A

Project Report

On

**Separation of Azeotropic mixture by extractive distillation
and pressure-swing distillation:Computer simulation
and economic optimization**

Submitted by

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In partial fulfilment of the requirements for the degree in Bachelor
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Under the supervision of

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<u>CERTIFICATE</u>

This is to certify that the thesis entitled, **"Separation of azeotropic mixture by extractive distillation and pressure-swing distillation: Computer simulation and economic optimization",** submitted by **Mr Apurva Agarwal, Roll no. 110CH0500**, in partial fulfilment of the requirements for the award of degree of Bachelor of Technology in Chemical Engineering at National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the report has not been submitted to any other University / Institute for the award of any Degree or Diploma.

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<u>Acknowledgements</u>

<u>ABSTRACT</u>

The Separation of Di-n-propyl ether and n-propyl alcohol is difficult because the highly non-ideal vapour-liquid equilibrium forms a azeotrope. It is very difficult to separate the azeotropic mixture by ordinary processes of distillation. The most common methods for separating the azeotropic mixture are pressure swing distillation and extractive distillation process. Pressure swing distillation is a better process for the case where the azeotropic composition changes significantly with the change in pressure whereas the extractive distillation process is effective only if we are able to find a suitable solvent.

This thesis equates these two different process to separate the mixture consisting of 50-50 mole % of di-n-propyl ether and n-propyl alcohol by means of a practical case of a industry. We have studied and simulated these two separate alternatives of the mixture for the case of a plant to treat 12000 Tm/year of the original mixture. The simulation is carried out satisfactorily by means of a package of commercial software i.e. Aspen Plus using the thermodynamic model UNIQUAC with the help of other parameters obtained. Aspen plus is a very important tool for the simulation of various processes with different thermodynamic models. In the result we have calculated different parameters required such as number of plates, feed plate etc. We have also calculated the amount of heat required for the reboiler and the cooling required in the condensers. We have also calculated the reflux ratio and the graph between the reflux ratio and the no. of stages is plotted. We have also simulated the stream results required for the valves and the mixer. The pump efficiency electricity required and the pressure drop across the pump has also been accounted.

Keywords: Pressure swing distillation, extractive distillation, computer simulation, di-n-propyl ether, n-propyl alcohol.

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Nomenclature And Abbreviations

S_{ij}	Selectivity coefficient
α_{ij}	Relative volatility of key components(Di-propyl ether and n-propyl ether)
γ_i & γ_j	Activity coefficients of the components of i and j
γ_i^∞ & γ_j^∞	Activity coefficient at infinite dilution
S_{ij}^∞	Selectivity coefficient at infinite dilution
T	Temperature
P	Pressure
x_i	Mole fraction of i component
C_v	Process variable cost, \$/year
C_f	Annual fixed cost, \$/year
i_r	Fixed capital recovery rate
i_m	Minimum acceptable rate of return
FCI	Fixed capital investment
A_{ij}	UNIQUAC binary interaction parameter
RHD	Reboiler heat duty
F	Feed flow rate
CEPCI	Chemical Engineering plant cost index
EC	Extractive column
PSD	Pressure Swing Distillation
HPC	High pressure column
LPC	Low pressure Column
PA	n-Propyl Alcohol
DPE	di-n-Propyl Ether
VLE	Vapour-Liquid equilibrium
SRC	Solvent Recovery Column

1. <u>INTRODUCTION</u>

In any substance industry distillation is a standout amongst the most broadly utilized synthetic detachment process. In any general substance plant, something like one third of aggregate financing is on the distillation sections and their help offices. Also the energy utilization in light of distillation segments constitutes s more than half of the aggregate energy needed. Remembering these things it has gotten truly important to plan and upgrade these distillation strategies as they have an enormous effect on the matters of trade and profit of the entire methodology. Anyway when we need to independent azeotropic mixtures, we require more thorough, solid and powerful thermodynamic models that are critical for the outline and union of the partition framework.

In the event that the compound segments are different and repulsive powers are solid, activity coefficients are more than unity solidarity and least-boiling azeotropes can structure. On the off chance that the synthetic parts draw in one another, activity coefficients are less than unity and most maximum-boiling azeotropes can structure. Paired mixtures with non-perfect vapour–liquid equilibrium conduct produce azeotropes in some compound frameworks.

Both frameworks requires two segments to generate two item streams that are rich in the two key parts. A few procedures are utilized as a part of industry to independent azeotropic Mixtures. A few routines require the expansion of a third concoction segment that movements the vapour–liquid harmony. Extractive distillation uses a higher boiling dissolvable. Azeotropic heterogeneous distillation uses an entraining chemical segment.

We realize that the mixture of di-n-propyl ether and n-propyl liquor structures an azeotropic mixture. So they can't be differentiated by typical strategies. One of them is aliphatic ether which could be structured by the lack of hydration of the comparing liquor by suitable impetus. For this case in vicinity of sulphuric corrosive DPE might be structured from lack of hydration of PA. However as indicated by the customary strategies last decontamination is a moderately complex strategy in light of the vicinity of azeotropic mixture at encompassing pressure.

For the division of azeotropic mixture numerous procedures are accessible, for example, extractive distillation, pressure swing distillation, vanishing by the utilization of film, by the expansion of salts and so forth. From the different methods accessible how we can select legitimate sought and suitable method for such a complex work.in our work we have acknowledged division with extractive distillation and pressure swing distillation. We

additionally need to advance the over two procedure such that they might be monetarily suitable.

Extractive distillation uses a higher boiling dissolvable that is sustained close to the highest point of the first extraction section to specially douse up one of the key parts in the paired crisp food. This part and the dissolvable leave in the bottoms stream[2]. The other key segment goes overhead as a high-virtue distillate stream. The ideal dissolvable-to-encourage degree and the ideal reflux proportion are two critical outline improvement variables in the extraction section. The bottoms stream is bolstered to the second segment that processes a high-virtue key-part distillate item and a dissolvable bottoms item for reuse again to the first section. The decision of a fitting dissolvable is basic in the outline of extractive frameworks. Dissolvable choice firmly influences energy utilization and capital financing in view of contrasts in selectivity, limit and breaking points. Dissolvable choice additionally influences controllability [2].

When we take a gander at the stream sheet of these two choices they are really comparative that is both have two distillation sections. If there should arise an occurrence of PSD we have one high pressure distillation section and one low pressure distillation segment and in the event of extractive distillation we have one ED section and one dissolvable recuperation segment. The principle issue with the ED methodology is the expansion of third segment. We need to think about third part in such a path, to the point that it must be prudent and also it ought not hurt nature's domain. The methodology of PSD is known structure 1920s yet from that point forward it have not gained that much consideration.

Heterogeneous azeotropic distillation, homogeneous azeotropic distillation film courses of action and pressure-swing distillation are regular techniques to independent azeotropic mixtures. Azeotropic distillation methods oblige expansion of a third part as an entrainer to arrive at complete division. Nonetheless, the utilization of performers, for example, benzene has a negative ecological effect due to danger issues. Also, they can undoubtedly enter into the climate and extra energy is needed for recuperation them. Right away, there is a quest for new, feasible items for the detachment of azeotropic mixtures utilizing new sort of solvents that show maintainable. Distillation/layer setups are an alternate path for getting dried out ethanol. Despite the fact that the significant outcomes with layers utilizing reenactment instruments and pilot plant examinations the usage at modern scale can come about troublesome as a result of working issues.

Extractive distillation has discovered a tremendous exhibit of different provisions from the division of natural mixes in smoke to the partition of unpredictable mixes from products of the soil. Different zones of extractive distillation frameworks have been explored at one time,

for example, dissolvable choice strategies, the improvement of new extractive distillation frameworks and the acquaintance of a salt with the dissolvable to enhance the detachment .

An alternate prevalent technique for differentiating azeotropes, which does not include the expansion of a third segment, is pressure-swing azeotropic distillation. Two sections working at two separate pressures are utilized. High-immaculateness item streams are prepared from one end of the sections and reuse streams are processed from the flip side with structures close to the two azeotropes. This arrangement might be financially utilized when changes within pressure fundamentally move the piece of the azeotrope[7]. The bigger the movement, the littler the obliged reuse stream rates, so the more diminutive the energy prerequisites in the two reboiler.

Pressure-swing distillation could be connected to both least boiling and most extreme-boiling homogeneous azeotropic mixtures. With least-boiling frameworks, the distillate streams are reused. With greatest-boiling frameworks, the bottoms streams are reused. Since processing distillate reuses obliges that they be bubbled overhead, handling fluid bottoms reuse ought to take less energy. Consequently instinct may lead us to expect that less pressure reliance is required in a most extreme-boiling framework.

When we are leading the trials in the research facility then they are both drawn out and exceptionally exorbitant in light of the fact that a lot of parameters are included in it. So it gets extremely helpful that we do it with the assistance of some reenactment instrument as it is quick process and in addition less costly. Today the utilization of recreation projects has changed the substance of compound industry as an enormous measure of figuring is possible effectively. This engineering is likewise supporting the enhancement and advancement of the compound plants. The main test which we need to face is confining the utilization of demonstrating and evaluating databanks for themophysical properties. Real issue is to get a predictable and solid plant date.

Here we have chosen aspen in addition to as our test system in light of its recreation quality and also it fuses figurings utilizing spread sheet instrument.

1. **LITERATURE REVIEW**

1.1 **Pressure Swing Distillation**

From one perspective, homogeneous azeotropic arrangements that are pressure touchy might be separated utilizing pressure-swing distillation (PSD), which uses two or more distillation sections working at distinctive pressures together with fitting reuse methodologies to accomplish the desired separation. Lewis [9] was the initially, who proposed distillation the azeotropic mixtures by PSD. This methodology has been proposed by different creators to divided azeotropic mixture; e.g. Dark [10], Abu-Eihah and Luyben [11], Chang and Shih [12]. Phimister and Seider [13] were the first who mulled over the bunch provision of paired PSD by reproduction. They examined the detachment of a minimum azeotrope (THF-water) by semi persistent PSD.

The affectability of azeotropes to changes in pressure has been known and contemplated for a long time. The extent of pressure impacts relies on upon the mixture. At times, creation of azeotropes change almost no (e.g. the ethanol–water azeotrope). Then again, there are mixtures where pieces of a few azeotropes change quickly with pressure and even azeotropes that show up and vanish as pressure changes. For our situation, the DPE + PA azeotropic organization is pressure-sensitive.

To explore how the PSD functions with the DPE + PA azeotropic framework, we have done a computer re-enactment of the vapour–liquid equilibrium utilizing Aspen in addition to at distinctive pressures with the connection parameters got from test VLE information acquired by us [7]. In view of these outcomes we have chosen to complete the development and enhancement of the pressure-swing distillation process. Technical knowledge about the design and development of distillation process is widely available fot both pressure swing distillation and extractive distillation.
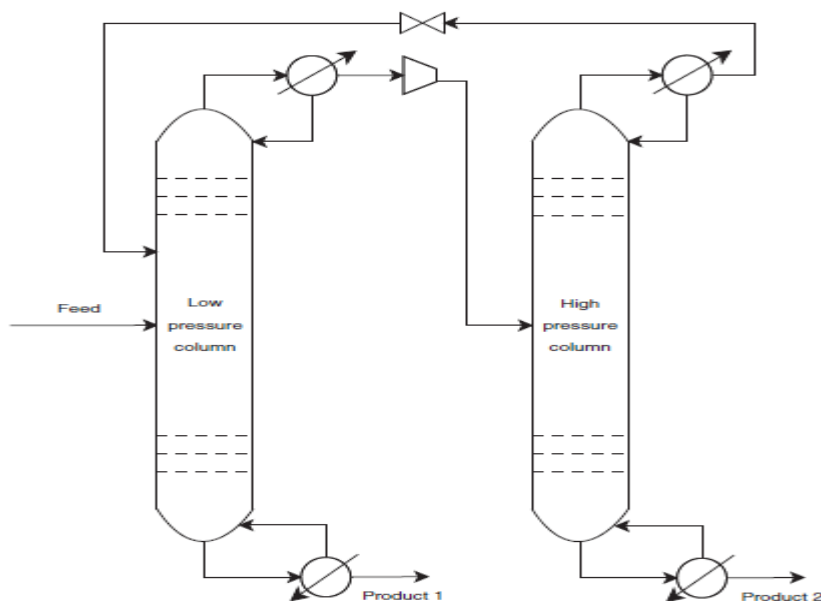
Fig-1 Flowsheet of conventional pressure swing distillation scheme

From the perspective of green compound standards, extra solvents ought to be evaded however much as could be expected in chemical process. Taking after these standards, PSD appears to be more alluring and ought to be specially chosen, contrasted with the azeotropic/extractive distillation. Be that as it may, it is not frequently misused economically, in light of the fact that in numerous case the relative volatility stays near 1.0 at the highest point of the column (for minimum boiling azeotrope) or at the bottom (for maximum boiling azeotrope). In such cases, a high reflux degree and an extensive number of balance stages are obliged to attain complete separation, so the power of energy utilization may prompt be a methodology financially non-eligible.

1.2 **EXTRACTIVE DISTILLATION**

Then again, extractive distillation (ED) might be utilized to independent the segments of an azeotropic mixture including a dissolvable (entrainer) that is fit for determinedly changing the relative volatility of the mixture. The synthesis and configuration of extractive distillation methods happen in two steps [14]. The first includes the determination of one or more hopeful solvents (which encourage the detachment by changing the relative volatilities in the mixture through physical or compound interaction with the first segments), and the decision of one or more section arrangements. The second step, methodology outline, includes the quest for ideal procedure parameter values. The accomplishment of the second step relies on upon the results acquired for the first in light of the fact that proficiency in extractive distillation is generally dictated by the decision of a suitable entrainer. In this work, taking into account the rules for the dissolvable screening, at first, it had been picked four solvents: 1-pentanol [15], n butyl propionate [16], N,n-dimethylformamide [17] and 2- ethoxyethanol [18].

therefore, keeping in mind the end goal to have the capacity to select the best solvent around them, we have done simulation with Aspen in addition to. Truth be told, the point of this work is to study the impact of the operation variable values a segment setup on the performance of the DPE + PA partition by extractive distillation utilizing an entertainer and by swing-pressure distillation with the assistance of a simualtion test system Finally, we have picked the best elective for the division of the azeotropic mixture under study from the financial perspective. The effects from the study will give essential outline data in applications connected with extractive distillation
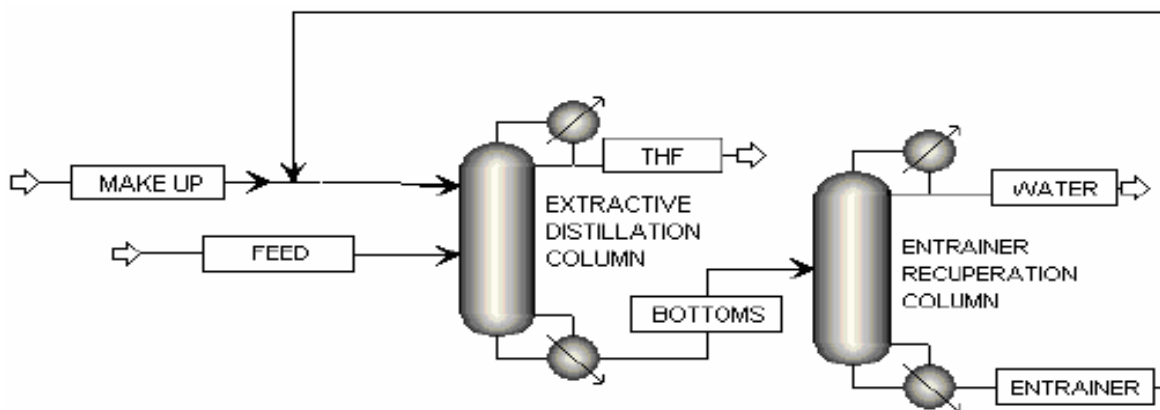
Fig-2 Flow sheet of conventional extractive distillation process

Azeotropes are unpredictable, non-perfect mixtures that happen when the segments of the mixture have low relative volatilities. The parts of these mixtures are extremely troublesome and thus unmanageable to separate. They could be differentiated effectively by method for extractive distillation whereby the addition of a dissolvable solvent is made to a distillation segment. The dissolvable demonstrations to expand the relative volatility of the mixture by increasing the activities of the parts, as given in the non-perfect binary component mixture relationship:

$$\alpha_{ab} = \gamma_a p_{ao} / \gamma_b p_{bo}$$

1.3 **Azeotrope**

An azeotrope is a mixture of two or more liquids in such a proportion, to the point that its composition can't be changed by straightforward distillation. This happens on the grounds that, when an azeotrope is heated up, the ensuing vapor has the same degree of constituents as the first mixture. Since their composition is unaltered by distillation, azeotropes are additionally called (particularly in more older writings) constant boiling mixtures. The statement azeotrope is inferred from the Greek words consolidated with the prefix α- (no) to give the general signifying, "no change on bubbling." Azeotropic mixtures of sets of mixes have been recorded. Numerous azeotropes of three or more mixes are likewise known.

1.3.1 **Minimum-boiling or Positive azeotrope**

The chart below shows a positive azeotrope of theoretical constituents, P and Q. The bottom follow explains the boiling temperature of different composition. Beneath the lowest part follow, just the liquid stage is in equilibrium. The top follow shows the vapor structure over the liquid at a given temperature. Over the top follow, just the vapor is in equilibrium. Between the two follow, liquid and vapor stages exist all the while in equilibrium: for instance, warming a 25% P : 75% Q mixture to temperature AB might produce vapor of arrangement B over liquid of organization A. The azeotrope is the point on the outline where the two bends touch. The level and vertical steps indicate the way of repeated distillation processes. Point A is the boiling point of a nonazeotropic mixture. The vapor that differentiates at that temperature has arrangement B. The state of the bends obliges that the vapor at B be wealthier in constituent P than the liquid at point A.The vapor is physically divided from the VLE (vapor-liquid harmony) framework and is cooled to point C, where it gathers. The ensuing liquid (point C) is currently wealthier in P than it was at point A. On the off chance that the gathered liquid is bubbled once more, it advances to point D, et cetera. The stepwise movement demonstrates how rehashed distillation can never transform a distillate that is wealthier in constituent P than the azeotrope. Note that beginning to the right of the azeotrope point brings about the same stepwise process surrounding the azeotrope point from the other direction.
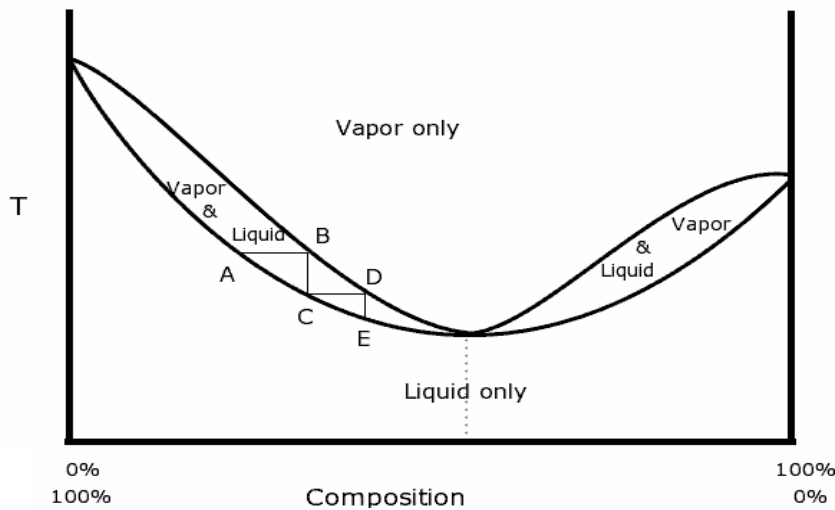
Fig-3 Phase diagram of a positive azeotrope. Vertical axis is temperature, horizontal axis is composition

1.3.2 **Maximum-boiling or Negative azeotrope**

The chart below shows a negative azeotrope of theoretical constituents, P and Q. Again the bottom follow represents the boiling temperature at different arrangements, and once more, beneath the lowest part follow the mixture must be completely liquid stage. The top follow again shows the condensation temperature of different syntheses, and once more, over the top follow the mixture must be completely vapor stage. The point, A, demonstrated here is a boiling point with a composition picked close to the azeotrope. The vapor is gathered at the same temperature at point B. That vapor is cooled, consolidated, and gathered at point C. Since this illustration is a negative azeotrope instead of a positive one, the distillate is more remote from the azeotrope than the first fluid mixture at point A was. So the distillate is poorer in constituent P and wealthier in constituent Q than the first mixture. Since this procedure has evacuated a more stupendous portion of Q from the fluid than it had initially, the deposit must be poorer in Q and wealthier in P after distillation than in the past one.
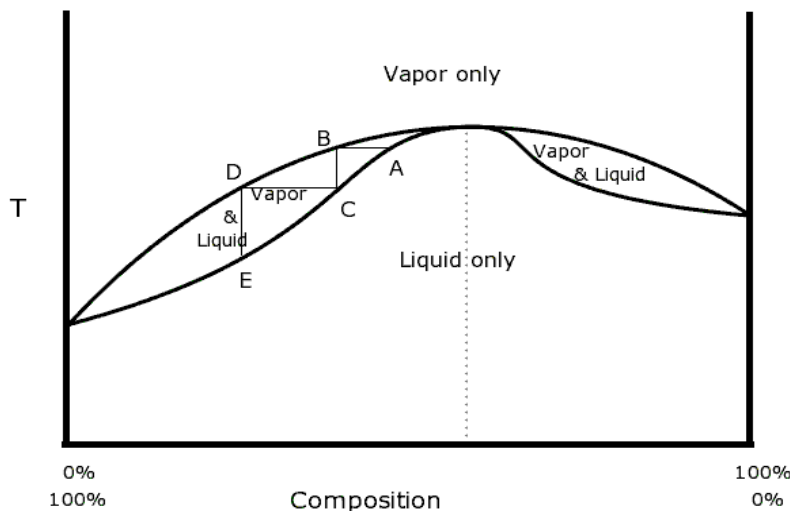
Fig-4 Phase diagram of a negative azeotrope. Vertical axis is temperature, horizontal axis is composition

If the point, A had been decided to the right of the azeotrope instead of to the left, the distillate at point C might be more distant to the right than A, which is to say that the distillate might be wealthier in P and poorer in Q than the first mixture. So for this situation too, the distillate moves far from the azeotrope and the residue moves to it. This is normal for negative azeotropes. No amount of distillation, be that as it may, can make either the distillate or the buildup land on the opposite side of the azeotrope from the first mixture. This is normal for all azeotropes.
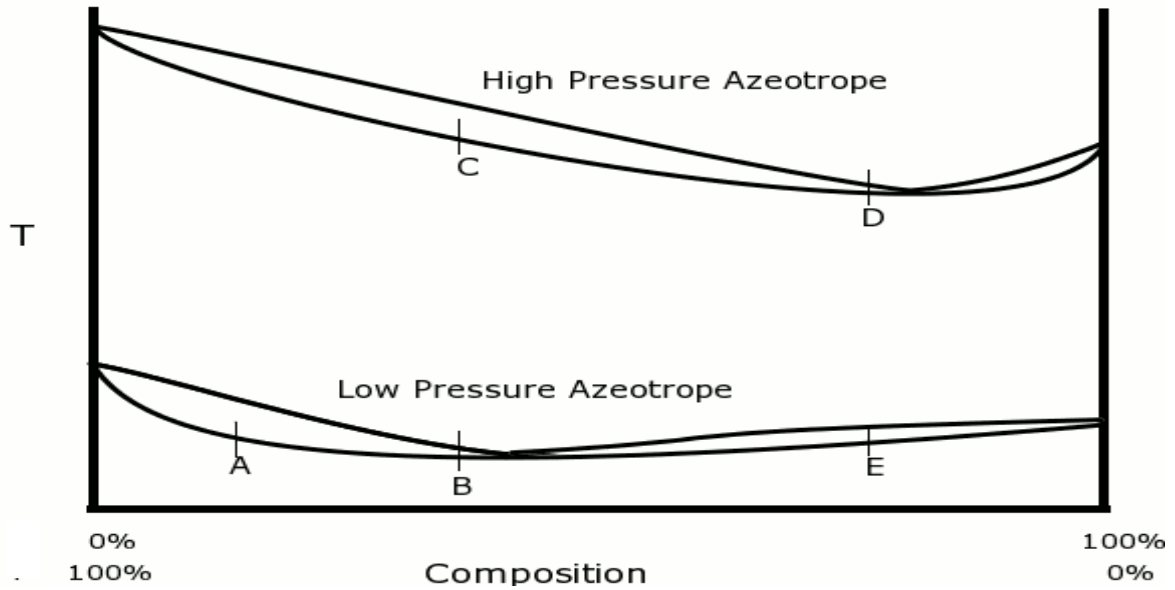
Fig-5 Azeotropic composition due to pressure swing distillation

A speculative azeotrope of constituents P and Q is demonstrated in the outline above. Two plots are demonstrated to, one at a comparatively low pressure and an alternate at a similarly discretionary, yet higher, presssure. The piece of the azeotrope is significantly distinctive between the high- and low-pressure plots – higher in P for the high-pressure framework. The objective is to divided P in as high as could be expected under the circumstances beginning from point A. At the lowpressuret, it is conceivable by dynamic distillation to achieve a distillate at the point, B, which is on the same side of the azeotrope as A. Note that progressive refining steps close to the azeotropic arrangement show next to no contrast in boiling temperature. On the off chance that this distillate is presently presented to the high pressure, it bubbles at point C. From C, by dynamic refining it is conceivable to achieve a distillate at the point D, which is on the same side of the high-pressure azeotrope as C. In the event that that distillate is then laid open again to the low pressure, it bubbles at point E, which is on the reverse side of the low-pressure azeotrope to A. Thus, by method for the pressure swing, it was conceivable to traverse the low-pressure azeotrope.

3. DESCRIPTION OF SIMULATION

3.1. Problem Definition

In this problem we are considering two processes i.e. PSD and ED .considering the same initial data we have to simulate both the processes. We have consider both components to be 50% each the annual stream rate is around12000Tm/year. Considering a total working 8000 hours according to which the mass stream is about 1500kg/hr.

3.2. Property Package

Today computer simulation has changed the face of optimization thousands of calculations can be done within minutes. Commercially the use has become so important. Today these process simulators has become a important tool to determine qualitatively the action of the variables on the system. The simulated results are very much accurate and also there accuracy depends upon the quality of the parameters from the activity models.

In this case, UNIQUAC activity model was chosen and we have used the binary interaction parameters. The parameters used are listed in Table 1.

3.3. Pressure-Swing Distillation

 We have seen that changing the operating pressure can change the VLE of the mixture. The VLE varies lot with a change in pressure. This technique might be used to separate a minimum boiling azeotropes given the composition is changed over a moderate range of pressure. It can be used as an important tool that changing the pressure will effect the vapor liquid equilibrium of the mixture.

3.3.1 Operating Pressure Selection

First thing is to select the operating pressure, to select it we start with the effect of pressure on DPE and PA azeotropic mixture, so we begin with a simulation of the VLE at different pressures. Here we are using UNIQUAC model for simulation. As seen in Fig. 6 the DPE temperature and mole fraction are plotted as a function of pressure for the azeotrope composition. We can see a great pressure effect on the azeotropic curve. We need to select the real pressure in such a way that we can use water as a coolant and steam can be used for heat in the reboiler.in the figure the dashed line represents pressure vs azeotrope creation and dark line represents pressure vs azeotropic temperature.

We can see that , the high pressure section (HPC) at ambient pressure (101.3 kpa) and the low pressure segment (LPC) will work at 30 kpa.
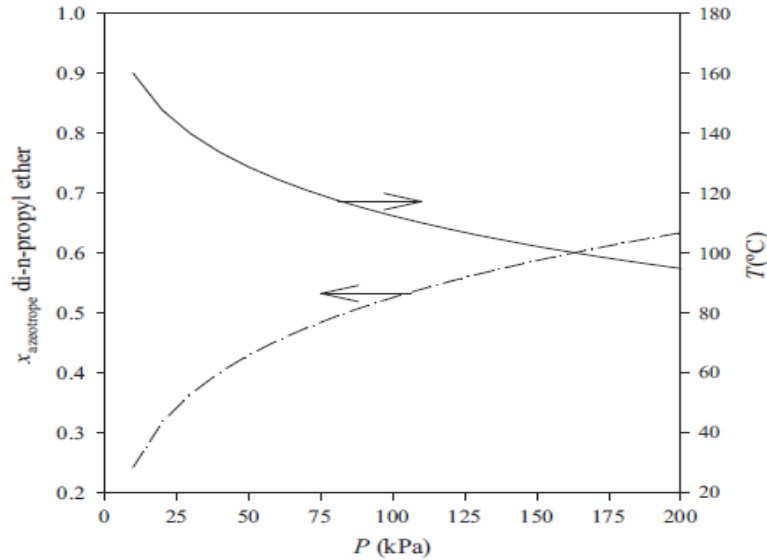
Fig-6 DPE mole fraction and temperature of the azeotrope as a function of pressure.

3.3.2. Sequencing of The Pressure-Swing Distillation Process

The arrangement is framed any two segments working at different pressures, when a binary mixture which is pressure sensitive least breaking azeotrope is introduced [20]. As shown in fig. 6 we have a parallel mixture forming a pressure sensitive minimum boiling azeotrope the partition acts as shown in the above fig. in the T-xy curve. . From Fig. 7 the new feed, F_0, is blended with the recycled stream from the second segment to structure the feed stream, F_1, to the first section, which works at 30 kPa. Since F_1 misleads the left of the azeotrope at 30 kpa, unadulterated n-propyl liquor could be acquired as a lowest part item, B_1 and a mixture close to the azeotropic arrangement at 30 kPa is the distillate, D_1. Stream D_1 is the feed stream to the following segment with distinctive pressure, for this situation 101.3 kpa. Since F_2 ($\sim= D_1$) now is in the right of the azeotrope at 101.3 kPa, the other pure component segment, di-n propyl ether, can recuperated in the lowest part product stream, B_1, and a close azeotropic mixture turns into the distillate, D_2, for reusing in the first section.

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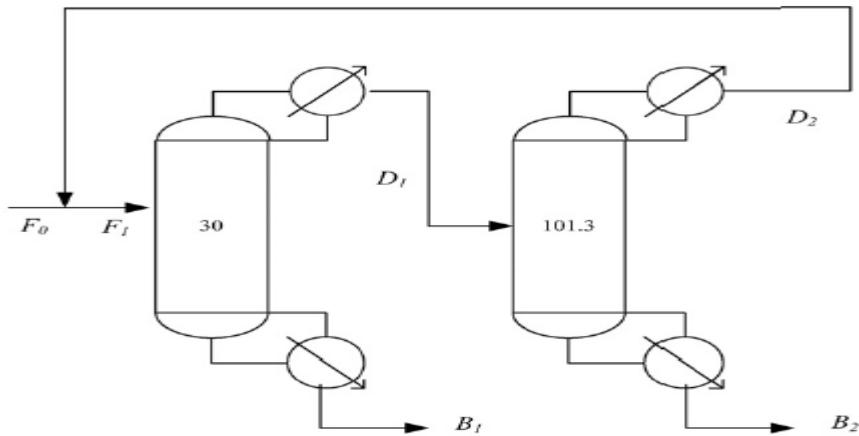
Fig-7 Pressure swing distillation sequence

Fig. 8 shows the pressure-swing succession for the division of DPE from PA. here our feed enters from the LPC at a relatively low pressure of 30kPa and the distillate which we are getting has a composition close to the minimum boiling azeotropes. The feed for the HPC is the distillate from the LPC at a higher pressure of 101.3kPa. where it forms a higher boiling azeotrope so we adopts methods for higher boiling azeotropes. The composition of the distillate is close to the feed composition so it is recycled back to blend with the feed to LPC . . High purified of PA (99 molar %) is processed as a bottom stream from the LPC and DPE (99 molar %) is generated as a lowest part stream from HPC
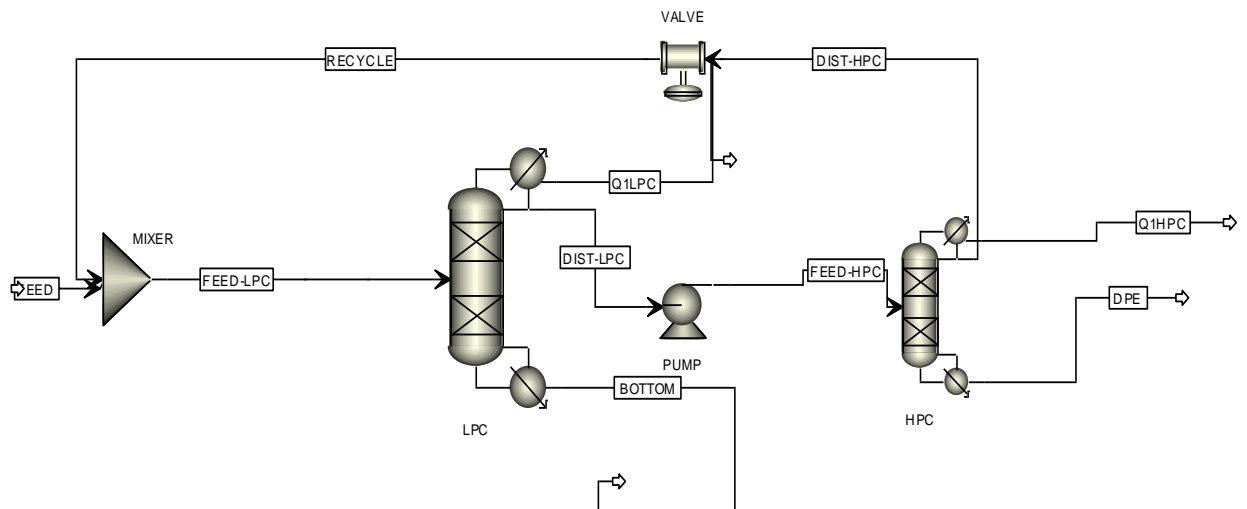
Aspen plus flow diagram for pressure swing distillation.

3.3.3. **Input Variables**

Table 1- Design variables in the pressure-swing distillation process

	Variable	Specification
Binary Feed	T (°C)	50.0
	Flow (kmol/h)	18.50
	Composition	50% DPE
(LPC)	P (kPa)	30.0
	PA bottom purity (molar %)	99.0
(HPC)	P (kPa)	101.3
	DPE bottom purity (molar %)	99.0

In table 1 we have listed all the variables that are required for the simulation. There are two types of variables which can be chosen one is optimization variables and the other is design variables. The values of the design variables are set by physical properties or by market demands. For our case design variables are flow rate ,composition operating pressure, bottom purity etc. Once the design variables are specified there values remains intact during whole process. Optimization variables are those whose values we have to choose arbitrarily to reach the optimum results. For this case we can say that the optimization variables are no. of stages, flow rate, distillate composition etc.

Table-2 Input variables for feed and feed to low pressure column for pressure swing distillation are given.

Feed		Feed LPC	
Temperature (°C)	30.0	Temperature (°C)	53.00
Pressure (kPa)	101.3	Pressure (kPa)	30.0
Molar flow (kgmole/h)	18.50	Molar flow (kgmole/h)	41.05
Molar fraction (DPE)	0.500	Molar fraction (DPE)	0.6000
Molar fraction (PA)	0.500	Molar fraction (PA)	0.4000

Table-3 Input variables for the feed to HPC and recycled feed to the mixer

Distillate HPC		Distillate LPC	
Temperature (°C)	52.76	Temperature (°C)	51.75
Pressure (kPa)	30.00	Pressure (kPa)	29.00
Molar flow (kgmole/h)	22.67	Molar flow (kgmole/h)	31.84
Molar fraction (DPE)	0.6740	Molar fraction (DPE)	0.7650
Molar fraction (PA)	0.3260	Molar fraction (PA)	0.2350

3.4 **Extractive Distillation**

Extractive distillation has the characteristic burden of bringing a third segment into the framework (the dissolvable) that will show up in the item streams, which essentially must be recuperated. Along these lines, the extractive framework must show noteworthy financial focal points over the pressure-swing framework to settle on it the procedure of decision.

3.4.1 **Solvent Selection**

Since the selection of solvent is the centre of extractive distillation, more consideration ought to be paid on the choice of potential solvents.

The extractive agent should have the following characteristics:
- Lesser volatility then the component volatility
- The relative volatility of the mixture should be increased
- Should not form azeotrope with the other part of the mixture
- Largely available
- Cheap

The Selectivity of solvents can be expressed as:
$S_{ij} = (\alpha_{ij})^T/(\alpha_{ij})^B$
Where
$(\alpha_{ij})^T$ is relative volatility for ternary mixture
$(\alpha_{ij})^B$ is relative volatility for binary mixture

At low pressures the selectivity can be written as

$S_{ij} = (\Upsilon_i/\Upsilon_j)^T/(\Upsilon_i/\Upsilon_j)^B$
Where (Υ_i and Υ_j are activity coefficient.
At infinite dilution the selectivity can be rewritten as:
$S_{ij}^\infty = (\Upsilon_i^\infty/\Upsilon_j^\infty)^T/(\Upsilon_i^\infty/\Upsilon_j^\infty)^B$

In an exhaustive study to discrete the DPE + PA azeotropic mixture with diverse solvents. Table 4 demonstrates to a few aspects of the diverse solvents. It might be watched that N, N-dimethylformamide is, past all uncertainty, the best dissolvable contemplated with a specific end goal to attain the division, despite the fact that 2-ethoxyethanol could be a great dissolvable. But, concurring natural(environmental) viewpoints (2-ethoxyethanol is significantly less forceful than N, N dimethylformamide) it was chosen to made the investigation of the extractive refining with 2- ethoxyethanol as entrainer.

Table 4 – Normal Boiling point and selectivity of different solvents for DPE+PA separation.

Solvent	T_{eb}	S^{∞}_{ij}
1-Pentanol	408.53	1.93
n-Butyl Propionate	416.69	0.799
N,N-dimethylformamide	420.58	5.1
2-Ethoxy ethanol	403.96	2.77

3.4.2 **Sequencing of Extractive Distillation Process**

After the entrainer has been chosen, consideration is directed to the arrangement of the distillation sections. The methodology arrangement is indicated in Fig. 9, in which the solvent is included at the top trays of the extractive section (EC). Since 2-ethoxyethanol is substantially less volatile than either DPE or PA, it streams down the section, dragging to PA, to leave with the base item.

The solvent recovery column (SRC) evacuates PA from 2- ethoxyethanol. This is a simple division on the grounds that the solvent is significantly less volatile than PA. The lean solvent is then cooled and reused again to the extractive segment. In the event that the recuperation of the solvent, in this section, is high a little measure of solvent make-up is obliged to keep up the solvent to feed degree constant.
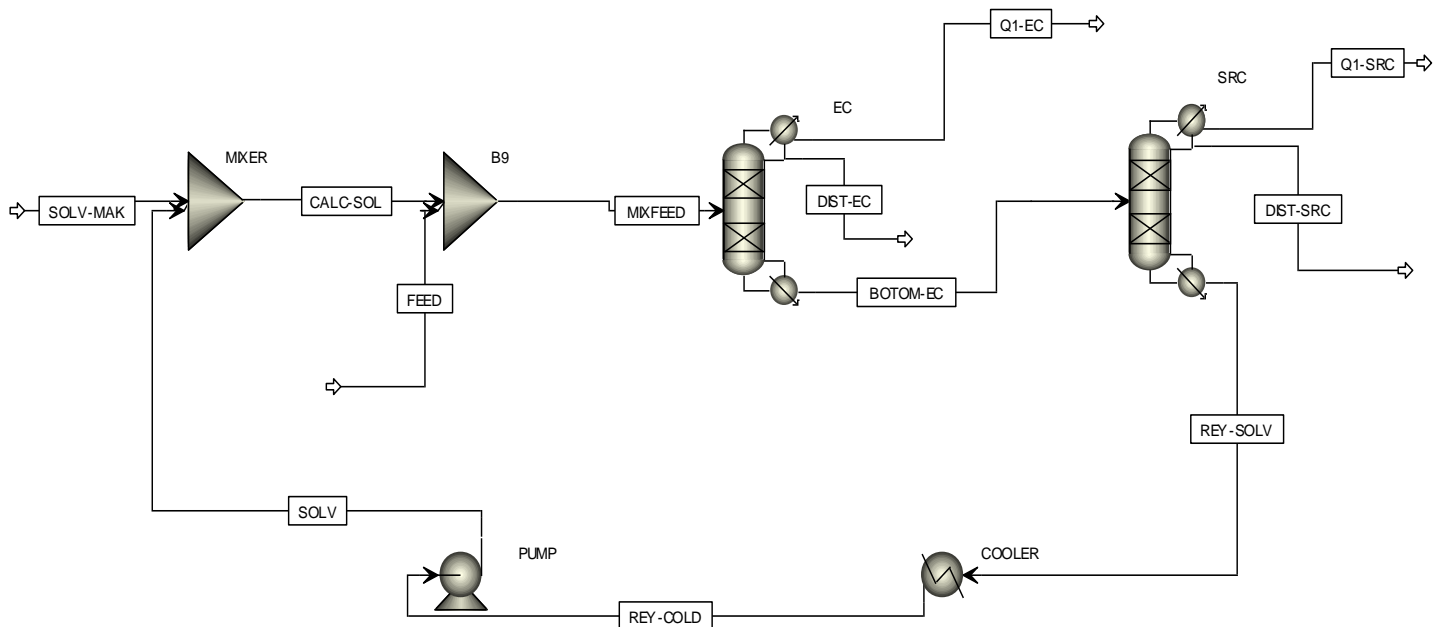
Fig-9 Aspen plus flow diagram for Extractive distillation.

3.4.3 **Input variables**

Table-5 Input conditions of feed and solvent entering into extractive distillation process.

Feed		Solvent	
Temperature (°C)	90.00	Temperature (°C)	95.0
Pressure (kPa)	101.3	Pressure (kPa)	101.3
Molar flow(kgmole/h)	18.50	Molar flow(kgmole/h)	35.20
Mole fraction(DPE)	0.5000	Mole fraction(DPE)	0.000
Mole fraction(PA)	0.5000	Mole fraction(PA)	0.9997
Mole fraction (Solvent)	0.000	Mole fraction (Solvent)	0.0003

Table-6 Input variables for make-up solvent

Solvent Make-Up		Distillate EC	
Temperature (°C)	33.00	Temperature (°C)	92.3
Pressure (kPa)	101.3	Pressure (kPa)	101.3
Molar flow(kgmole/h)	0.1390	Molar flow(kgmole/h)	9.31
Mole fraction(DPE)	0.000	Mole fraction(DPE)	0.0012
Mole fraction(PA)	0.000	Mole fraction(PA)	0.99
Mole fraction (Solvent)	1.000	Mole fraction (Solvent)	0.008

Table 5 and 6 shows the input variables of the feed entering, solvent and the recycled solvent entering into extractive distillation column. In this simulation we are using 2 ethoxyethanol as the solvent as it is much less volatile then propyl alcohol. Because of this it comes down with the solvent as the bottom product which can be separated easily.

Table-7 Specifications of design variables in the extractive distillation

Feed Streams	Variables	Specifications
Binary feed	Temperature (°C)	85
	Molar flow (kmol/h)	18.50
	Molar Composition	50% DPE
Solvent make-up	Temperature (°C)	25
	Molar Composition	100% 2-ethoxy ethanol
Extractive column Distillation	Purity of DPE (molar %)	99.0
	Recovery of DPE	99.9%
Solvent recovery column distillation	Purity of PA (molar %)	99.0
	Recovery of PA	99.9%

4. **RESULTS AND DISCUSSIONS**

Both the processes i.e. extractive distillation and pressure swing distillation are very much helpful in separating azeotropic mixtures as they are hard to separate by narmal distillation processes.

4.1 **Results For pressure swing Distillation**

Table 8 – Stream wise simulation results for pressure swing distillation

Stream ID		BOTTOM	DIST-HPC	DIST-LPC	DPE	FEED	FEED-HPC	FEED-LPC	Q1HPC	Q1LPC	RECYCLE
						pfd					
Temperature	K	376.9	376.9	376.9	376.9	326.2	459.3	376.9			505.0
Pressure	N/sqm	155000.00	155000.00	155000.00	155000.00	30000.00	29000.00	30000.00	155000.00	155000.00	30000.00
Vapor Frac		1.000	1.000	1.000	1.000	1.000	0.000	1.000			1.000
Mole Flow	kmol/sec	0.008	0.004	0.008	0.004	0.011	0.008	0.015	0.000	0.000	0.004
Mass Flow	kg/sec	0.777	0.388	0.777	0.388	1.165	0.777	1.553	0.000	0.000	0.388
Volume Flow	cum/sec	0.154	0.077	0.154	0.077	1.031	0.002	1.588	0.000	0.000	0.532
Enthalpy	MMBtu/hr	-7.925	-3.608	-7.925	-3.963	-12.242	-7.925	-15.850			-3.608
Mole Flow	kmol/sec										
DIISO-01		0.008	0.004	0.008	0.004	0.011	0.008	0.015			0.004
PROPANOL											
WATER											

As can be seen from the above table we can see the respected mole fraction of DPE in the respected units and the remaining fraction will be of propanol in the units. Also, we can see the Enthalpy ,pressure and temperature in all the units.
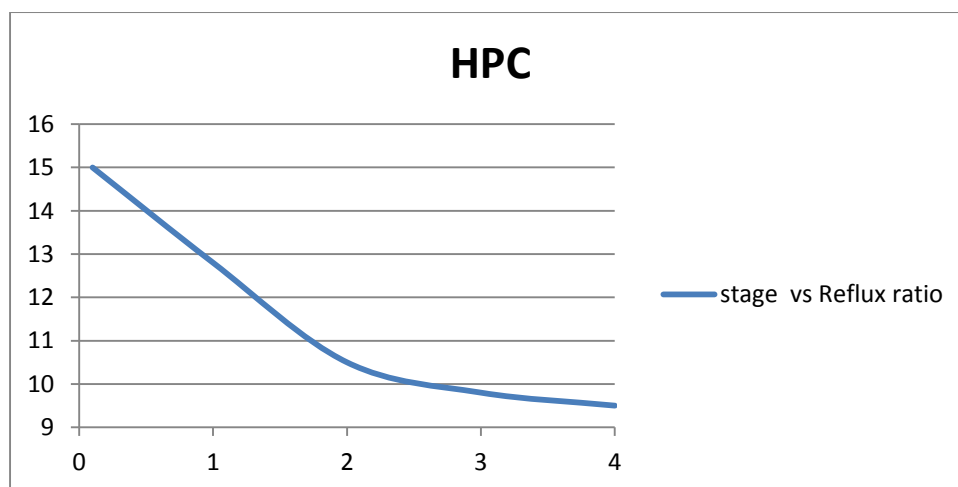
Fig-10 variation of stage no.vs reflux ratio of HPC
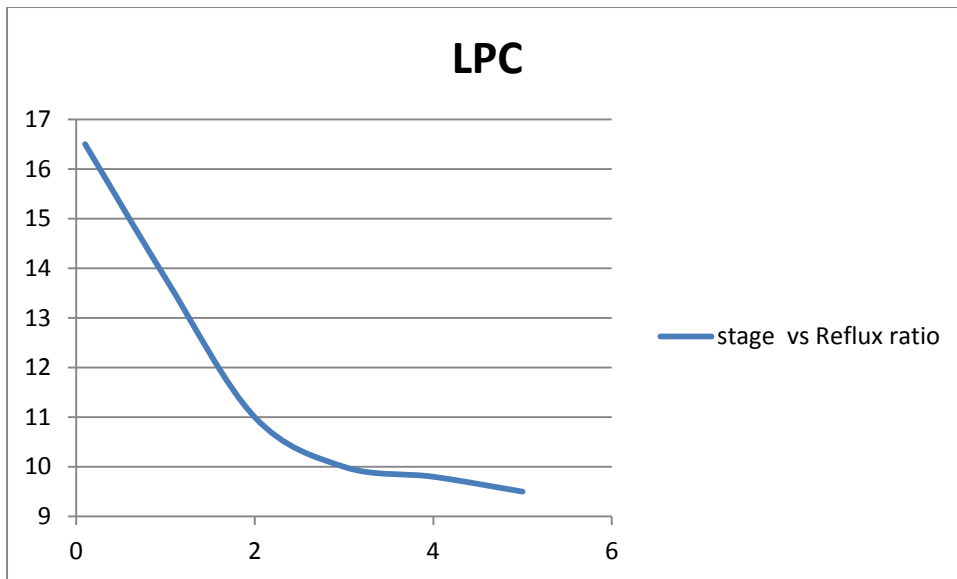
Fig-11 variation of stage no. vs reflux ratio of LPC

From the above graph we can see the variation of the stage with the reflux ratio and we observe that the stage no. decrease with the increase in the reflux ratio.

Table 9 Stream results of mixer

pfd				
Stream ID		RECYCLE	FEED	FEED-LPC
Temperature	K	505.0	326.2	376.9
Pressure	N/sqm	30000.00	30000.00	30000.00
Vapor Frac		1.000	1.000	1.000
Mole Flow	kmol/sec	0.004	0.011	0.015
Mass Flow	kg/sec	0.388	1.165	1.553
Volume Flow	cum/sec	0.532	1.031	1.588
Enthalpy	MMBtu/hr	-3.608	-12.242	-15.850
Mole Flow	kmol/sec			
DIISO-01		0.004	0.011	0.015
PROPANOL				
WATER				

Table 10 Stream results of Valve

pfd			
Stream ID		DIST-HPC	RECYCLE
Temperature	K	376.9	505.0
Pressure	N/sqm	155000.00	30000.00
Vapor Frac		1.000	1.000
Mole Flow	kmol/sec	0.004	0.004
Mass Flow	kg/sec	0.388	0.388
Volume Flow	cum/sec	0.077	0.532
Enthalpy	MMBtu/hr	-3.608	-3.608
Mole Flow	kmol/sec		
DIISO-01		0.004	0.004
PROPANOL			
WATER			
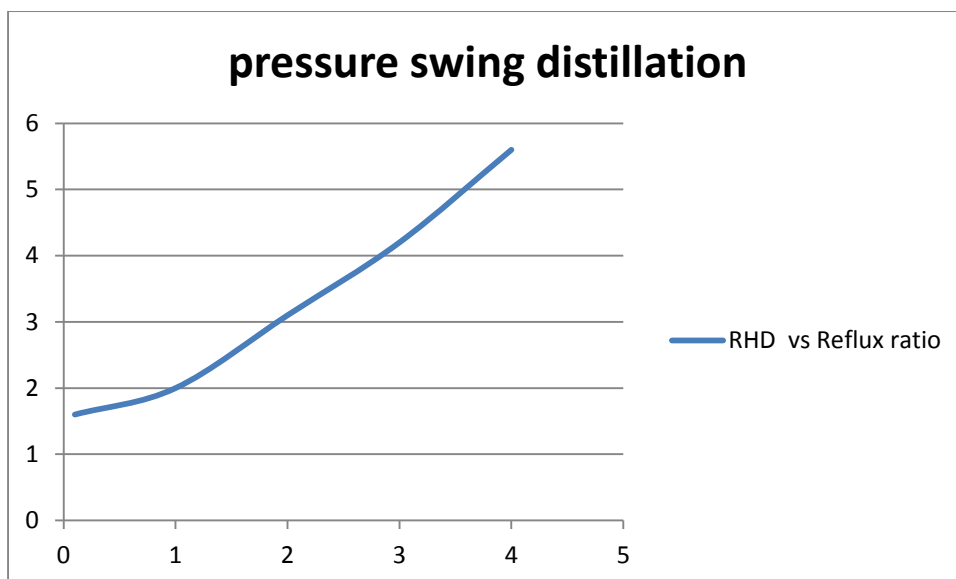
Fig.12- variation of RHD as a function of reflux ratio

Table 9 and Table 10 shows the stream results of the mixer and valve .From table 9 we can see that the outlet temperature of the fresh feed and the recycled feed after going through the mixer is around 376.7 and outlet pressure is 30 kPa. And, from table 10 we can see that the outlet pressure of the valve is 30kPa and the pressure drop across the valve is around 125 kPa as the distillate HPC is entering at 155 kPa and leaving at 30 kPa.

4.2 **Results for Extractive Distillation**

Table 11- Stream wise simulation results for extractive distillation

StreamID		BOTOM-EC	CALC-SOL	DIST-EC	DIST-SRC	FEED	MIXFEED	Q1-EC	Q1-SRC	REY-COLD	REY-SOLV	SOLV	SOLV-MAK
						Extractive Distillation							
Temperature	K	370.5	363.2	347.1	369.8	358.1	361.0			370.4	390.6	370.4	362.9
Pressure	N/sqm	102000.00	101300.00	101300.00	101300.00	101300.00	101300.00	101300.00	101300.00	101100.00	102000.00	101300.00	101300.00
Vapor Frac		0.000	0.000	0.000	0.000	1.000	0.320			0.000	0.000	0.000	0.000
Mole Flow	kmol/sec	0.009	0.010	0.006	0.009	0.005	0.015	0.000	0.000	<0.001	<0.001	<0.001	0.010
Mass Flow	kg/sec	0.539	0.610	0.488	0.516	0.417	1.027	0.000	0.000	0.023	0.023	0.023	0.588
Volume Flow	cum/sec	0.001	0.001	0.001	0.001	0.151	0.145	0.000	0.000	<0.001	<0.001	<0.001	0.001
Enthalpy	MMBtu/hr	-8.861	-10.100	-6.751	-8.491	-4.895	-14.995			-0.373	-0.369	-0.373	-9.726
Mole Flow	kmol/sec												
DIISO-01		<0.001	trace	0.003	<0.001	0.003	0.003			trace	trace	trace	
1-PRO-01		0.009	0.010	0.004	0.009	0.003	0.012			<0.001	<0.001	<0.001	0.010
2-ETH-01		<0.001	<0.001	trace	trace		<0.001			<0.001	<0.001	<0.001	trace
WATER													

As can be seen from the above table we can see the respected mole fraction of DPE in the respected units and the remaining fraction will be of propanol in the units. Also, we can see the Enthalpy ,pressure and temperature ,volume flow and mole flow in all the units. We can also see the concentration of PA, DPE and the solvent in the units.

Table 12- other results in simulation Extractive distillation column.

Minimum reflux ratio:	0.155949
Actual reflux ratio:	0.200647
Minimum number of stages:	2.978053
Number of actual stages:	12
Feed stage:	8.733791
Number of actual stages above feed:	7.733791
Reboiler heating required:	103251.7 Watt
Condenser cooling required:	283928.9 Watt
Distillate temperature:	347.1193 K
Bottom temperature:	370.4843 K

Table 13- other results in simulation solvent recovery column.

Minimum reflux ratio:	0.36959515
Actual reflux ratio:	0.86582742
Minimum number of stages:	7.06359742
Number of actual stages:	12
Feed stage:	6.99556257
Number of actual stages above feed:	5.99556257
Reboiler heating required:	669362.225 Watt
Condenser cooling required:	669165.603 Watt
Distillate temperature:	369.841846 K
Bottom temperature:	390.552472 K
Distillate to feed fraction:	0.9682534

From Table 12 and table 13 we have got the minimum and actual reflux ratio, the amount of heating required in the boiler and cooling for condenser, the feed stage and the respected distillate and bottom temperature of both the extractive distillation column and the solvent recovery column

Fig.13 Variation of RHD with reflux ratio

Extractive Distillation

RHD vs Reflux ratio
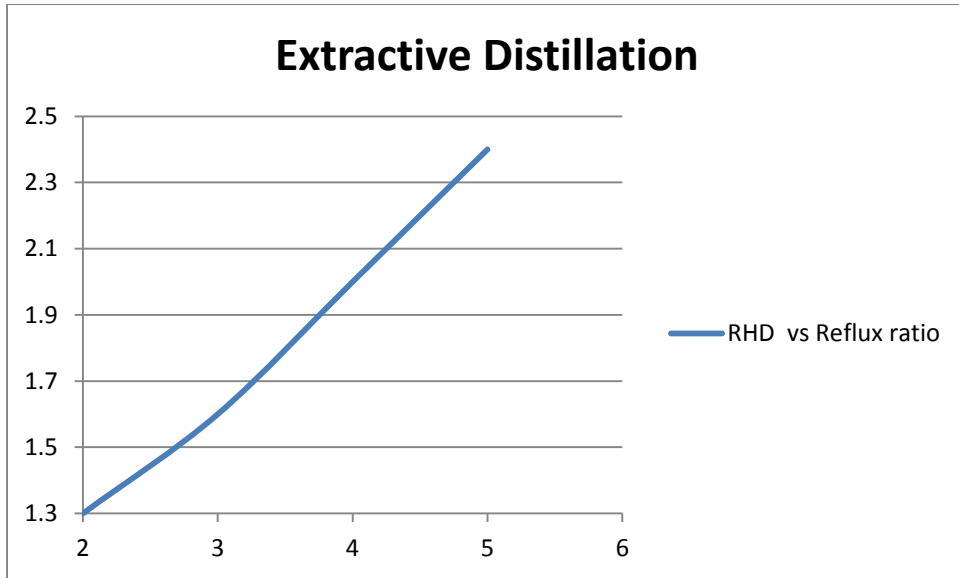
From table 14, we can find the amount of power required electricity required, the head developed and the pump efficiency, from the table we can see the pressure drop across the pump which is about 200N/sqm, and the output volumetric flow is about $2.780*e^{.05}$ cum/sec.

Table 14 - Pump results

Pump results		
Fluid power:	0.00556119	Watt
Brake power:	0.01880957	Watt
Electricity:	0.01880957	Watt
Volumetric flow rate:	2.7806E-05	cum/sec
Pressure change:	200	N/sqm
NPSH available:	62.464012	J/kg
NPSH required:		
Head developed:	0.24462275	J/kg
Pump efficiency used:	0.29565764	
Net work required:	0.01880957	Watt

5. OPTIMIZATION

5.1 PSD Optimization

5.1.1 Partial optimization based on total reboiler heat duty

For optimization we have considered reference variable as total reboiler heat duty. We have to select the best conditions to consider the global economic optimization, so we begin with partial optimization considering some variables and using RHD as reference variable. We can characterize the variables into two categories as optimization variables and design variables. Optimization variables are those whose value needed to be assigned arbitrarily. In case of PSD we can consider number of trays as optimization variable, recycle flow rate and low pressure column distillate composition. The value keeps on changing as we proceed from base to optimization.

The design variables are needed to be assigned once, and they are specified then their value remains unaltered during the process. The design variables selected are flow rate, operating column   pressure, purities of bottom streams, composition, and temperature of binary feed. Table 1 shows the specification chosen for all variables.

Here we are using Aspen plus as our simulation software. First we have to fix the number of trays for both the columns. We consider using shortcut method of aspen plus. We did the initial optimization considering the variation of stage number and reboiler heat duty as a function of reflux ration to calculate the optimum number of trays and feed position for both of the columns. From the graphs below we can see that the ideal number of trays for both the columns should be 12.
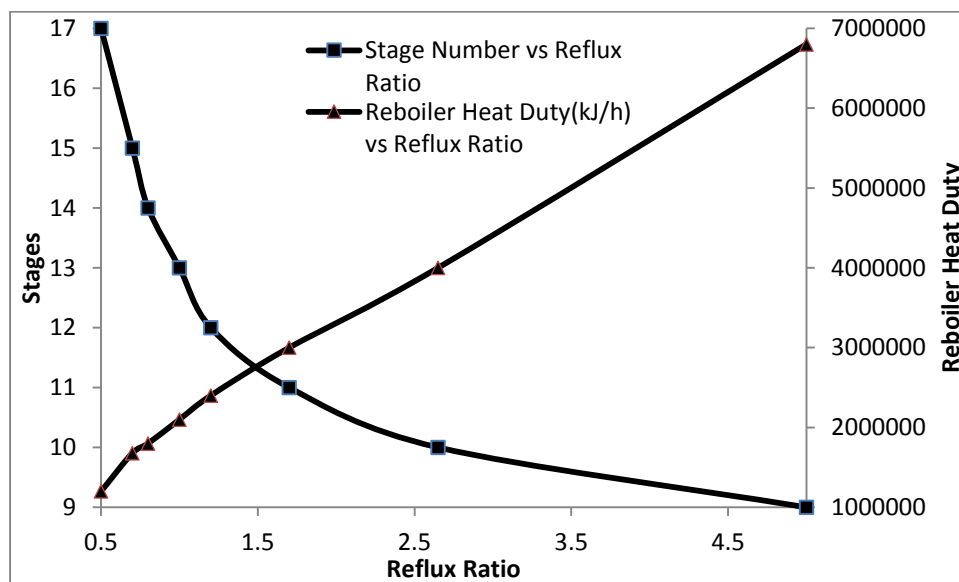
Fig. 14 Stage number and reboiler heat duty as a function of reflux ratio for LPC
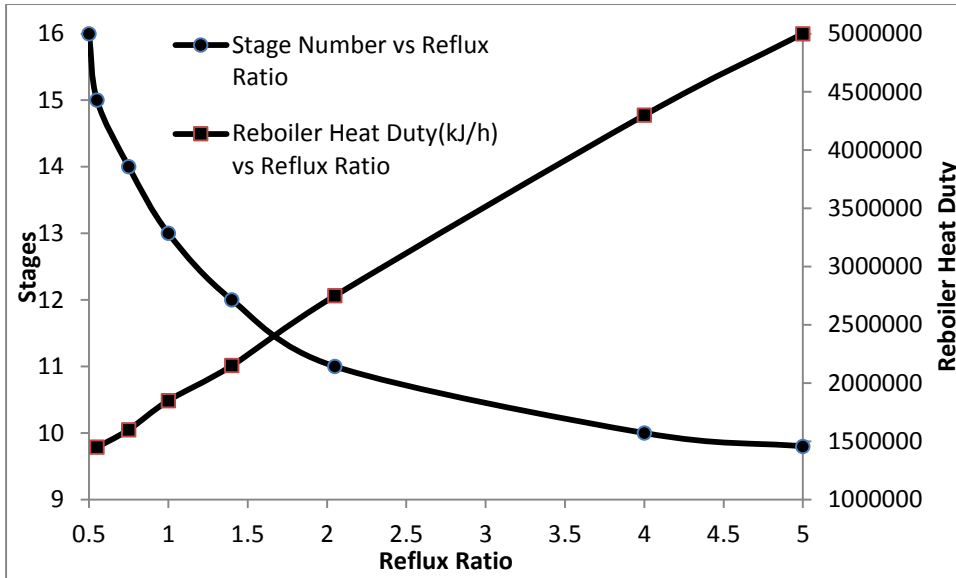
Fig.15 Stage number and reboiler heat duty as a function of reflux ratio for HPC

Once the number of trays are fixed we consider eight cases varying the distillate composition varying from 0.72 to 0.78 and selecting the case which minimizes total reboiler heat duty.From the figure below we can see that the minimum reboiler heat duty occurs at a mole fraction of DPE is 0.765 that is optimum.

Fig. 16 Variation of total reboiler heat duty vs composition

5.1.2 **Economic Evaluation**

Table 15 PSD process global economic optimum

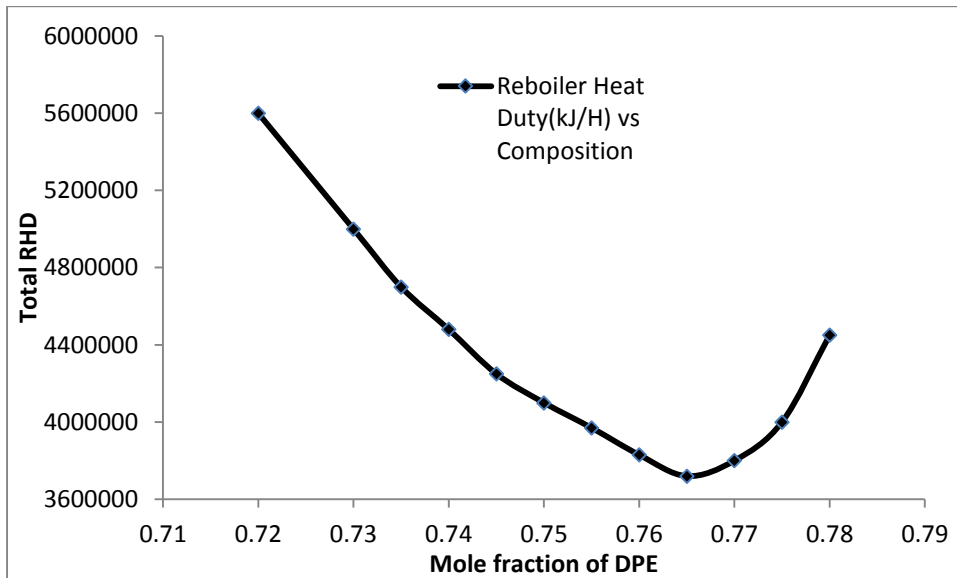| Design Parameter	Low Pressure Column(LPC)	High Pressure Column(HPC)
Number of stages	12	12
Feed(top down stage number)	7	7
Assumed tray efficiency(%)	70	70
Reflux ratio	.75	1.1
Reflux rate(kg/h)	3629.19	4419.51
RHD(kJ/h)	$234.7 \ P \ 10^6$	$247.4 \ P \ 10^6$
Total Annual Cost(TAC) =Rs $489 \ P \ 10^5$		

As it can be seen from Fig 16 the optimum mole fraction is 0.765 of DPE. This is based on minimum reboiler heat duty. We need to calculate total annual costs using the following objective function [21]:

$TAC = C_v + C_f + (i_r + i_m) \cdot FCI$

Where,

C_v : Process variable cost

i_r : Fixed capital recovery rate which is 8.3% corresponding to linear recovery in 12 years.

C_f : Annual fixed costs

I_m : Minimum rate of return assumed to be 13% of FCI

For Economic Evaluation 10 years of project life is considered. Capital investment of each unit is shown in Table 16

Unit	Price(Rs 10^5)
Low pressure Column	
Tower + Trays	336
Reboiler	50.4
Condenser	27.7
Reflux pump	54.6
Reflux vessel	43.6
Vacuum System	89.9
Total	602.2
High pressure Column	
Tower + Trays	319.2
Reboiler	33.6
Condenser	21
Reflux pump	54.6
Reflux vessel	43.7
Total	472.1
Recycled Pump	28.6
Total fixed capital investment for PSD process	1102.9

Hence, the above equation can be rewritten as:

TAC = C$_v$ + 0.30 FCI

Utility prices are shown in Table 17

Utility	Price (Rs)
Low pressure steam(Rs/t)	1000
Electricity(Rs/kWh)	6

5.2 **Extractive Distillation Optimization**

Extractive distillation has a disadvantage of introducing a third material into the system(solvent)that comes in the product streams and needed to be recovered from the product streams. So extractive distillation should show some excellent advantages over pressure swing distillation in order to prefer extractive distillation.

5.2.1 **Partial optimization on the basis of total reboiler heat duty**

As done previously in case of PSD optimization we start with choosing some variables and using total reboiler heat duty as a reference variable. Specifying flow rate, temperature, composition and pressure of binary feed. In addition we also specify distillate purity and recovery of PA in solvent recovery column. We have chosen the design variables shown in Table 7, once they are specified their value remain unchanged during the process.in case of extractive distillation the optimization variables are number of trays and solvent to feed ratio.

As done in the previous case using short cut method for designing we analyse the variation of reboiler heat duty and stage number as a function of reflux ratio.the next plot shows the required plot.
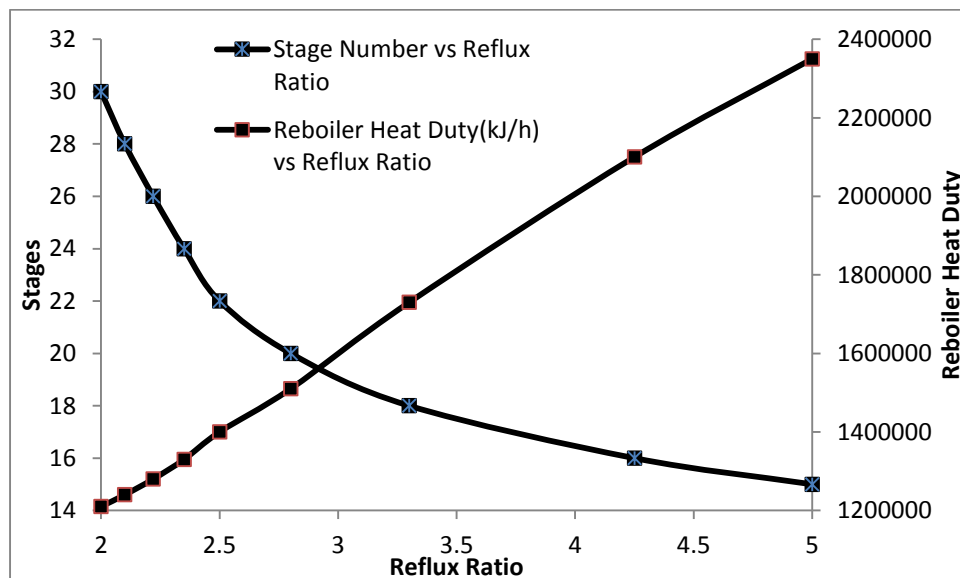

Fig.17 Stage number and reboiler heat duty as a function of reflux ratio for SRC

From the above graph we see that theoretical stage region that minimizes the cost will be located at the point where the curvature is changing most rapidly. So it should lie between 19 to 23. So we can use 22 as ideal no of stages. But since it is a ternary mixture we have to use rigorous method. Considering six different cases varying the tray number from 35 to 55,and considering the best solvent and feed entry stage.the solvent to feed ratio has a significant effect on reflux ratio and so on RHD. Hence in each case the solvent to feed ratio is adjusted so as to get minimum reboiler heat duty.

Table 18 shows the summary of variation of RHD with the tray number and solvent to feed ratio.

Case	Ideal Tray Number	Solvent to Feed ratio	Total RHD(kJ/h)
EC-1	35	3.7	4500000
EC-2	37	3.1	3970000
EC-3	40	2.4	3400000
EC-4	45	1.8	2930000
EC-5	50	1.6	2690000
EC-6	55	1.4	2550000

5.2.2 **Global economic optimization**

As seen from the above table the minimum RHD corresponds to case EC-6 but it require large number of trays which is economically not feasible, therefore we need to carry out the calculation based on minimum TAC. In this case TAC will also include cost of solvent that is 2-ethoxyethanol.therefore taking EC-4 as the most optimum case which meets the design objectives.

Table 19 optimum parameter for ED process

Design Parameter	Extractive Column(EC)	Solvent Recovery Column(SRC)
Number of stages	45	22
Feed(top down stage number)	15	10
Assumed tray efficiency(%)	70	70
Reflux ratio	3.67	2.02
Reflux rate(kg/h)	3445.69	1072.47
RHD(kJ/h)	1.64×10^6	1.17×10^6
Total Annual Cost(TAC) = Rs 768 P 10^5		

Estimated capital investments for the case in ED unit for each unit is shown in Table 20

Unit	Price(Rs 10^5)
Extractive Column	
Tower + Trays	1040
Reboiler	25.2
Condenser	23.5
Reflux pump	58
Reflux vessel	34.4
Total	1181.1
Solvent recovery Column	
Tower + Trays	518
Reboiler	24.3
Condenser	23.5
Reflux pump	60
Reflux vessel	34.4
Total	660
Recycled Pump	28.6
Cooler	35.7
Total fixed capital investment for PSD process	1905

5.3 **ALTERNATIVES COMPARISION**

As we can see from Table 13 and 17 the total annual costs fot the extractive distillation are quite higher than the pressure swing distillation acquired using the same evaluation procedure. These results may seem case of extractive distillation is significantly higher then that of pressure swing distillation unit surprising, since Ed is usually more better then PSD process but we should have appropriate solvent which can easily be recovered.

So if we look at the table of economic results more slowly then we can see that the capital investment value in pressure swing distillation. This huge difference of fixed capital investment led to a good difference in capital investment(mainly fixed capital recovery and minimum acceptable rate of return. By looking at these we can say PSD is more favourable then extractive distillation. On the other hand the cost of steam in case of pressure swing distillation is higher then that in extractive distillation because the reflux rates are higher in the PSD.

Table 21 Economic Results Summary

Cost	Pressure Swing Distillation	Extractive Distillation
Fixed capital investment	1102.9	1905
Cost proportional to FCI	330.87	571.5
Steam	142	104.3
Cooling water	13.4	9.6
Electric power	3	1
Solvent make-up	-	77.3
Total annual costs	489.2	763.7

We have done this optimization for the practical case based on the plant treatment of 12000Tm/year of a DPE+PA mixture. But if we consider larger plants the difference between the both method becomes less and less as in case of PSD the steam costs are higher as they are growing proportional to the flow rate, on the other hand the cost associated with the initial investment will grow much slowly, so the cost become more and more closer. For our case PSD is much more economical then extractive distillation process.

CONCLUSION AND FUTURE WORKS

The simulation of processes with a commercial software program used appropriately is a very powerful tool to analyse the separation of complex mixtures. In this case, steady-state comparisons have been presented of a pressure-swing distillation process and an extractive distillation process to separate the di-n-propyl ether and n-propyl alcohol azeotropic mixture.

The optimization of both pressure swing distillation and extractive distillation has to be carried out by changing the respected variables that are tray number, solvent entry stage and feed entry stage. Also the economic cost of both the processes has been calculated including all the costs i.e. initial investment, running cost and the raw materials cost. Then we have evaluated which process will be better for the separation of di-n-propyl ether and n-propyl alcohol.

The computer simulation and economic evaluation of the two separation alternatives allow us to conclude that, to process 12,000 Tm/year (approximately, 1500 kg/h). We can clearly see that in case of extractive distillation the total annual cost is around Rs 7.64 crores and in case of pressure swing distillation the total annual cost reduces to Rs 490 crores. This difference is mainly because of the large difference in fixed capital investment as in the case of extractive distillation we require large number of plates so the cost increases. But if we consider using very large flow rate and getting large production then we can prefer PSD over ED but here also we have to consider that the solvent cost will also increase. So we can say that the process that uses PSD is much more attractive in terms of steady-state economics.

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