Application of Extractive Distillation for the Separation of Benzene and Cyclohexane Mixture

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ABSTRACT

Distillation is the most widely used separation technique in the chemical process industries. Not all liquid mixtures can be separated by ordinary fractional distillation, however. When the components to be separated of system have relative volatilities of close to 1.00 (i.e. close boiling mixture), separation becomes difficult and expensive because a large number of trays and a high reflux ratio are necessary. Both the equipment and utility will costs increase markedly and the separation by ordinary distillation can become uneconomical. If the mixture forms azeotropes, a different problem arises - the azeotropic composition can limit the separation. In such a case, the azeotrope must be "broken" to enable separation. This paper discusses the procedure for separating two close boiling components; i.e. benzene (C_6H_6) and cyclohexane (C_2H_{12}) by extractive distillation technique to overcome the "azeotrope barrier". A computer simulation has been performed to enable performance comparison among a few candidate solvents which include phenol, aniline and 1,2-propanediol to achieve cyclohexane purity specification in excess of 99%.

INTRODUCTION

The mixture of cyclohexane and benzene is encountered in the production of cyclohexane through hydrogenation of benzene via the reaction path as below:

$$3H_2 + C_6H_6 \rightarrow C_6H_{12}$$

Unreacted gaseous hydrogen may easily be purged from the product stream which left a azeotropic mixture consists of liquid benzene (unreacted raw material) and cyclohexane (product), which will be separated by a rigorous distillation technique, i.e. the extractive distillation.

TEORY

At low to moderate pressure, with the assumption of ideal-gas model for the vapor phase, the vapor-liquid phase equilibrium (VLE) of many mixture can be adequately describe by the following Modified Raoult's Law:

$$y_i P = x_i \gamma_i P^{sat} \quad for \quad i = 1, \ldots, c \qquad [1]$$

When $\gamma_i = 1$, the mixture is said to be ideal and equation 1 simplifies to Raoult's Law. Non-ideal mixtures ($\gamma_i \neq 1$) can exhibit either positive ($\gamma_i > 1$) or negative deviations ($\gamma_i < 1$) from Raoult's Law. In many highly non-ideal mixtures these deviations become so large that the pressure-composition (P-x, y) and temperature-composition (T-x, y) phase diagrams exhibit a minimum or maximum azeotrope point. In the content of T - x, y phase diagram, these points are so called minimum boiling azeotrope (where the boiling temperature of the azeotrope is less than that of the pure component) or maximum boiling azeotrope (the boiling temperature of the azeotrope is higher than that of the pure components). About 90% of the known azeotropes are of the minimum variety. At these minimum and maximum boiling azeotrope, the liquid phase and its equilibrium vapor phase have the same composition, i.e.,

$$x_i = y_i \quad \text{for } i = 1, \ldots, c \qquad [2]$$

The five methods for separating azeotropic mixtures (Ruthven D.M., 1997) are: (i) Extractive distillation and homogeneous Azeotropic Distillation; (ii) Heterogeneous azeotropic distillation, or more commonly, azeotropic distillation; (iii) Distillation using ionic salts; (iv) Pressure-swing distillation; and (v) Reactive distillation

Extractive Distillation

Extractive distillation works because an heavy solvent is specially chosen to interact differently with the components of the original mixture, thereby altering their relative volatilities. Because these interactions occur predominantly in the liquid phase, the solvent is continuously added near the top of the extractive distillation column so that an appreciable amount is present in the liquid phase on all of the trays below. The mixture to be separated is added through second feed point further down the column. In the extractive column the component having the greater volatility, not necessary the component having the lowest boiling point, is taken overhead as a relatively pure distillate. The other component leaves with the solvent via the column bottoms. The solvent is separated from the remaining components in a second distillation column and then recycled back to the first column.

As the azeotropic distillation, design of extractive distillation system will also requires significant preliminary work including: (i) Choosing the solvent; (ii) Developing or finding necessary data, such as azeotropic condition or residue curve; (iii) Preliminary screening of solvent; (iv) Computer simulation; (v) Small scale testing. This paper will just deal with the first four steps describe above.

Solvent Screening and Selection

One of the most important steps in developing a successful (economical) extractive distillation sequence is to select a good solvent. Berg, Ewell et al. and Tassions in their paper have well discussed the approaches in selecting an extractive distillation solvent. Perry's handbook serves as a good reference for the solvent selection procedure, which can be thought of as a two-step process, i.e.: (i) broad screening by functional group or chemical family; (ii) identification of individual candidate solvents

Residue Curve Maps

The most simple form of distillation, called simple distillation, is a process in which a multi-components liquid mixture is slowly boiled in an open pot and the vapors are continuously removed as they form. At any instant in time the vapor is in equilibrium with the liquid remaining on the still. Because the vapor is always richer in the more volatile components than the liquid, the liquid composition changes continuously with time, becoming more and more concentrated in the least volatile species. A simple *distillation residue curve* is a graph showing how the composition of the liquid residue curves on the pot changes over time. A *residue curve map* is a collection of the liquid residue curves originating from different initial compositions. Residue curve maps contain the same information as phase diagrams, but represent this information in a way that is more useful for understanding how to synthesize a distillation sequence to separate a mixture.

A simple residue curve map may be view in FIGURE 1. Notice that the trajectories move from the lowest temperature component (*unstable* node) towards the highest (stable node). The point that the trajectories approach from one direction and live in the other (as always is the point of intermediate boiling component) is termed *saddle point* (S).

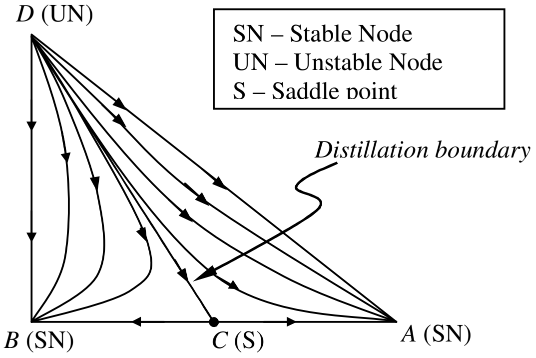

FIGURE 1 Residue Curve Map for a Ternary Mixture with a Distillation Boundary Running from Pure Component *D* to the Binary Azeotrope *C*.

Residue curve maps would be of limited usefulness if they could only be generated experimentally. Fortunately that is not the case. Throughout various of reference, the simple distillation process can be described by the set of equations:

$$\frac{dx_i}{d\xi} = x_i - y_i \quad \text{for } i = 1, \ldots, c \qquad [3]$$

Research studies has also been done to determine the relationship between the number of nodes (stable and unstable) and saddle points one can have in a legitimately drawn ternary residue plot. The equation is based on topological arguments. One form for this equation is (Biegler L.T., Grossmann E.I., Westerberg A.W., 1997):

$$4(N_3 - S_3) + 2(N_2 - S_2) + (N_1 - S_1) = 1 \qquad [4]$$

THE SCENARIO OF BENZENE AND CYCLOHEXANE SYSTEM

The Azeotropic Condition

The feed to the extractive distillation unit consist mostly of cyclohexane and benzene with the mole % of 44.86 and 54.85 respectively. Thus, we will consider this to be a binary mixture in our further discussion.

At the operational pressure of the distillation column of 150kPa, cyclohexane and benzene will perform a boiling point of 94.34^{o}C and 93.49^{o}C respectively (**FIGURE 3**). This is the typical case where conventional distillation is hardly perform to separate these type of close boiling mixture. Thus, a special type of distillation technique, i.e. extractive distillation has been chosen in order to purify the desire product, i.e. cyclohexane to our desire purity of 99.3%.

As can be shown from **FIGURE 3**, this binary composition will form a minimum boiling, homogeneous azeotrope at the temperature of 91^{o}C and the corresponding composition at this point will be 45.5 mole % for cyclohexane and 55.5 mole % for benzene (**FIGURE 4**).

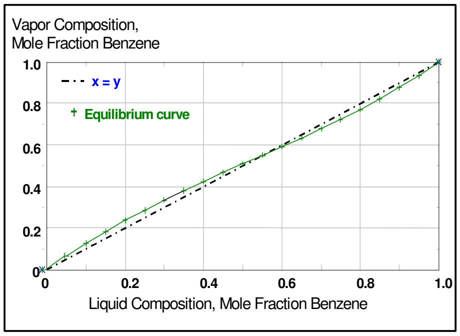

Fig 3. T-x, y Plot for Benzene and Cyclohexane at 150 kPa.

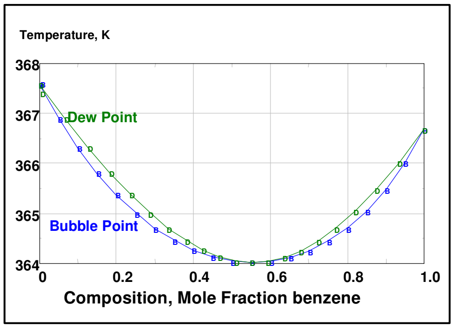

FIGURE 4 X-y Plot for Benzene and Cyclohexane at 150 kPa

Solvent Selection for Benzene-Cyclohexane Binary Mixture.

In extractive distillation suitable, a suitable solvent is required to break the azeotrope formed at the prevailing operating pressure. Recommended solvent for the benzene-cyclohexane mixture from the literature (Green, Perry, 1997; Michael F. D., Jeffrey P. K., 1997) is *aniline,* with a solvent to feed ratio (S/F) of 4, which will shift the azeotropic point toward the corner of the high-boiling component cyclohexane, and the equilibrium curve of the original components fall below the diagonal.

As were stated in the above section, the primary effort of solvent selection is to identify a group of feasible solvents to perform a good separation. Our desire product, i.e. cyclohexane should have a purity of above 99% to meet the market standard. Aniline was the first solvent that had been put to the simulator to be tried out, as it is of the same homologous group as benzene. This solvent will produce the desire production rate of 150 with the solvent flow rate of 3500, i.e. a S/F ratio of 9.85. However, the product purity can only reach to 76.20% and definitely, this do not meet our product specification. As a result, other solvent may have to be searched to perform the desire separation.

We will have to perform the solvent selection criteria as stated in the preceding section. At the column pressure of 150 kPa, cyclohexane and benzene boil at 94.34^{o}C and 93.49^{o}C respectively and form a minimum-boiling azeotrope at 91^{o}C. The natural volatility of the system is benzene > cyclohexane, so the favor solvents most likely will be those that cause the benzene to be recovered in the distillate. However, in order to get a better quality of product, we would like to recover cyclohexane as the distillate rather than from the bottom stream. Thus, solvent to be chosen should give positive deviations from Raoult's law for cyclohexane and negative (or zero) deviation for benzene.

Turning to the *Robbins Chart* (**TABLE 4**), we note that solvent that may cause the positive deviation for cyclohexane (Class 12) and negative (or zero) to benzene (Class 11) came from the groups of 4, 7, 8 and 9, which consist of polyol, amine and ether. We further consider the solubility, the hydrogen bonding effects and also the homologous characteristic of the solvent with the corresponding components in the feed mixture. Few candidate solvents that had been put to the computer simulation, included *phenol* (homologous to benzene), *1,2-benzenediol* (homologous to benzene, with -OH group that will produce hydrogen bonding), *1,3-butanediol* (with -OH group that will produce hydrogen bonding), and also *1,2-propanediol* (same characteristic as with *1,3-butanediol*).

1,2-propanediol (often known as *propylene glycol*), gave the most promising result compared to the other solvents (**TABLE 3**). This result may cause from the highly solubility of benzene in this solvent and the hydrogen bonding that were formed between the two constituents. Simulation result showing that this solvent will produce the desire production rate of more than 150 kg-mole/hr with the solvent flow rate of 3600, i.e. a S/F ratio of 10 with a product purity of 99.3%.

Solvent	**Cyclohexane flow rate achieved**	**Purity**
Aniline	120.59 kg mole/hour	76.2 %
Phenol	61.508 kg mole/hour	38.9 %
1,2-benzenediol	158.26 kg mole/hour with 9.8134 kg mole/hour benzene	Unseparated Condition
1,3-butanediol	31.2 kg mole/hour	19.7%

TABLE 3 Purity of Cyclohexane by Utilizing Different Solvents

Solute class	Group	Solvent class											
		1	2	3	4	5	6	7	8	9	10	11	12
11	Aromatic, olefin, halogen aromatic, multihalo paraffin without active H, monohalo paraffin.	+	+	+	0	+	0	0	-	0	+	0	0
12	Paraffin, carbon disulfide	+	+	+	+	+	0	+	+	+	+	0	+

Solvent/solute class	Group
4	Active -H in multihalo paraffin
7	Secamine
8	Pri amine, ammonia, amide with 2H or N
9	Ether, oxide, sulfoxide

TABLE 2 Part of *Robbins Chart* Taken from Perry's Chemical Handbook.

Construction of the Residue Curves

Equation [3] and [4] were used to sketch the corresponding residue curve for the three species. From the above information, we know that these species have boiling points of 94.34 (cyclohexane), 93.49 (benzene) and 200.35^{o}C (propylene glycol) at the pressure of 150 kPa, with a minimum boiling azeotrope boiling at 91^{o}C between the two more volatile species. As shown from **FIGURE 6** and **FIGURE 7** there are no new azeotropes formed between the solvent 1,2-propanediol respectively with the another two component in the feed.

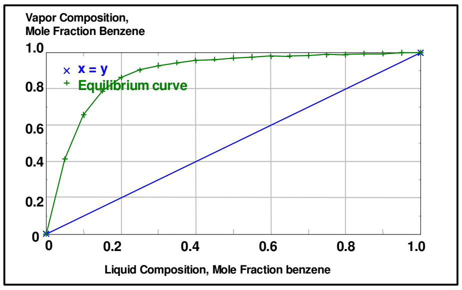

FIGURE 6 X-y Plot for Benzene and Propylene Glycol

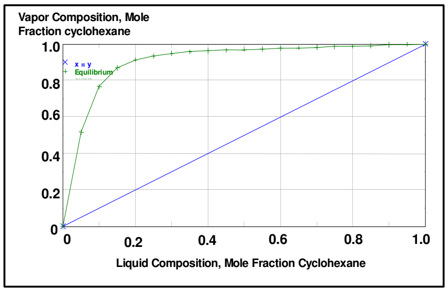

FIGURE 7 X-y Plot for Cyclohexane and Propylene Glycol

We then start to sketch our residue curve map by sketching the triangular diagram in **FIGURE 8**, and placing the arrows pointing from the lower to higher temperatures around the edge. The corner points for benzene and cyclohexane are single species point, and both are unstable nodes - all residue curves leave. The corner point for propylene glycol is a single species point which is a stable node - all residue curve enter. All three are nodes; none are saddles, thus: $N_1 = 3$ and $S_1 = 0$. We then further determine that there will be no ternary azeotrope been form among the three constituents, i.e., $N_3 = S_3 = 0$.

The remaining steps here require us to identify the only binary azeotrope that form between benzene and cyclohexane, to be either a node or a saddle point. From Equation [4]: $N_2 - S_2 = -1$. Thus, the only way we can satisfy the above equation is letting $N_2 = 0$ and $S_2 = 1$, i.e. the binary azeotrope is a saddle point, which direct the trajectories to another direction. We then sketch our residue curve map as in **FIGURE 9**.

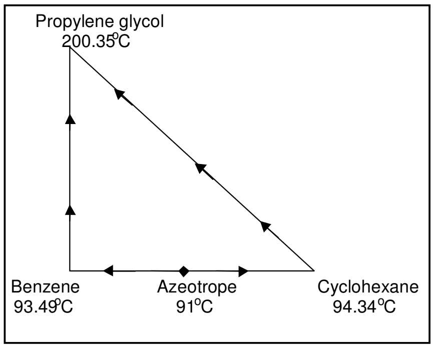

FIGURE 8 Starting Sketch for Residue Curve Species with a Minimum Boiling Azeotrope

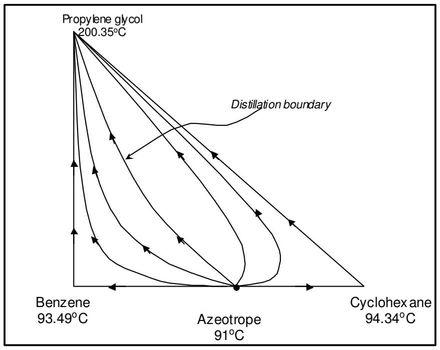

FIGURE 9 Complete Sketch of the Residue Curve of the Benzene-cyclohexane-propylene glycol Ternary Mixture

Column Operation

The extractive distillation unit of this cyclohexane production plant consists of two distillation columns (**FIGURE 10**), which is classified as the *direct sequence*. The first column (T-20) acts as an extractive column where the solvent is introduced on the second tray of the column, in order to provide better contact with the binary mixtures throughout the column. As were stated above, the solvent alter the natural volatility of the binary mixture by forming hydrogen bond with benzene and causing it to be recovered as the bottom product.

Bottom product of the first column enters the second column (T-21), i.e. the solvent recovery column to undergo the normal distillation to separate both the component for further usage, i.e. benzene been recycled to the reactor for further conversion while solvent to the first column for reuse. The main operation parameter of the distillation unit is shown in **TABLE 3**.

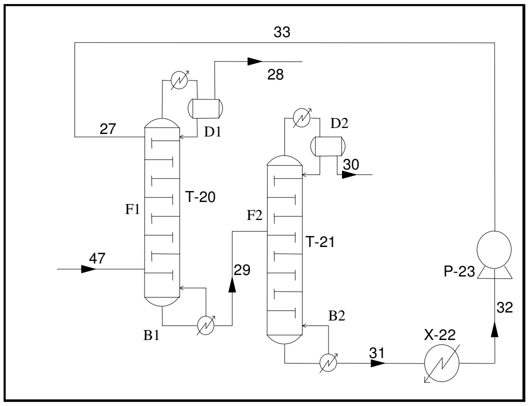

FIGURE 10 Extractive Distillation Unit for Cyclohexane Production Plant

Unit Tag	Description	Operating parameter
T-20	First column (extractive column)	• Operating pressure: 150 kPa • Number of tray: 45 • Solvent (Stream 27) feed tray = 2 • Feed (Stream 47) tray = 28
T-21	Second column (Solvent recover column)	Operating pressure = 105 kPa • Number of tray: 20 • Feed stream: 10
S27	Solvent stream of 1,2-propanediol (propylene glycol)	Molar flowrate = 3600 kgmol/hr
S47	Feed stream	Total molar flowrate = 355.43 kgmol/hr
S28	Product stream of Column T-20 distillate (cyclohexane)	Molar flowrate = 158.75 kgmol/hr with the purity of 99.3%.
S29	Benzene-Solvent stream of bottom product from Column T-20, fed to solvent recovery column T-21.	Total molar flowrate = 3795.5 kgmol/hr with 94.8% of solvent
S30	Product stream of Column T-21 distillate (Benzene) for recycle.	Total molar flowrate = 223.91 kgmol/hr with 84.96% of benzene
S31	Solvent stream of bottom product from Column T-21 (Solvent) for recycle.	Total molar flowrate = 3571.6 kgmol/hr with 99.87% of solvent

TABLE 3 Distillation Unit Summary

CONCLUSIONS

A better understanding of an extractive distillation technique can be performed by constructing a residue curve as clearly shown by the distillation boundaries of the respective azeotropic system. *Robbins Chart* serves as a good reference where types of solvent candidates can be chosen to further compare their separation performances. This study shows that among the candidate solvents compared, the most suitable solvent for the separation of benzene and cyclohexane is 1, 2- propanediol (propylene glycol) which can achieve in excess of purity specification of 99%.

ACKNOWLEDGEMENT

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NOMENCLATURE

y_i	mole fraction of component *i* in vapor phase	x_i	mole fraction of component *i* in liquid phase
P	system pressure	P^{sat}	vapor pressure of component *i*
γ_i	liquid-phase activity coefficient of component *i*	ξ	nonlinear time scale
c	number of components in the mixture	N_i	number of nodes (stable and unstable) involving *i* species
S_i	number of saddles involving *i* species		

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