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Extractive Distillation Of Ethanol From Ethanol- Water Mixture For Medicinal Purpose

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Abstract: ***Ethanol-Water mixture forms an azeotrope (constant boiling mixture) at specific temperature, due to which it cannot be separated using simple distillation. Azeotropic Distillation or Extractive Distillation methods would then come into account. Ethanol can be used as fuel by extracting it from water using benzene easily, but if we want to use ethanol for medicinal purpose then we can't use benzene for extracting ethanol as benzene is carcinogenic compound. Hence, it will not be suitable to use it in medicinal applications. The solution of this is to extract it from a solvent which is not carcinogenic and easily available in the market at low cost.***

Keywords: Azeotrope, ethanol, fuel, extracting, medicinal purpose, carcinogenic, solvent.

I. INTRODUCTION

A. GENERAL INTRODUCTION

In this we have discussed the fundamentals of distillation in general and extractive distillation in particular. To separate azeotropic mixtures formed between various components constituting mixtures have been an area of research for several decades and literatures on that are highlighted here. Distillation is one of the most fundamental and sought alter techniques prevalent in various process industries. The success of distillation as a unit operation depends on the fundamental factor called relative volatility. The higher the relative volatility, the easier the separation would be. Here the purpose is to extract ethanol from ethanol water mixture by using such solvent that it can be used for medicinal purpose.

B. AZEOTROPIC DISTILLATION

Azeotropes are constant boiling mixtures when vapor and liquid phase compositions are equal and no separation by conventional distillation is possible beyond that point. The greater the non-ideality in the mixture, the more probable is the chance of an azeotrope formation. Ideal solutions obey Raoult's law and non-ideal solutions deviate from that. There are two possibilities:- positive deviation or negative deviation. Generally this deviation occurs large because of the dissimilarity in the chemical configuration of the constituting species. This differences leads to non-uniformity in the inter-molecular forces of attraction between them. The occurrence of minimum boiling azeotropes are more common. Extractive distillation is defined as distillation in the presence of a miscible, high boiling, relatively non-volatile component, the solvent that forms no azeotrope with the other components in the mixture. The method is used for mixtures having a low value of relative volatility, nearing unity. Such mixtures

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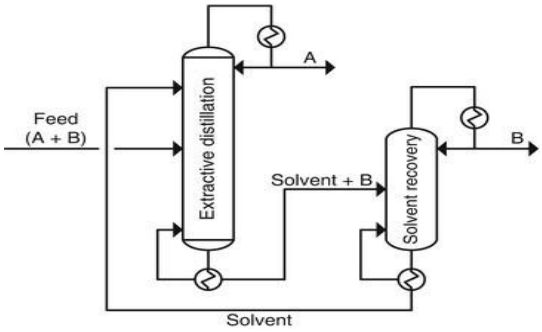
cannot be separated by simple distillation, because the volatility of the two components in the mixture is nearly the same, causing them to evaporate at nearly the same temperature at a similar rate, making normal distillation impractical. The method of extractive distillation uses a separation solvent, which is generally non-volatile, has a high boiling point and is miscible with the mixture, but doesn't form an azeotropic mixture. The solvent interacts differently with the components of the mixture thereby causing there relative volatilies to change. This enables the new three part mixture to be separated by normal distillation. The original component with the greayesy volatility separates out as the top product. The bottom product consists of a mixture of the solvent and the other components which can again be



separated easily because the solvent does not form an azeotrope with it.

Figure 1: Extractive distillation flowsheet

II. SIMULATION

Performing experiment is not possible everytime as it is not affordable, hence simulation is carried out. There are many softwares for performing simulation and in our case we are using Aspen Plus. Aspen Plus is a computer based steady state process simulation. It is developed for simulation of, chemical and petrochemical processes, coal based process, petroleum refining and polymer processes. In addition to process simulation, Aspen Plus allows user to perform a wide range of other tasks such as estimating and regressing physical properties, generating custom graphical and tabular output results, fitting plant data to simulation models, optimizing the process and interfacing the results to spreadsheets.

To start this, we need the Vapor-Liquid Equilibrium data (VLE) of the specific components. So the experimental VLE data of three mixtures (i.e. Ethanol-Water, Ethanol-Ethylene Glycol and Ethylene Glycol-Water) is obtained from book "

J. Gmehling – Vapor Liquid Equilibrium data collection" at 760mmHg of pressure. After it by using the experimentl data we can proceed with the simulation in Aspen Plus.

III. CONSISTENCY TEST

The thermodynamic consistency is then checked, to know whether the experimental VLE data is reliable or not. The thermodynamic test is carried out for all three systems with different thermodynamic model equations like Wilson, NRTL, Vanlar and UNIQUAC. This test is used to carry out in thermodynamic model consistency test by using all these various models in Aspen Plus. If the consistency data entered are passed then they are reliable and can be used for further simulation and no need of regression is there. And if the test failed, then we need to do regression and then we can obtain the particular data of VLE for further simulation.

In this case of ethanol-water-ethylene glycol mixture consistency test are passed in Aspen due to which that VLE data obtained can be directly used for further simulation without going for regression. As the consistency test are passed successfully we can say that the experimental VLE data is reliable and can be used in simulation without any regression. Moving further, now we have to do analysis in Aspen Plus and obtain the VLE as result (aspen generated VLE), which will be used for selecting the suitable Thermodynamic model equations by comparing it with experimental VLE. The comparison between experimental VLE data and aspen generated VLE data is done and the error between them is found for all 3 binary systems, and the model equation with minimum error is used for further simulation.

NRTL METHOD					
ETHANOL AND ETHYLENE GLYCOL SYSTEM					
SELECTED CORDINATES					
EXPERIMENTAL			ASPEN		% ERROR
X1	Y1		X1	Y1	
0	0		0	0	0
0.0253	0.7799		0.025	0.095222	87.79049
0.055	0.9121		0.05	0.096444	89.42616
0.104	0.9479		0.1	0.25567	73.02775
0.204	0.975		0.2	0.974104	0.091897
0.318	0.9855		0.3	0.98465	0.086251
0.48	0.9892		0.475	0.991586	0.241205
0.5701	0.9901		0.575	0.993408	0.334108
0.898	0.9963		0.9	0.996548	0.024922
0.9815	0.9992		0.975	0.998484	0.071647
				AVERAGE	27.89938

Table 1: Sample % Error calculation between experimental data and data obtained from Aspen

As above shown in the figure, % error is calculated between the experimental and aspen data and further the average value of % error is calculated. This is done for all Thermodynamic model and consistency test methods and further average value of all three systems for a particular method is carried out.

SELECTION OF THERMODYNAMIC MODEL EQUATION					
		NRTL	UNIQUAC	VANLAAR	WILSON
WATER+ETHYLENE GLYCOL		0.9066	0.9089	0.7895	0.91293
ETHANOL+ETHYLENE GLYCOL		27.89938	2.106102	1.705748	2.20795
ETHANOL+WATER		2.517055	0.8144	2.3008	2.92683
	AVERAGE	10.44101	1.2764673	1.5986827	2.0159

Table 2: Average % Error calculation of all three systems by different thermodynamic model.

We found that:

- ✓ The minimum error (1.27%) is obtained using UNIQUAC thermodynamic model equation for all 3 binary systems and so for performing simulation we are going to use UNIQUAC thermodynamic model equation.
- ✓ As the error is less than 5% and the thermodynamic consistency is passed, so there is no need of regressing the VLE data for performing simulation.

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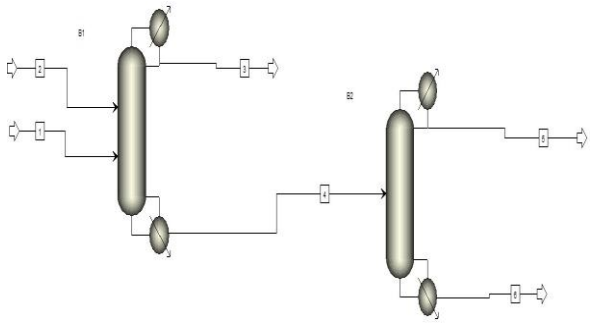
IV. SIMULATION ON EXTRACTIVE DISTILLATION COLUMN

RadFrac is a rigorous model for simulating all types of multi-stage vapor-liquid fractionation operation. These

operation includes:

- ✓ Simple Distillation
- ✓ Absorption
- ✓ Stripping
- ✓ Extractive and azeotropic Distillation It is suitable for:
- ✓ Two phase systems
- ✓ Three phase systems
- ✓ Narrow and wide boiling systems
- ✓ Systems exhibiting strong liquid phase non-ideality

In this work the Reflux Ratio, Distillate Rate, Number of Theoretical Stages required for Separation, Azeotropic Mixture Feed Stage, Solvent Feed Stage, Column



Temperature, Column Pressure, Total Feed Flow, Total Solvent Flow etc.

Figure 2: Model drawn in Aspen Plus for Simulation

V. EXPERIMENTAL WORK

A. GAS CHROMATOGRAPHY AND ITS ANALYSIS

Gas chromatography (GC) is a common type of chromatography used in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance, or separating the different components of a mixture (the relative amounts of such components can also be determined). In some situations, GC may help in identifying a compound. In preparative chromatography, GC can be used to prepare pure compounds from a mixture.

In gas chromatography, the mobile phase (or "moving phase") is a carrier gas, usually an inert gas such as helium or an unreactive gas such as nitrogen. Helium remains the most commonly used carrier gas in about 90% of instruments although hydrogen is preferred for improved separations. The stationary phase is a microscopic layer of liquid or polymer on an inert solid support, inside a piece of glass or metal tubing called a column (an homage to the fractionating column used in distillation). The instrument used to perform gas chromatography is called a gas chromatograph (or "aerograph", "gas separator").

The gaseous compounds being analyzed interact with the walls of the column, which is coated with a stationary phase. This causes each compound to elute at a different time, known as the retention time of the compound. The comparison of retention times is what gives GC its analytical usefulness.

Gas chromatography is in principle similar to column chromatography (as well as other forms of chromatography, such as HPLC, TLC), but has several notable differences. First, the process of separating the compounds in a mixture is carried out between a liquid stationary phase and a gas mobile phase, whereas in column chromatography the stationary phase is a solid and the mobile phase is a liquid. (Hence the full name of the procedure is "Gas–liquid chromatography", referring to the mobile and stationary phases, respectively.) Second, the column through which the gas phase passes is located in an oven where the temperature of the gas can be controlled, whereas column chromatography (typically) has no such temperature control. Finally, the concentration of a compound in the gas phase is solely a function of the vapor pressure of the gas.

Gas chromatography is also similar to fractional distillation, since both processes separate the components of a mixture primarily based on boiling point (or vapor pressure) differences. However, fractional distillation is typically used to separate components of a mixture on a large scale; whereas GC can be used on a much smaller scale (i.e. Micro scale).

A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex sample. A gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas stream (carrier gas, mobile phase) at different rates depending on their various chemical and physical properties and their interaction with a specific column filling, called the stationary phase. As the chemicals exit the end of the column, they are detected and identified electronically. The function of the stationary phase in the column is to separate different components, causing each one to exit the column at a different time (retention time). Other parameters that can be used to alter the order or time of retention are the carrier gas flow rate, column length and the temperature.

In a GC analysis, a known volume of gaseous or liquid analyst is injected into the "entrance" (head) of the column, usually using a micro syringe (or, solid phase micro extraction fibers, or a gas source switching system). As the carrier gas sweeps the analyst molecules through the column, this motion is inhibited by the adsorption of the analyst molecules either onto the column walls or onto packing materials in the column.

The rate at which the molecules progress along the column depends on the strength of adsorption, which in turn depends on the type of molecule and on the stationary phase materials. Since each type of molecule has a different rate of progression, the various components of the analyst mixture are separated as they progress along the column and reach the end of the column at different times (retention time). A detector is used to monitor the outlet stream from the column; thus, the time at which each component reaches the outlet and the amount of that component can be determined. Generally, substances are identified (qualitatively) by the order in which

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they emerge (elute) from the column and by the retention time of the analyst in the column.

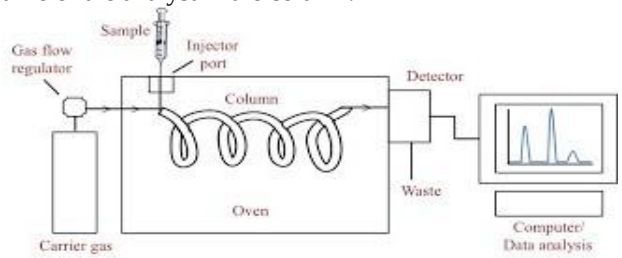

Figure 3: Schematic representation of Gas Chromatography

B. CALIBRATION

Further the calibration of chemicals is done by using Gas chromatography. In this, we analyse all three systems and look into it whether the graph plotting while analyzing is straight line or not. Graph prepared is of Mass ratio Vs Area ratio. Analyzing all three systems we get the following graph. Calibration of all three chemicals is done my making a three different samples of each by Iso-Propyl Alcohol (IPA). Mostly IPA is used as a solvent for calibration in Gas Chromatography.

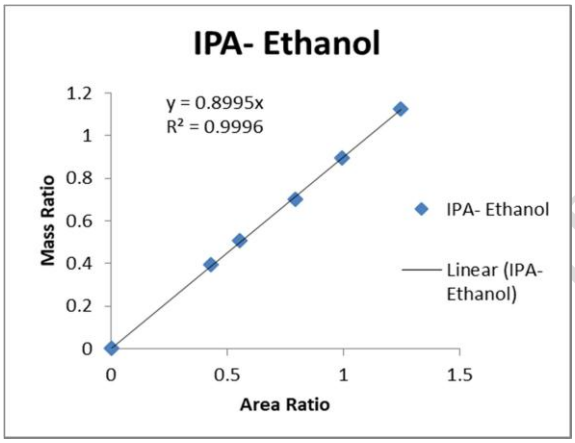

Figure 4: Calibration of IPA and Ethanol

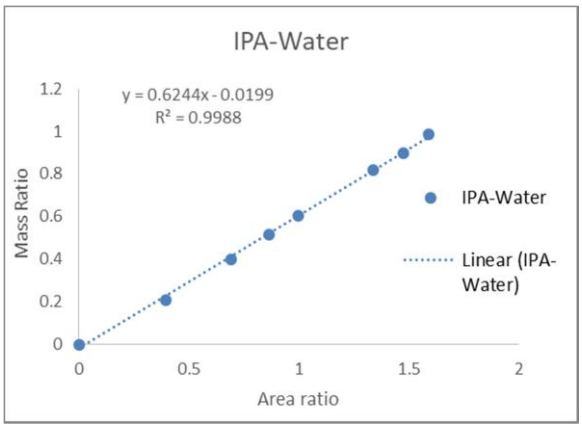

Figure 5: Calibration of IPA and water

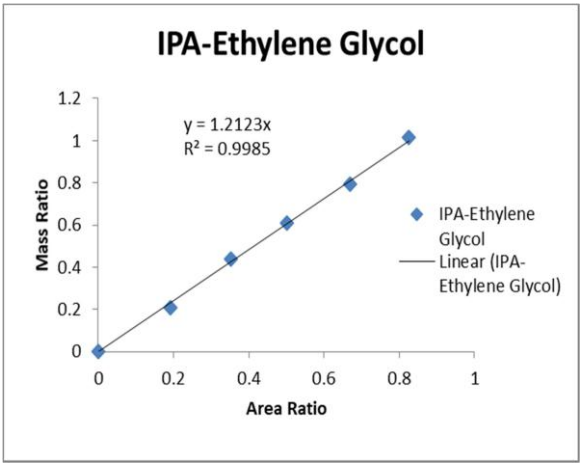

Figure 6: Calibration of IPA and Ethylene Glycol

C. BATCH-1

Take 90:10 concentration of Ethanol-Water mixture and increase the concentration of ethanol to 95.4 Wt% and show that the concentration cannot be further increased due to formation of minimum boiling azeotrope. Hence to add Ethylene Glycol as solvent and perform Extractive Distillation to further increases the concentration of ethanol.

In Distillate		
Time, min	Ethanol mass%	Water mass %
0	92.71730653	7.282693471
10	93.13171057	6.868289428
20	93.27464613	6.725353869
30	93.74269216	6.257307837
40	93.67648661	6.323513392
50	94.04982191	5.950178087
60	94.07575691	5.924243089
70	94.14007316	5.859926842
80	94.22403301	5.775966989
90	94.07773966	5.922260343
100	94.10784703	5.892152973
110	94.12060053	5.87939947
120	94.09891389	5.901086112
130	94.23714479	5.762855214
140	94.84002832	5.667370983

Table 3: Results for Batch-1, Mass% of ethanol and Mass% of water Vs Time

As we can see that an azeotropic mixture is formed at point where ethanol is having 94.84 mass% and remaining is mass% of water. This clearly shows that ethanol and water cannot be separated completely by simple distillation. Hence, we need to add the third component to separate ethanol completely from water. So further process can be done by using azeotropic distillation or extractive distillation. Azeotropic distillation will somewhat be costly as compared to extractive distillation, because the entrainer which we will add to separate ethanol and water will again form an azeotrope of entrainer and water. So, solvent recovery will then be costly. Hence, we will go with extractive distillation.

D. BATCH-2

Take the Azeotropic concentration of Ethanol-Water mixture and then increase the concentration of Ethanol above the azeotropic concentration and take it to 99.9 Wt% by adding suitable solvent; Ethylene Glycol which will break the azeotrope between ethanol-water mixture.

Following will be the result of batch-2 in which after a particular period of time we will get a distillate having an ethanol concentration of 98.89 mass% and remaining will be mass% of water. Hence, by using Ethylene glycol as a solvent we can approximately separate pure ethanol from ethanol water mixture.

At the Top (Distillate)		
Time	Ethanol Mass %	Water Mass %
0	95.219652	4.780347995
10	95.23610894	4.763891063
20	96.45794624	3.542053761
50	97.01670108	2.983298917
80	98.19603803	1.80396197
110	98.58769906	1.412300938
140	98.89311819	1.386881805

Table 4: Results for Batch-2, Mass% of Ethanol and Mass% of Water Vs Time

VI. CONCLUSIONS

After reviewing and by doing experiments at different conditions, the following conclusions were drawn:

- ✓ The experimental VLE data obtained from "Gmehling" was reliable for simulation as it passed the consistency test and hence no regression required.
- ✓ The UNIQUAC thermodynamic model equation was selected for calculation of activity coefficients used for phase equilibrium calculations, as it showed minimum error for the VLE.
- ✓ After performing simulation we got 99.8 Wt% of ethanol from the top of distillation column in the form of distillate.
- ✓ From simulation we also came to know composition and temperature on each stage.
- ✓ We also came to know how to do calibration and analysis on GC (Gas Chromatography).
- ✓ Performing experiment based on the simulation we got 98.8 Wt% ethanol from the top of column in the form of distillate.
- ✓ For further concentration of ethanol upto 99.5 Wt % we must add suitable adsorbent and do adsorbtion with molecular sieves.

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