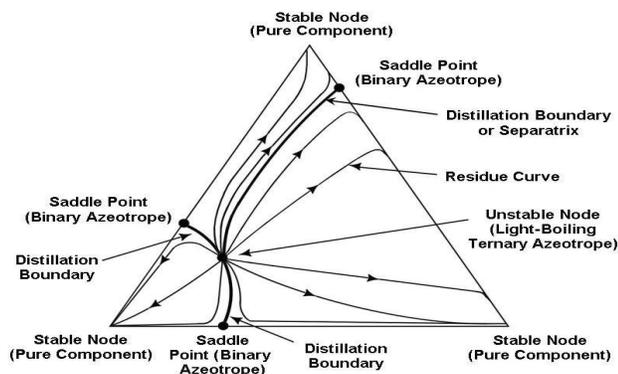
Figure 1. Phase diagram of the relationship between the three-component mixtures (Modified from Villiers et al., 2002). Where; Node: Every location on the phase diagram where the initial and final point are located, Stable node: Single point on the phase diagram where the component has its highest purity and its highest boiling point, Unstable node: The point where the ternary mixture has its lowest boiling point or "ternary azeotropic" point, Saddle point: The point on a phase diagram where a binary azeotrope is formed. The behavior of any ternary azeotrope on the phase diagram will coincide with the residual curve.

tion of ethanol by azeotropic distillation requires knowledge of VLE and the LLE of the water, ethanol and hydrocarbon system. However, despite the extensive use of this technique and the fact that *n*-heptane can be a good entrainer to dehydrate ethanol, a complete experi-mental study of the isomeric VLE and LLE of water, etha-nol and *n*-heptane is not available in the literature. The advantage of this entrainer is that the remaining quantity of *n*-heptane in the ethanol will not be a problem for its subsequent use as a fuel since it is one of the common compounds in gasoline (Gomis et al., 2006).

In this research, design and installation of a continuous ethanol distillation unit based on the heterogeneous azeotropic approach using *n*-heptane as the entrainer was performed. The optimization process for an overall azeo-tropic distillation unit can be understood by the relation-ship between feed flow, reflux flow, entrainer flow and the percentage of ethanol in the bottom.

MATERIALS AND METHODS

Azeotropic phase diagram

The phase diagram will demonstrate the proportion of the three components that can be used to predict the needed feed and the corresponding amount of distillate obtained. Included in the phase diagram as well are borderline region and a residue curve (Wang and Mansoori, 1994; Urdaneta et al., 2002). In-depth details are shown in Figure 1.

In Figure 1, the relationship between the three-component mixture and the two-component-mixture can be found. In Figure 2, the binary and ternary azeotrope can be seen. As a result, the proportion of each component can be simply estimated from the filled point on the ternary phase diagram (water, ethanol and *n*-heptane).
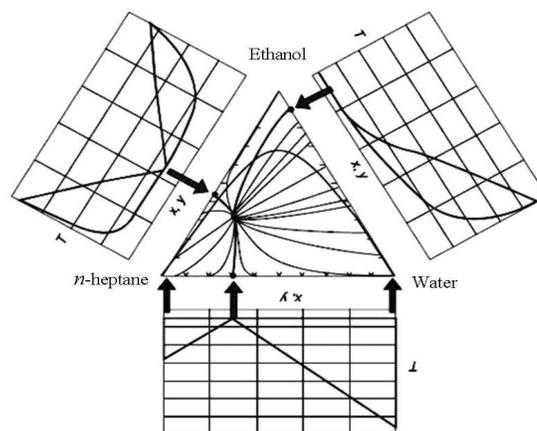
Figure 2. Phase diagram of water: ethanol: *n*-heptane (Modified from Villiers et al., 2002).

Calculation for continuous distillation of the binary system

Mass balance, is expressed as the following equation:

$$F\,X_F = D\,X_D + W\,X_W \tag{1}$$

Where; F, D, W are flow rates (kg·mol/h) of feed, distillate, and waste or the bottom, respectively. X_F, X_D, X_W are mole ratios of the most volatile components in feed, distillate, and waste or the bottom, respectively.

Operation line

Given X_n and L_n as the mole ratio and flow rate of the liquid phase flowing out of tray number n, counting from the overhead, and given Y_{n+1} and V_{n+1} as component and flow rate of vapor rising up from tray number $n+1$, the operation line of the enriching section (particular point where location is above the feed point) can be drawn.

$$
\begin{aligned}
Y_{n+1} &= \frac{L_n}{V_{n+1}} X_n + \frac{D}{V_{n+1}} X_D \\
&= \frac{L_n}{L_n + D} X_n + \frac{D}{L_n + D} X_D
\end{aligned}
$$

The reflux ratio is considered as $R = L_n/D$ and substituted into the above equation to give;

$$Y_{n+1} = \frac{R}{R+1} X_n + \frac{1}{R+1} X_D \tag{2}$$

In the meantime, given Y_m and V_m as proportional ratio and flow rate of vapor rising up from tray number m (counting from the bottom) and given X_{m+1} and L_{m+1} as proportional ratio and flow rate of liquid phase falling down from tray number $m+1$, the operation line of stripping
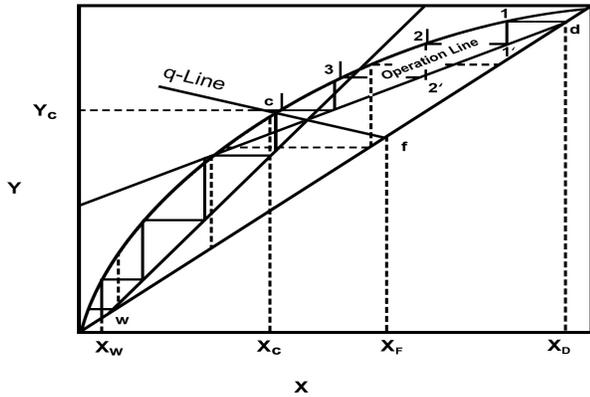
Figure 3. Demonstration of the theoretical number of stages predicted using McCabe-Thiele method (Camdee et al., 2004).

Figure 4. Reboiler and heating generator set.

section (particular point where the location is lower than the feed point) can be built.

$$Y_m = \left(\frac{L_{m+1}}{V_m}\right) X_{m+1} - \left(\frac{W}{V_m}\right) X_W$$

$$= \left(\frac{L_{m+1}}{L_{m+1} - W}\right) X_{m+1} - \left(\frac{W}{L_{m+1} - W}\right) X_W$$

In circumstances where the feed of 1 mole consists of liquid q mole and vapor $1-q$ mole, the relationship can be denoted by $L_{m+1} = L_n + qF$ and $V_m = V_{n+1} - (1-q) F$. So,

$$Y_m = \left(\frac{R + q\frac{F}{D}}{R + 1 + (1-q)\frac{F}{D}}\right) X_{m+1} - \left(\frac{\frac{F}{D} - 1}{R + 1 - (1-q)\frac{F}{D}}\right) X_W \qquad (3)$$

If the reflux ratio R is assumed constant, equation (2) and (3) are represented in graph (X-axis, Y-axis), considering X_n, Y_{n+1}, X_{m+1}, Y_m as variable factors, the operation line will be linear. q-Line is the linear line following the expression;
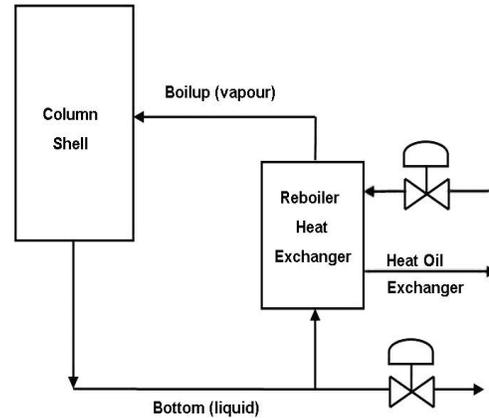
$$qX + (1 - q)Y = X_F \qquad (4)$$

Practically, X from both q-line and the operation line should be close in value to the component of mixture fed in.

Number of stages following McCabe-Thiele (Camdee et al., 2004)

Drawing the line of the vapor-liquid equilibrium on the X-Y axis and pointing d, f, and w on the diagonal line represents the concentrations of X_D, X_F, X_W, respectively (Figure 3). Using equations (2), (3) and (4), dragging to depict the operation line of enriching section, stripping section, and q-line, respectively. These three lines will be crossed somewhere at a particular point.

Starting at d and drawing horizontally a line crossing an equilibrium line at 1, thereafter drawing vertically a line crossing the operation line at 1′, from 1′ drawing horizontally a line crossing an equilibrium line at 2, continuing to do so until reaching w. Accumulating numbers of feeding trays at enriching section; n trays, assuming the number of trays of easy volatile components be m trays, to provide the theoretical number of stages totally $n+m$.

Minimum of stage number; n_m

In the case where the reflux ratio is considered infinite, by applying McCabe-Thiele method, the operation line became diagonal where the minimum stage number generated the least, as represented by the dashed line in Figure 3.

We used the Raoult law to determine the number of stages depending on the relative volatility index (α) to express;

$$n_m + 1 = \frac{\log\left[\left(\frac{X_D}{1 - X_D}\right)\left(\frac{1 - X_W}{X_W}\right)\right]}{\log \alpha} \qquad (5)$$

Minimum of reflux ratio; R_m

In the case where viewing the number of stage are vastly unlimited, by applying the McCabe-Thiele method, the cross over between the operation line and the q-line will coincide on the equilibrium line, denoted by point c located in Figure 3. This certain reflux ratio is named "minimum of reflux ratio", expressed as follows;

$$R_m = \frac{X_D - Y_C}{Y_C - X_C} \qquad (6)$$

DESIGN AND INSTALLATION

The objective of the distillation column in this study refers to the minimum of the stage and reflux ratio. The reboiler consists of a cylindrical heater drum made from stainless steel of 0.500 x 0.650 x 0.003 m (diameter x height x thickness) containing heating oil as the heat transferring media. Inside it has a cylindrical drum reboiler of 0.350 x 0.600 x 0.003 m (diameter x height x thickness). The heat generator contains 3 electrical wires of 1,500 W each regulated by using a panel controller (Figure 4). The decanter or reflux drum is a stainless steel cylindrical drum of 0.1150 x 0.1750 x 0.003 m (diameter x height x thickness), with a reflux flow height of 0.1020 m. Feed storage and the third component or entrainer storage drums are stainless and designed in a cylinder shape with a thickness of 0.0150 m and a volume of 25 L.

The internal distillation column is polished stainless with a thickness of 0.0015 m. The internal design is detailed as follows; column inner diameter, 0.0380 m; tray spacing, 0.0320 m; liquid flow path length, 0.0300 m; downcomer clearance 0.0040 m; deck thick-ness, 0.0030 m; tray-hole diameter, 0.0160 m; weir type, spiral current, weir
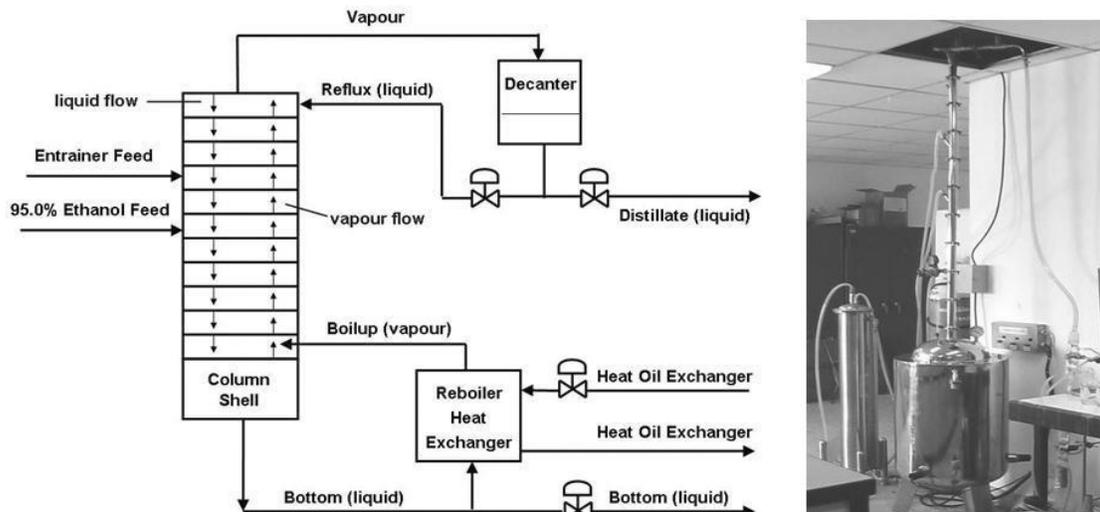
Figure 5. Distillation prototype and experimental apparatus.

length, 0.0280 m; weir height, 0.0100 m; weir diameter, 0.0082 m; hole pitch, 0.0160 m; cap diameter, 0.0262m; skirt clearance, 0.0025 m; slot height, 0.0045 m; active area, 82.28%; total hole area, 22.37%; number of stage, 11; stage height, 0.1500m.

The distillation prototype when completely installed is pictured in Figure 5.

EXPERIMENT OF DISTILLATION PROTOTYPE

Chemical agents

All chemical used were "for analysis" grade and obtained from LAB-SCAN Analytical Science, since ethanol 99.99 mass% and 99.9 mass% *n*-heptane for GC standard analytical ethanol 95 mass%, *n*-heptane 99.8 mass% for feed and entrainer respectively.

Apparatus and procedure

An all-stainless steel of the distillation prototype, flow meter from cole/Parmer, Chicago II 60648, pressure gauge from WEGA, TES-COM EUROPE GMBH and CO.HG, Germany, fluid pump from Pro-Minent, HEIDELBERG, GE.

All analytical work, ethanol and *n*-heptane analysis were carried out by chromatography on a varian GC: star 3400 cx, column: 10% Carbowax 20 Mon Chromosorb, detector: Frame Ionization Detector (FID), GC condition, column temperature, 373 K; injector, 423 K; detector, 423 K.

DISTILLATION AND CALCULATION

The characteristics of the column are summarized as follows by the equation (5), which has 11 stages. The minimum of reflux ratio follows as the equation (6). The feed flow and entrainer flow are over stage 5 and 7, respectively. The distillation column prototype is shown in Figure 5. The column separates a two component mixture of water and ethanol. Since the volatile relative between water and ethanol is very small, an entrainer is needed for efficient separation. In this column, *n*-heptane is used as an entrainer. Water is obtained from the heavy phase in the decanter and ethanol is withdrawn from the bottom of the column. This 3 component mixture re-sults in a liquid-liquid equilibrium for a wide range of compositions. A liquid phase becomes heterogeneous not only in the decanter but also in the upper part of the column. This column has two reflux flows, that

is, the entrainer reflux and the water reflux. Therefore, there are three manipulated variables, that is, the entrainer reflux flow rate, the water reflux flow rate, and the feed flow rate. This azeotropic distillation apparatus were tested for 10 experimental conditions to observe the relation of column temperature, column pressure, and the percentage of ethanol in the bottom column. The three conditions that gave a higher percentage of ethanol were selected as the following;

Condition 1: 95.0% ethanol feed flow rate, 0.250 kg·mol/h; entrainer feed flow rate (*n*-heptane), 0.050 kg·mol/h; reflux feed flow rate, 0.005 kg·mol/h; column pressure, 106.9 kPa; column temperature, 363.2 K; feed temperature, 303.2 K.

Condition 2: 95.0% ethanol feed flow rate, 0.200 kg·mol/h; entrainer feed flow rate (*n*-heptane), 0.030 kg·mol/h; reflux feed flow rate, 0.006 kg·mol/h; column pressure, 104.8 kPa; column temperature, 362.7 K; feed temperature, 302.7 K.

Condition 3: 95.0% ethanol feed flow rate, 0.170 kg·mol/h; entrainer feed flow rate (*n*-heptane), 0.020 kg·mol/h; reflux feed flow rate, 0.009 kg·mol/h; column pressure, 115.1 kPa; column temperature, 362.2 K; feed temperature, 302.2 K.

The experimentally determined composition trajectories for a set of three experimental conditions are shown in Figures 6 - 8. The feed flow rate, entrainer flow rate, reflux flow rate, column pressure, column temperature, and feed temperature are varied in each condition. The components of the distillate and bottom were analyzed by gas chromatography (GC).

RESULTS AND DISCUSSION

The experimental data results are shown in Figures 6 - 8. The test results of each condition indicated that the liquid began to reflux and distillate at temperature 353.0 K and pressure 103 kPa. When the column temperature and column pressure were increased, the percentage of ethanol was higher, but each experimental condition had its own maximum percentage. From 3 conditions, only condition 2 produced the maximum percentage of absolute ethanol at
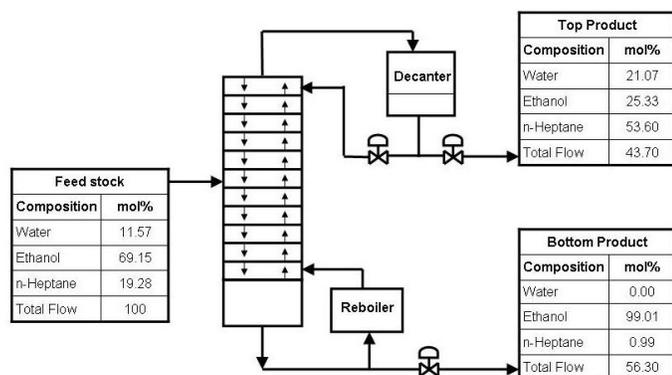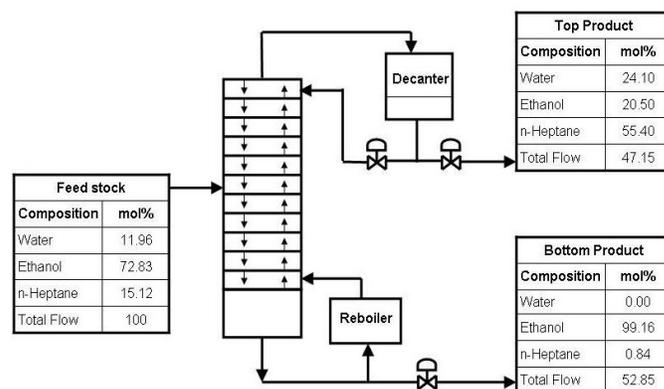
Figure 6. Result of condition 1.

Top Product	
Composition	mol%
Water	21.07
Ethanol	25.33
n-Heptane	53.60
Total Flow	43.70

Feed stock	
Composition	mol%
Water	11.57
Ethanol	69.15
n-Heptane	19.28
Total Flow	100

Bottom Product	
Composition	mol%
Water	0.00
Ethanol	99.01
n-Heptane	0.99
Total Flow	56.30

Figure 8. Result of condition 3.

Top Product	
Composition	mol%
Water	20.53
Ethanol	27.05
n-Heptane	52.42
Total Flow	46.70

Feed stock	
Composition	mol%
Water	13.15
Ethanol	78.40
n-Heptane	8.45
Total Flow	100

Bottom Product	
Composition	mol%
Water	0.00
Ethanol	98.20
n-Heptane	1.80
Total Flow	55.30

Figure 7. Result of condition 2.

Top Product	
Composition	mol%
Water	24.10
Ethanol	20.50
n-Heptane	55.40
Total Flow	47.15

Feed stock	
Composition	mol%
Water	11.96
Ethanol	72.83
n-Heptane	15.12
Total Flow	100

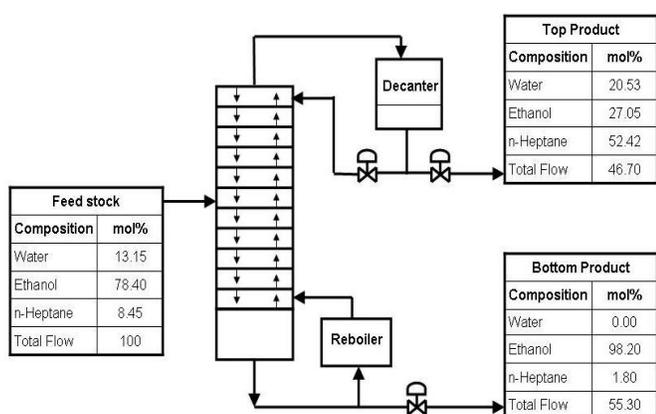| Bottom Product	
Composition	mol%
Water	0.00
Ethanol	99.16
n-Heptane	0.84
Total Flow	52.85

at the bottom of the azeo-tropic column that is 99.2 mol% absolute ethanol. That, was because its minimum reflux ratio (R_m) as the equa-tion (6) was not too high thus the system gave a higher pure ethanol product than conditions 1 and 3. If R_m is too high, the efficiency will decrease. But if R_m is too low, the separation could take forever. The optimization was per-formed separately to obtain over 99.0 mol% of ethanol from 95.0 mol% of aqueous ethanol using n-heptane as an entrainer through an azeotropic distillation. This study provides the fundamental basis so that researchers can strive for the mathematical relationships of each variable factor to be correlated. For example, feed flow rate, the third component or entrainer flow rate, vapour tempe-rature, liquid mole fractional component, reflux flow rate, percent ethanol out, percent liquid component, energy ba-lance, and mass balance are drawn into mathematical equation. A comparison concerning the production cost of ethanol from various feed stock (corn, sugar cane juice, molasses, sugar beet, wheat and cassava), the average production costs 0.20-0.48 USD/L (Sriroth, 2006; Anony-mous, 2006; Dai, 2006).

For the comparative of benzene and n-heptane, the entrai-ner of heterogeneous azeotropic distillation using n-hep-tane is not much difference from using benzene, but n-heptane better than benzene that it is not carcinogenic compound and n-heptane is one of the usual hydrocar-bons in the gasoline engines.

Conclusion

In this study, the best condition for production of absolute ethanol was following: 95.0% ethanol feed flow rate, 0.200 kg·mol/h; n-heptane feed flow rate, 0.030 kg·mol/h; reflux feed flow rate, 0.006 kg·mol/h; column pressure, 104.8 kPa; column temperature, 362.7 K; feed tempera-ture, 302.7 K.

Nomenclature: D, Distillate flow rate (kg·mol/h); **F**, feed flow rate (kg·mol/h); $\mathbf{L_{m+1}}$, flow rate of liquid phase falling down from tray number m+1 (kg·mol/h); $\mathbf{L_n}$, flow rate of li-quid phase flowing out of tray number n (kg·mol/h); $\mathbf{n_m}$, mi-nimum of stage number; **m**, tray number counting from bottom; **n**, tray number counting from the overhead; **q**, li-quid within 1 mole feed (mol); **R**, reflux ratio; $\mathbf{R_m}$, minimum of reflux ratio; **T**, absolute temperature (K); $\mathbf{V_m}$, flow rate of vapor rising up from tray number m (kg·mol/h); $\mathbf{V_{n+1}}$, flow rate of vapor rising up from tray number n+1, (kg·mol/h); **W**, bottom flow rate (kg·mol/h); $\mathbf{X_D}$, mole ratio of most vola-tile component in distillate; $\mathbf{X_F}$, mole ratio of most volatile component in feed; $\mathbf{X_W}$, mole ratio of most volatile com-ponent in bottom; $\mathbf{X_{m+1}}$, mole ratio of liquid phase falling down from tray number m+1; $\mathbf{X_n}$, mole ratio of liquid phase flowing out of tray number n; $\mathbf{Y_m}$, mole ratio of vapor rising up from tray number m; $\mathbf{Y_{n+1}}$, mole ratio of vapor rising up from tray number n+1.

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