Recovery of n-butanol from its Ternary Azeotropic Mixture with Methanol and Water

Leena V. Bora

***Abstract*--This paper is one of the numerous efforts in reducing the organic content of effluent streams. The effluent is the top product of a distillation column. This distillate is a ternary azeotrope consisting of methanol, n-butanol and water. The feed to this distillation column is through a separator, separating as much organic content from the water as possible, leaving some quantity in the leaner phase. This separator was found to be under-designed. Redesigning drastically reduced the organic content of the leaner phase. Next, in order to separate as much n-butanol from methanol and water, and vice versa, as possible, the unit operation of Liquid-Liquid Extraction was utilized. Two solvents were tried, viz., toluene and mixed xylene. It was found that toluene not only gave better extraction results, but also, did not need to be separated from n-butanol as it could be reused and re-fed into the process at some point. Thirdly, it was also tried whether process parameter modification proved passable and could be used a fortiori. It was checked if vacuum operation of the process was admissible. The variation in the azeotropic composition with vacuum was first numerically checked using computer spreadsheets. These spreadsheets give information whether vacuum operation increased or decreased the organics in the effluent. It was found that reducing the pressure gives two-edged results. It reduces the loss of n-butanol to all intents and purposes; antithetically, it increases that of toluene. And the methanol just doesn't form any azeotrope with water.**

***Index Terms*—liquid-liquid extraction, n-butanol, ternary azeotrope.**

I. PROCESS DESCRIPTION

THE effluent contains some amount of methanol, some toluene and a majority of n-butanol. This stream comes out from the reactor as vapours. This is then condensed in the condenser. The condensed stream enters a separator, where two distinct layers are formed. The upper one is an organic-rich layer containing majority of the n-butanol and the lower one is water-rich. n-Butanol is recycled back to the reactor. The lower water-rich layer now becomes the new effluent to be treated. In the next step, this stream is fed to a distillation column. The bottom product is almost water. The top product from this distillation column or the distillate is a multi-component azeotrope. It is a ternary azeotrope containing methanol, n-butanol and water. This is now the new effluent to be treated.

II. OBJECTIVE

Removal of as much quantity of organics as possible is desired. If these organic chemicals can, in turn, be reused or be of any economical value, this would prove to be savour of dual benefits- effluent treatment plus recovery of chemicals. This is the driving force or the objective behind the work. Two methods: To reduce the C.O.D value of the effluent stream the following two strategies could be used:

1) *Process Parameter Modification:* The other method to limit the organic content of the effluent is changing the parameters of the process itself so that minimum amount of chemicals goes into the effluent stream. As a trial, the plant can be operated in vacuum. But before going for vacuum operation, the variation in the organic content of the azeotrope with change in vacuum pressure needs to be checked through theoretical calculations. Hence, spreadsheets giving the azeotropic compositions were prepared.

2) *Process Redesigning (Recovery of Raw Materials):* The first unit operation through which the condensed vapours pass, is decantation in a settler. The settler, therefore, should be designed properly so as to separate as much organics (mainly n–butanol) [12] as possible. Next, the stream is fed to a distillation column; the bottom product of which is sent to CETP. The top product is a ternary azeotrope and high in its organic content. Recovery of the organics is desired. Of the multifarious unit operations available, Liquid-liquid Extraction was chosen. Experimentation was carried out with different solvents and in different proportions and the best option was found out.

III. EFFECT OF VACUUM PRESSURE ON AZEOTROPIC COMPOSITION

This effect was studied with the help of a spreadsheet prepared for three systems[28] , viz.,

- Water-Butanol
- Water-Toluene, and
- Water-Methanol

with the help of the following equations:

Margules equations:

$$\ln \gamma_1 = x_2^2 \, [A + 2(B-A)x_1] \qquad (1)$$

$$\ln \gamma_2 = x_1^2 \, [B + 2(A-B)x_2] \qquad (2)$$

Modified Raoult's law:

$$y_i \, P = x_i \, \gamma_i^{az} \, P_i^{sat} \qquad (3)$$

or
$$\frac{\gamma_1^{az}}{\gamma_2^{az}} = \frac{P_2^{az}}{P_1^{az}} \quad (4)$$

Antoine equation:

$$\ln P_i^{sat} = A - \frac{B}{t + C} \quad (5)$$

The spreadsheet was used to calculate and study the azeotropic composition as the pressure varies from atmospheric to about 100 mm Hg abs.

An effort was made to study the effect for the ternary azeotrope formed between methanol(1)/n-butanol(2) /water(3) [5],[6]. A separate spreadsheet was prepared for the same. The controlling equations are as follows:

Wilson Equation [16],[22] giving the activity coefficients:

$$\ln \gamma_i = 1 - \ln\left[\sum_{j=1}^{n}\left(A_{ij}x_j\right)\right] - \sum_{l=1}^{n}\frac{A_{li}x_l}{\sum_{j}^{n} A_{lj}x_j} \quad (6)$$

And finally the set of equations to be solved is [5],[6]

$$\ln P - \ln P_i^{sat} - \ln \gamma_i^L = 0, \forall i \in N \quad (7)$$

subject to
$$\sum_{i=1}^{N} x_i - 1 = 0 \quad (8)$$

We get N number of equations for N components, which need to be solved simultaneously or sequentially to get the desired mole fraction values.

A. *Abbreviations and Acronyms*

A	Parameter, in Margules empirical equations
A	Area, m^2
A	Antoine constant, equation
A	Parameter showing whether or not a binary azeotrope exists
B	Antoine constant, equation (43)
D	Diameter of settler, m
d_d	Droplet diameter, m
G	Acceleration due to gravity, 9.81 m/s^2
L	Length of settler, m
N	Total number of components
N	Total number of components
P	Pressure
Q	Volumetric flow rate, m^3/s
T	Absolute temperature, Kelvin or Celsius
T	Separation time, hrs
u_d	Settling (terminal) velocity of the dispersed phase droplets with diameter *d*, m/s
X	Mole fraction
X	Mole fraction in liquid phase
Y	Mole fraction in vapour phase

B. *Subscripts*

1	Component one
2	Component two
C	Continuous phase
C	Critical property
D	Dispersed phase
D	Droplet
I	Arbitrary component, one
J	Arbitrary component, two
K	Arbitrary component, three

C. *Superscripts*

∞	Value at infinite dilution
az	Azeotrope
L	Liquid phase
sat	Saturated state

D. *Greek Letters*

γ	Activity coefficient
α	Relative volatility
λ	Wilson interaction parameter, cal/mol
μ	Viscosity, N s/m^2
ρ	Density, kg/m^3

IV. DESIGN OF SETTLER

There are three approaches to the design[21],[26],[29]; the corresponding equations are:

1) *Coulson and Richardson’s Method:*

$$u_d = \frac{d_d^{\,2} g\left(\rho_d - \rho_c\right)}{18\mu_c} \quad (9)$$

2) *Treybal’s Method :*

$$D = 8.4\sqrt{q_{\text{Water}} + q_{\text{Butanol}}} \quad (10)$$

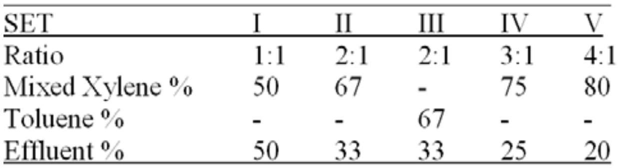
3) *McCabe-Smith-Harriott Method:*

$$t = \frac{100\mu}{\left(\rho_C - \rho_D\right)} \quad (11)$$

V. EXPERIMENTAL WORK

Literature survey suggests that for the separation of n-Butanol from Water, the two better solvents are Toluene and Mixed Xylene. Hence, the experiment was conducted with these two solvents. Following are the various solvent-feed volume proportions that were taken for the two solvents for the LLE[2], [27] operation:

TABLE I
EXPERIMENTAL SETUP DATA FOR LIQUID-LIQUID SEPARATION



SET	I	II	III	IV	V
Ratio	1:1	2:1	2:1	3:1	4:1
Mixed Xylene %	50	67	-	75	80
Toluene %	-	-	67	-	-
Effluent %	50	33	33	25	20

Three trials of the above sets were taken and results were studied after the gas chromatographic analysis of each.

VI. RESULTS

Spreadsheet results: The main points can be highlighted as follows:

The spreadsheets confirm the formation of azeotrope of n-butanol and toluene with water. As opposed to this, methanol and water do not form azeotrope.

1) The n-butanol–water spreadsheet showed that as the vacuum increases the amount of butanol in the azeotrope decreases. This implies that there is less loss of the organic

through the vapour and hence the effluent. But the vacuum of about 650 mm of Hg showed just 3% reduction in the amount of dissolved butanol. But this figure becomes an essential quantity to reckon with when it is applied to the plant process. This is because the plant handles tons of liquid per batch. Hence vacuum operation is beneficial.

2) It was also seen that the azeotrope forms at a reduced temperature. This may be useful in avoiding degradation of heat-sensitive material or excessive polymerization of the resinous product, which may take place due to high temperatures. Evidently, lesser amounts of heating oil would be required to achieve comparatively lower temperatures.

3) Antithetically, the reverse trend was seen with toluene – water azeotrope. As pressure reduces, more and more toluene moves into water. Hence, operating this system under vacuum is not favourable.

An effort was made to find the azeotropic composition of a multi-component system involving three components. This was based on trial and error. But this proved futile. The futility can be burdened on the number of variables to be handled simultaneously. As stated earlier, this task would be well handled by professional software packages. Two high powered modeling programs that can provide all possible azeotropic compositions formed by multi-component systems having four or even five components, with guarantee and accuracy, are INTLIB and INTBIS[6]. The system of equations required to be solved were:

$$\ln\gamma_a = 1 - \ln\left(x_a + 0.2959x_b + 2.7621x_c\right) - \frac{x_a}{x_a + 0.2959x_b + 2.7621x_c} - \frac{1.0941.x_b}{1.0941x_a + x_b + 0.3964x_c} - \frac{5.78469\times10^{-8}x_c}{5.78469\times10^{-8}.x_a + 0.0121.x_b + x_c} \tag{12}$$

$$\ln\gamma_b = 1 - \ln\left(1.0941x_a + x_b + 0.3964x_c\right) - \frac{0.2959x_a}{x_a + 0.2959x_b + 2.7621x_c} - \frac{x_b}{1.0941x_a + x_b + 0.3964x_c} - \frac{0.0121x_c}{5.78469\times10^{-8}.x_a + 0.0121.x_b + x_c} \tag{13}$$

$$\ln\gamma_c = 1 - \ln\left(5.78469\times10^{-8}.x_a + 0.0121.x_b + x_c\right) - \frac{2.7621x_a}{x_a + 0.2959x_b + 2.7621x_c} - \frac{0.3964x_b}{1.0941x_a + x_b + 0.3964x_c} - \frac{x_c}{5.78469\times10^{-8}.x_a + 0.0121.x_b + x_c} \tag{14}$$

Settler design results:

TABLE II
SETTLER DESIGN RESULTS

Method	D(m)	L(m)
Coulson- Richardson's Method	0.06	0.24
Treybal's Method	0.1	0.4
McCabe-Smith-Harriott Method	0.4	2

The third value which is the largest is the final design value as it encompasses scope within itself for still better separation, if possible.

L-L-E results: Obviously, it was found that increasing the amount of solvent increased the percentage reduction in the total volume of the water phase; in other words, extraction was more effective. The result table of one of the trials is as follows:

TABLE III
LIQUID-LIQUID EXTRACTION RESULTS

SET	I	II	III	IV	V
Ratio	1:1	2:1	2:1	3:1	4:1
Mixed xylene %	50	67	-	75	80
Toluene %	-	-	67	-	-
Effluent %	50	33	33	25	20
Initial interfacial level	125	85	85	62.5	50
Final interfacial level	98	64	62	46	36
Change in volume (ml)	27	21	23	16.5	14
% Reduction in vol. of water layer	21.6	24.7	27.7	26.4	28
% Reduction in vol. of organic layer	21.6	12.73	13.94	8.8	7
% Recovery of n-butanol	-	-	75	70	74
% Separation of Methanol	-	-	83	76	88

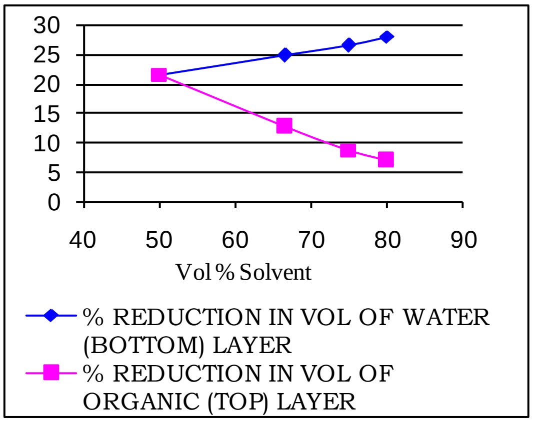


Fig. 1. Recovery of organics

The percentage recovery of butanol with toluene as solvent is about 75% and that with mixed xylene is also near about the same. In other words, toluene as solvent, with an amount equal to half the quantity of that required by mixed xylene, yields nearly same the amount of extraction as that by mixed xylene. n-Butanol is a principal reagent required for alkylation and toluene is also used at certain point in the reactor. Hence, toluene with dissolved n-butanol can directly be fed to the reactor. Thus, eliminating altogether the need of further separation of the two chemicals.

Calculations show that the recovery of n-butanol with the help of toluene saved Rs. 13,500 per batch. If the batch is run 10 times a month, this would imply a saving of about Rs. 1,35,000 per month. In contrast with this, the new separator, along with all its accessories, costs about Rs.3,00,000, which is expected to be recovered in ten weeks.

VII. CONCLUSION

1) The final dimensions of the settler are:
- Diameter = 0.4 m
- Length = 2 m

When the redesigned separator was installed in the factory, a drastic reduction in the organic content of the effluent was noticed. It was noticed that the original COD value of about 4,00,000 mg/l got dropped down to about 2,50,000 mg/l.

2) Two solvents, namely, toluene and mixed xylene were selected for extraction of the desired components. In one case, toluene and the distillate were mixed in 2:1 ratio and allowed to separate in two layers. In another case, mixed xylene was mixed with the distillate in 4:1 ratio and allowed to separate.

3) In the manufacture of amino resins, before starting the reaction, nearly 250 litres of toluene is required per batch with nearly 4000 litres of n-butanol. Since toluene has been found as a better extractive agent, it is suggested that toluene rich in n-butanol can be fed into the separator instead of pure toluene. In this way, addition of toluene in the separator can be eliminated and nearly 75% n-butanol recovery is achieved. As stated before, this implies a saving of about Rs. 1,35,000 per month, at the cost of about Rs. 3 lacs for the new separator, which is expected to be recovered in ten weeks.

4) The bottom layer is an aqueous layer rich in methanol. It is suggested that it may be distilled in the distillation tower. Here also, methanol and n-butanol can be recovered again as a distillate from the top. This distillate can be mixed with the distillate of aqueous layer obtained during the reaction, i.e., top product of first distillation column (recovered butanol). Else, it can be sold in the market as about 30% methanol solution. This methanol solution may also find its takers as brine in chillers. In this way, it is hoped that sufficient recovery of n-butanol and methanol can be achieved. The bottom product from the distillation column will be water, nearly free from organics and can be disposed off.

5) Based on the results obtained by the prepared spreadsheet, in the plant, one of the 4 reactors was operated in vacuum. The vacuum pressure was about 400 mm Hg. Substantial improvements were noticed:

- Reduced n-butanol loss- The spreadsheet showed that the amount of n-butanol in the azeotrope decreases as the system pressure reduces. It was found that the effluent contained less n-butanol.
- Enhanced product purity- It was found that there was less amount of formaldehyde in product.
- Time saved- The time required for azeotrope formation and its removal was reduced from about 6 hrs to nearly 4 hrs. This may be attributed to the fact that lesser amount of the organic is in the stream.
- Reduction in fuel consumption- The required temperature in the system is brought about from heat oil. This heat oil is, in turn, heated by furnace oil. Substantial reduction in the consumption of furnace oil was observed. This may be due to lesser time requirement and lower temperature achievement.

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