

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Process for Dehydration of Alcohol. [2]

In a typical configuration for the dehydration of an alcohol, one or more towers concentrate the dilute alcohol to compositions approaching the alcohol-water azeotrope (see Figure 2.1). The resulting stream is fed to the azeotropic tower along with an entrainer-rich reflux stream. A pure alcohol stream is withdrawn from the bottom of the azeotropic tower, and an overhead stream that condenses into two liquid phases is sent to a decanter. The aqueous phase from the decanter is fed to the top tray of a stripping tower, where most of the water in the feed to the azeotropic tower is recovered in high purity. The overhead vapor, containing alcohol, water and entrainer, is condensed and recycled to the decanter. A small make up stream of entrainer is necessary to replace small losses in the alcohol and water product streams.

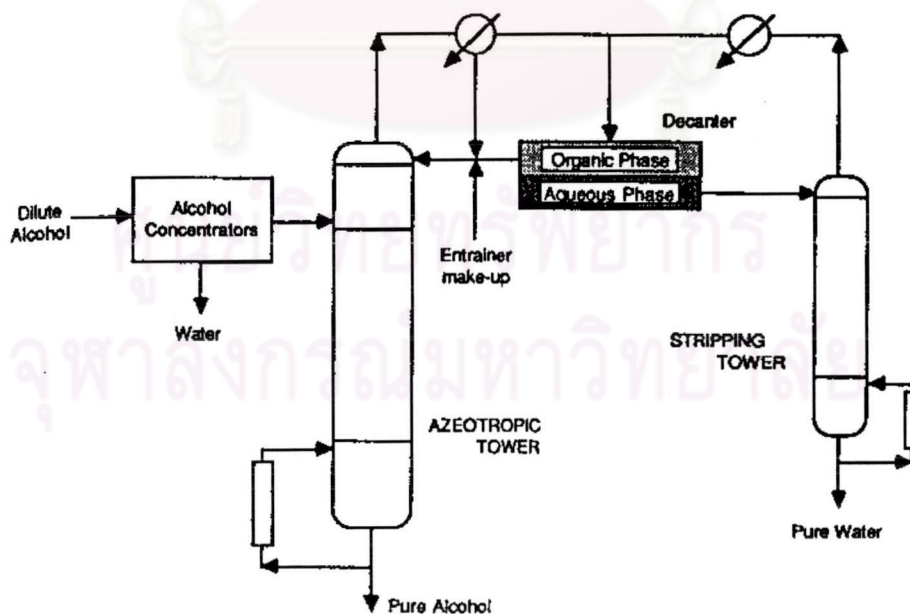


Figure 2.1 Typical configuration for dehydration of alcohol [3]

2.2 Properties of Isopropyl Alcohol and Cyclohexane.

Table 2.1 The properties of IPA and CHX [4]

Description	IPA	CHX
1. Properties	Colorless liquid Flammable liquid Miscible with water and ethyl alcohol	Colorless liquid Flammable liquid Immiscible with water
2. Molecular Weight	60.09	84.16
3. Density at 20 °C	0.786	0.779
4. Melting Point	- 88.5 °C	6.55 °C
5. Boiling Point	82.5 °C	80.8 °C
6. Autoignition Temperature	399 °C	245 °C
7. Explosive Limits in air		
Lower	2.3 vol%	1.35 vol%
Upper	12.1 vol%	8.35 vol%
8. Flash Point Closed Cup	11.7 °C	- 18.4 °C
9. Vapor Density (air = 1)	2.07	2.91

2.3 Azeotropic Mixture [5]

An azeotrope is a liquid mixture that exhibits a maximum or minimum boiling point relative to the boiling points of surrounding mixture compositions. Boiling point of the pure components in the mixture must be sufficiently close to permit formation of an azeotrope. If only one liquid phase exists, the mixture is said to form a homogeneous azeotrope; if more than one liquid phase is present, the azeotrope is said to be heterogeneous.

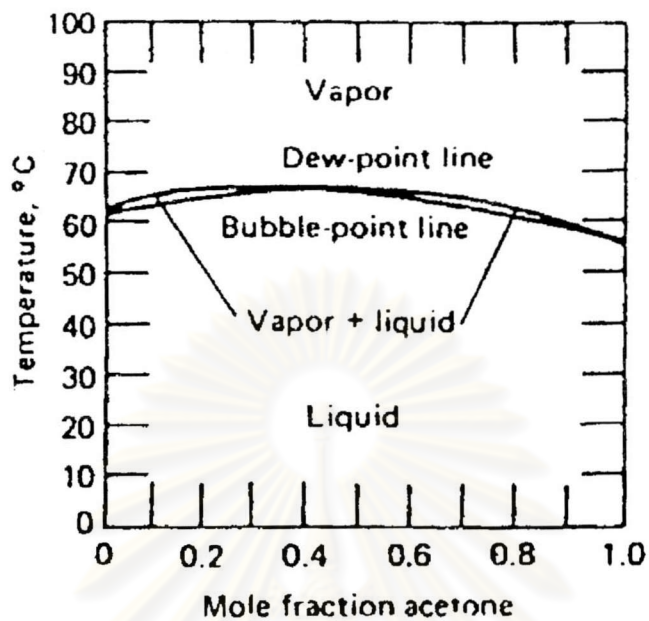


Figure 2.2 Maximum boiling point azeotrope, acetone-chloroform system. [5]

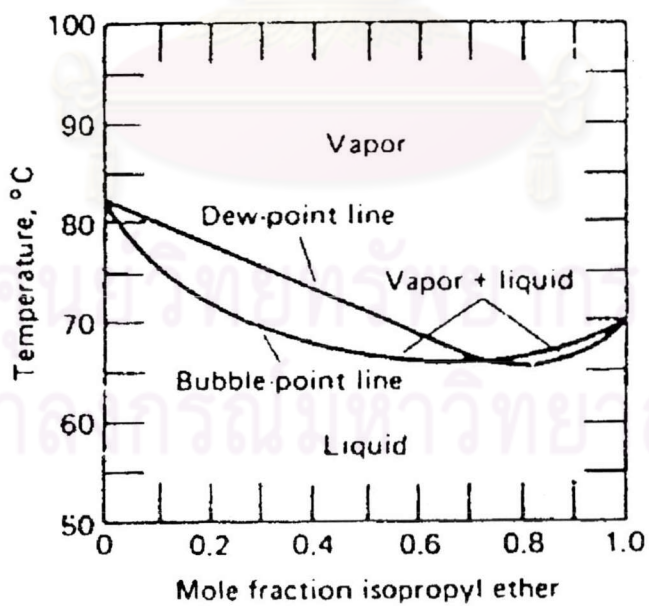


Figure 2.3 Minimum boiling point azeotrope, isopropyl ether-isopropyl alcohol system. [5]

For the maximum boiling azeotropic, acetone-chloroform system in Figure 2.2, the maximum boiling point is higher than the boiling point of the pure components, and the azeotrope would concentrate in the bottom in a distillation operation.

For the minimum boiling azeotropic, isopropyl ether-isopropyl alcohol system in Figure 2.3, the minimum boiling point is below the boiling point of the pure components. Thus, in distillation, the azeotrope mixture would be the overhead product. Heterogeneous azeotropes are always minimum boiling mixtures.

Table 2.2 Ternary azeotropic mixtures. (pressure 760 mmHg) [6]

Component A Mole %A = 100-(B+C)	Components B and C	Mole % B and C	Temperature, °C
Water	Carbon tetrachloride	57.6	61.8
	Ethanol	23.0	2 phase
	Trichloroethylene	38.4	67.25
	Ethanol	41.2	2 phase
	Ethanol	12.4	70.3
Carbon disulfide	Ethyl acetate	60.1	
	Methanol	24.1	33.92
Methyl formate	Ethyl bromide	35.4	
	Isopentane	23.8	16.95
Propyl lactate (n)	Phenetol	31.0	
	Menthene	35.2	163.0
		34.1	

2.4 The Methods for Separating Azeotropic Mixtures. [7]

The methods for separating azeotropic mixtures are:

1. Extractive distillation and homogeneous azeotropic distillation where the liquid separating agent is completely miscible.
2. Heterogeneous azeotropic distillation, or more commonly, azeotropic distillation where the liquid separating agent, called the entrainer, forms one or more azeotropes with the other components in the mixture and causes two liquid phases to exist over a wide range of compositions. This immiscibility is the key to making the distillation sequence work.
3. Distillation using ionic salts. The salt dissociates in the liquid mixture and alters the relative volatilities sufficiently that the separation become possible.
4. Pressure-swing distillation where a series of column operating at different pressures are used to separate binary azeotropes which change appreciably in composition over a moderate pressure range or where a separating agent which forms a pressure-sensitive azeotrope is added to separate a pressure-insensitive azeotrope.
5. Reactive distillation where the separating agent reacts preferentially and reversibly with one of the azeotropic constituents. The reaction product is then distilled from the nonreacting components and the reaction is reversed to recover the initial component.

2.5 Heterogeneous Azeotropic Distillation. [8]

Heterogeneous azeotropic distillation is an economically interesting process to separate azeotropic or close boiling mixture at low energy consumption. Azeotropic distillation refers to those processes in which a component (called the solvent or entrainer) is added above the main feed tray to form (or nearly form) with one or more of the feed components an azeotrope, which is removed as either the distillate or the bottom, but usually the former. Azeotropic distillation can also refer to process in which an entrainer is added to break an azeotrope that otherwise would

be formed by components in the feed. In this case, the process is distinguished from extractive distillation because the entrainer appears in the distillate, from which it must be separated and recycled back to the top section of the column.

Many heterogeneous azeotropic distillation systems show a very high sensitivity to small changes in the operating conditions or requirements. To mention just a few;

- Small changes in bottom products purity specs can significantly impact the column temperature profile and entrainer requirements.
- Small change in the reflux ratio can dramatically change the temperature profile.
- Small fluctuations in pressure can move the overhead composition outside the heterogeneous region, thus causing column failure.
- Small losses of decanter interface can cause the entire column sequence to shutdown.

2.6 Selection of an Entrainer [6,8]

In azeotropic distillation, an entrainer or solvent is added deliberately to the mixture to be separated so as nearly to form an azeotrope. In that way, the vapor-liquid equilibrium is shifted in a favorable direction. Thus, the purpose of the entrainer is either to separate one component of a closely boiling pair or to separate one component of an azeotrope.

Entrainers or solvents may be divided into two groups. Those that form azeotropes with some types of compounds but fail to form azeotropes with another type are called selective entrainers. Those that do not exhibit these properties are nonselective entrainers.

An alternative approach is to use the azeotropic-range values discussed earlier. In the case of a binary system for instance, it is advisable to compile substances that form azeotropes with either component 1 or component 2, or both. The final choice should consider whether the entrainer has a low heat of vaporization, is noncorrosive to the equipment, is nonreactive with the feed components, and is thermally stable, nontoxic and inexpensive.

The choice of entrainer is based on a large number of chemical engineering design considerations and can be rationalized by completing a design that maximizes the profit taking into account safety and environmental questions. cyclohexane stands up well in this design procedure because of its cost, availability, low toxicity and its normal boiling point temperature.

In a commercial process, it is necessary to recover the entrainer from the azeotrope and recycle it to the azeotropic distillation column. This is an economic aspect and requires that the entrainer be separated easily and cheaply. The easier separation occurs when entrainer and separated substance are insoluble at room temperature. When they are miscible, it is desirable that the entrainer be water-soluble so that water washing can be accomplished. The water-entrainer mixture should be easily separated. When the entrainer is water-insoluble, a different washing component that is inexpensive and easily removed from the entrainer must be used.

2.7 Production Process of Nitrocellulose.

Nitro Chemical Industry Co.,Ltd is the manufacturer of nitrocellulose in Thailand. Nitrocellulose made from nature fibres (cellulose) remains one of the most widely used and important film formers in printing inks, wood lacquers, foil and film lacquers, auto refinish paints, nail lacquers and leather finishes. Nitrocellulose is manufactured and transported as cuboid granules wetted with a choice of water, isopropyl alcohol or ethanol.

The manufacturer of nitrocellulose is illustrated in Figure 2.4 and the wet product is dried by alcohol displacement.

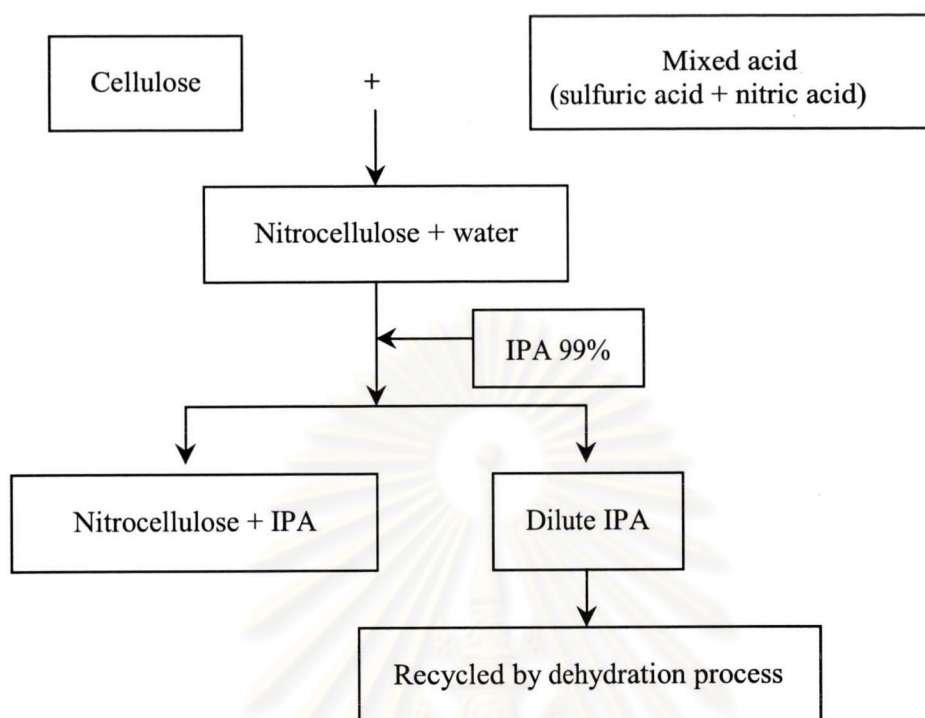


Figure 2.4 The process for manufacturer of nitrocellulose.

2.8 Literature Reviews

Müller, D. and Marquardt, W. [9] studied the ethanol dehydration with CHX as the entrainer. It has been carried out in order to verify the existence of multiple steady states in heterogeneous azeotropic distillation. The different composition profiles, and the hysteresis, measured in a dynamic experiment, confirm the existence of multiple steady states as predicted in simulation. The experiment data are very close to simulation results obtained for the laboratory column using the equilibrium stage model with an overall column efficiency of 70%. In addition, the results were in good agreement with predictions from thermodynamic considerations for columns with an infinite number of trays and infinite reflux. This agreement implies that the existence of the validated multiple steady states were caused by the thermodynamic behavior for the system ethanol/water/CHX.

Bekiaris, N., Meski, G.A. and Morari, M. [10] studied the multiple steady states in ternary heterogeneous azeotropic distillation. The experiment shows that in

the case of infinite reflux and an infinite number of trays, one can construct bifurcation diagrams on physical grounds with the distillate flow as the bifurcation parameter. Multiple steady states exist when the distillate flow varies nonmonotonically along the continuation path of the bifurcation diagram. They showed how the distillate and bottom product paths can be located for tray or packed columns, with or without decanter and with different types of condenser and reboiler. A necessary and sufficient condition for the existence of these multiple steady states based on the geometry of the product paths was derived and the feed compositions that led to these multiple steady states in the triangle were located. The prediction of the existence of multiple steady states in the case of infinite reflux and an infinite number of trays has relevant implications for columns operating at finite reflux and with a finite number of trays.

Kovach, J.W. and Seider, W.D. [3] studied the dehydration process of secondary butyl alcohol by using industrial azeotropic distillation tower. The dehydration of secondary butyl alcohol shows erratic operation that only approaches a steady state. These were explained with steady state simulations which show that slight variations in the aqueous reflux rate cause many trays to shift from homogeneous to heterogeneous operation, accompanied by significant changes in the secondary butyl alcohol purity, with water or entrainer contaminating the bottoms product. When the entrainer entering the tower was increased, the fronts moved down the tower as predicted. However, the mechanism for the movement was different. For the secondary butyl alcohol – di-secondary butyl ether – water system, a small amount of di-secondary butyl ether (3 mol %) significantly decreased the solubility of secondary butyl alcohol and water. Thus, when a pulse of di-secondary butyl ether moved down the tower, leaving fewer trays for stripping the entrainer, and consequently the entrainer often contaminated the bottom product.

Müller, D., Marquardt, W., Esbjerg, K., Anderson, T.R. and Jorgensen, S.B. [11] studied the multiplicity in heterogeneous azeotropic distillation sequences. Two sequences suitable for ethanol dehydration were treated as sample problems and compared. As a basis the ∞/∞ -analysis method, which assumes infinite reflux and

infinite number of trays, was extended to and applied on heterogeneous azeotropic distillation sequences with the objective to determine steady state bifurcation diagrams from thermodynamic considerations. The ∞/∞ -predictions were very different for the two sequences despite their similar structures. In particular, it was predicted that output multiplicity of the azeotropic column, can be induced output multiplicity of the entire sequence. It was further predicted that output multiplicity can be avoided by the choice of a different sequence structure. Furthermore, ∞/∞ -analysis predicts state multiplicities in heterogeneous azeotropic distillation sequences. This phenomenon was also discussed and it is shown that this sequence behavior in the ∞/∞ -case can either be induced by a corresponding single column behavior or by the closing of the sequence. Finally, the implications on column sequences operating at finite reflux and with finite number of stages were investigated by rigorous simulation.

Müller, D., Marquardt, W., Hauschild, T., Ronge, G. and Steude, H. [12] studied the validation of an equilibrium stage model for three-phase distillation. The experimental studied with ethanol/water/CHX has been carried out at a laboratory tray column in order to validate the equilibrium stage model for three-phase distillation columns. Composition profiles were measured both at total reflux and in the production case. Comparisons of experimental data with simulation results were shown generally a good agreement and an overall column efficiency of about 70% but also indicate kinetic phenomena motivating the development of detailed nonequilibrium models.

Esbjerg, K., Andersen, T.R. and Jorgensen, S.B. [13] studied the static multiplicities in heterogeneous azeotropic distillation sequences. The results of a bifurcation analysis on heterogeneous azeotropic distillation sequences were given. Two sequences suitable for ethanol dehydration were compared, the direct and the indirect sequences. It was shown that the two sequences, despite their similarities, exhibit very different static behaviors. The method of Petlyuks and Avet'yan [14], Bekiaris et al.[15], which assume infinite reflux and infinite number of stages, was

extended to and applied on heterogeneous azeotropic distillation sequences. The predictions were substantiated through simulations. The static sequence exhibits output multiplicity, while the indirect sequence exhibits state multiplicity. The latter multiplicity may be avoided by accepting a slightly increased impurity in the ethanol product.

Prokopakis, G.J., and Seider, W.D. [16] studied the operating conditions for an azeotropic distillation tower using a nonlinear programming algorithm. The boil-up rate, fractional recovery of product, and the bottom purities of entrainer and by-product were adjusted to locate an overhead vapor stream that condenses into two liquid phases, but was in equilibrium with a single liquid phase on the top tray. A new objective function was introduced and minimized, subject to inequality constraints, using Powell's algorithm. Results were obtained for dehydration of alcohol with benzene.



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