GHG Emissions and Energy Minimization using Heat Integrated Pressure Swing Distillation Sequence (HiPSDS) for the Separation of Azeotropic Mixture

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ABSTRACT

The present work elaborates the process design methodology for the evaluation of the distillation systems based on the economic, exergetic and environmental point of view, the greenhouse gas (GHG) emissions. The methodology proposes the Heat Integrated Pressure Swing Distillation Sequence (HiPSDS) is economic and reduces the GHG emissions than the conventional Extractive Distillation Sequence (EDS) and the Pressure Swing Distillation Sequence (PSDS) for the case study of isobutyl alcohol and isobutyl acetate with the solvents for EDS and with low pressure variations for PSDS and HiPSDS. The study demonstrates that the exergy analysis can predict the results of the economic and environmental evaluation associated with the process design.

Keywords: *EDS, PSDS, HiPSDS, Simulation, GHG emissions*

1. INTRODUCTION

Energy consumption and Greenhouse gas (mainly carbon dioxide) emissions are strongly related in distillation. Therefore, to meet the environmental targets as per the Kyoto protocol, reducing the carbon dioxide emissions is the absolute necessity and an expensive challenge in the chemical process Industries. Effort should be focused on energy savings techniques and carbon dioxide emissions to meet the stringent environmental specifications. The research efforts are mostly at increasing the heat integration within the distillation unit[1]. The use of columns with the thermal coupling has received the considerable attention in recent years, with a special development reported for the case of separation of ternary mixtures[2]. Thermally coupled distillation systems are obtained through the implementation of interconnecting streams (one in the vapor phase and the other one in the liquid phase) between two columns; each interconnection replaces one condenser or one reboiler from one of the columns, thus providing potential savings in the capital investment[3]. Through proper selection of the distillation sequence among the Extractive Distillation Sequence (EDS)[4], Pressure Swing Distillation Sequence (PSDS) and the Heat Integrated Pressure Swing Distillation Sequence (HiPSDS), significant energy savings and reduction in CO_2 emissions with respect to energy consumptions of the conventional extractive distillation sequence can be obtained. Plenty of literature is available analyzing the relative advantages of distillation for the ternary separations with the equilibrium and non-equilibrium stage models.

The separation methods like extractive distillation used to separate compounds with similar or close boiling points or the compounds which forms azeotropes, by using an additional entrainer to alter the relative volatility. Thus, it is possible to obtain one pure compound at the top of the column and the other, together with the entrainer component at the bottom, which may be separated easily in the secondary distillation column, due to the high boiling point of the entrainer. Extractive Distillation is widely used in several different chemical engineering processes. Pressure Swing Distillation Sequence uses the behavior of the molecules in the low pressure region. In this type of distillation, the azeotropic composition is either break or can be altered to some desired level for the separation to occur[5]. In this paper, we have studied the purification of isobutyl alcohol and isobutyl acetate using conventional EDS, PSDS, HiPSDS and using Dimethylsulfoxide (DMSO)[6], *1*-Hexanol and *n*-Butyl Propionate as an entrainers for the EDS. The results show that the PSDS is more economic than the conventional EDS but the greenhouse gas emissions are more in case of the conventional PSDS. We have shown using CHEMCAD design, simulation and optimization, the same greenhouse gas emissions and the energy requirement can be reduced to the acceptable range and the economic viability using the HiPSDS [7].

2. Case Study:

The feed is a mixture of isobutyl alcohol and isobutyl acetate, with a flow rate of 8000 working hours per year and the mass flow of 1500 kg/hr to 3600 kg/hr. Isobutyl acetate (IBAc) is a solvent widely used in Chemical Industry. It is used alone or in solvent blends in application including coating, inks, adhesives, industrial cleaners and degreasers. The IBAc is produced by etherification of acetic acid with isobutyl alcohol (IBA) in presence of Amberlite IR-120.

$$CH_3COOH + (CH_3)_2CH_2CH_2OH \\ \rightarrow CH_3COOCH_2CH_2(CH_3)_2 + H_2O$$
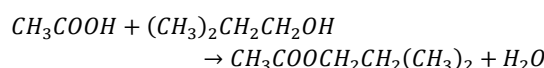
Final purification of acetate by traditional technologies is a relatively complex procedure due to the existence of minimum boiling point azeotrope in the IBA and IBAc mixture at atmospheric pressure[8].

3. Design of Extractive Distillation Sequences

The extractive distillation experiments in the laboratory are time consuming and expensive because of the large number of parameters involved. It would be desirable to predict the experimental data with the help of available simulation programs [3]. Computer simulations using the process simulators have been used with success as an aid for the process development as shown in Fig.
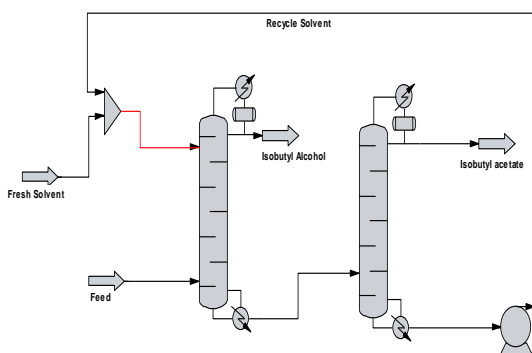
Figure 1. CHEMCAD Simulated flow diagram of Extractive Distillation Sequence

They were used to set up the guidelines for further pilot plant experiments and to optimize the operating parameters governing the process at steady state [9]. The synthesis and design of extractive distillation processes take place in two steps. The first one involves the selection of one or more candidate solvents (which facilitate the separation by changing the relative volatilities in the mixtures through physical or chemical interactions with the original components), and the choice of one or more columns configurations. The second step, process design, involves the search for optimal process parameter values. The success of the second step depends on the solutions obtained for the first step because, efficiency in the extractive distillation is determined by the choice of suitable entrainer [2].

4. Design of Pressure Swing Distillation Sequences (PSDS and HiPSDS)

The preliminary design for the distillation systems starting from the design aspects of the conventional distillation columns. The design of the recycle pressure swing distillation column sequence is obtained by using the conventional direct sequence of the distillation columns as shown in Fig 2.
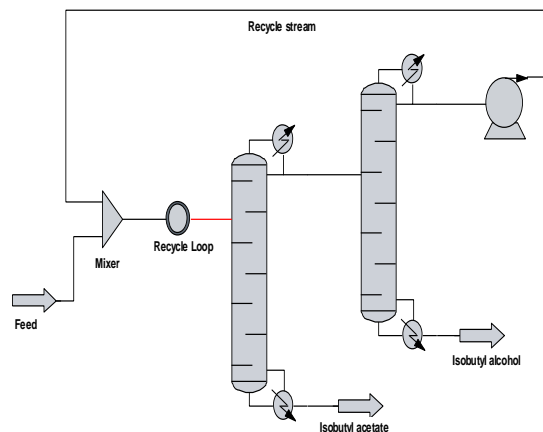
Figure 2. CHEMCAD simulated flow diagram of Pressure Swing Distillation Sequence

After the tray arrangement for the Extractive and Pressure Swing Distillation Sequence (EDS and PSDS), an optimization procedure is used to minimize the heat duty supplied to the reboilers of the schemes called as Heat Integrated Pressure Swing Distillation Column Sequence (HiPSDS), taking the constraints imposed by the required purity of the product streams i.e. the desired product purity required for isobutyl alcohol is 98.5 % and for isobutyl acetate 99.5 % are the constraint for the optimization of the sequences (Berg et al, 1988). The degree of freedom after design specifications and tray arrangement are used to obtain the operating conditions that provide minimum energy consumption [10].

Rigorous model for the simulation of the schemes with the proposed tray specification is solved. In this study, CHEMCAD was used for the simulation. If product compositions and desired separations are obtained within the specified number of trays with reflux ratio, then the design is appropriate or the design should be simulate once again with the appropriate adjustment within the process parameters. With the optimized design of the EDS, PSDS and HiPSDS, thermodynamic efficiencies can be calculated with the help of thermodynamic principles.

5. Thermal Analysis:

With the optimized design of the extractive and pressure swing distillation schemes, thermodynamic efficiencies can be calculated using the laws of thermodynamics.

Energy Conservation:

$$\sum_{output} (nh + Q + Ws) - \sum_{input} (nh + Q + Ws) = 0 \ldots\ldots\ldots (1)$$

Entropy Analysis:

$$\sum_{output} \left(ns + \frac{Q}{Ts}\right) - \sum_{input} \left(ns + \frac{Q}{Ts}\right) = \Delta Sirr \ldots\ldots (2)$$

Exergy balance:

$$\sum_{output}\left[nb + Q\left(1 - \frac{To}{Ts}\right) + Ws\right] - \sum_{input}\left[nb + Q\left(1 - \frac{To}{Ts}\right) + Ws\right] = LW \dots \dots (3)$$

Minimum work of separation:

$$Wmin = \sum_{output} nb - \sum_{input} nb \dots \dots (4)$$

Second law efficiency:

$$n = \frac{Wmin}{LW + Wmin} \dots \dots \dots (5)$$

6. Calculation of CO₂ emissions:

In distillation systems, carbon dioxide is generated mainly from furnaces, gas turbines, and boilers. These utility devices are the fuel consumers and are used to provide heat, stream and power to the process by burning a fuel. Therefore, these units are key drivers in energy savings oriented projects and for reducing environmental impact of emissions. Fuel is combusted when mixed with air, producing CO_2 according to the following stoichiometric equation:

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 \frac{y}{2}H_2O \dots \dots (6)$$
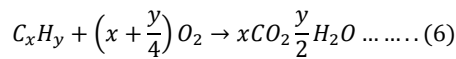
Where x and y denotes the number of carbon, *C* and hydrogen, *H* atoms, respectively, present in the fuel compositions and where complete oxidation of carbon is assumed.

In the combustion of fuels, air is assumed to be in excess to ensure complete combustion, so that no carbon monoxide is formed. CO_2 emission (kg/s) are related to the amount of fuel burnt, Q_{Fuel}(kw), in a heating device as follows

$$[CO_2]_{Emiss} = \left(\frac{Q_{Fuel}}{NHV}\right)\left(\frac{C\%}{100}\right)\alpha \dots \dots (7)$$

Where α is the ratio of molar masses of CO_2 and C (α =3.64), while *NHV* (kJ/kg) represents the net heating value of the fuel with carbon content of C %.

Boilers produce steam from the combustion of fuel. This steam is delivered to the process at the temperature required by the process or obtained at a higher temperature and then throttled. In distillation systems, steam is used either for heating purposes, indirectly in reboilers, or as a direct stripping agent in so-called steam distillations. The flame temperature is lower than in a furnace because the heat of combustion is removed immediately to the steam [11]. However, the same theoretical flame temperature, T_{FTB} of 1800⁰C may still be used. The stack temperature, T_{stack} of 160⁰C is also used in the calculations. The amount of fuel burnt can be calculated as

$$Q_{Fuel} = \frac{Q_{Proc}}{\lambda_{Proc}}(h_{Proc} - 419)\frac{T_{FTB} - T_o}{T_{FTB} - T_{Stack}} \dots (8)$$

Where λ_{Proc} and h_{Proc} (kJ/Kg) are the latent heat and enthalpy of steam delivered to the process. T_{FTB} is the flame temperature of the boiler flue gases.

7. Results and Discussion:

The resulting designs and their performance with respect to energy consumption, CO_2 emissions and thermodynamic efficiency are the preliminary aim of the study. To compare the behavior of the sequences, mixtures of isobutyl alcohol and isobutyl acetate were considered which forms the minimum boiling azeotrope. The number of ideal stages, the feed stage and the initial extractant stage in the EDS, PSDS and HiPSDS were set after the optimization of the structure of the conventional sequences were carried out. These parameters enabled a successful separation of the azeotropic mixtures of isobutyl alcohol and isobutyl acetate. The NRTL, UNIQUAC and the group contribution method UNIFAC models were used to describe thermodynamic properties. Different Extractant/Feed (E/F) ratios using DMSO [12], 1-hexanol, Butyl propionate were investigated for the EDS and various vacuum ranges for the PSDS and HiPSDS. The design pressure for each separation was chosen to ensure the use of cooling water in the condensers. The pressure drop for a single tray is given based on the heuristics. Purities of 99.5% in mole in the products were assumed for isobutyl acetate and 98.5% for isobutyl alcohol.

Table 1. Design variables for EDS and PSDS

Design variables	Extractive Distillation Sequence (EDS)		Pressure Swing Distillation Sequence (PSDS) and HiPSDS	
	Main Column (kPa)	Solvent Recovery Column(SRC) kPa	High Pressure Column (HPC)	Low Pressure Column (LPC)
Pressure kPa	110	101	101.3	22
No. of stages	50	30	30	16
Feed stage	35	13	8	4
Solvent entry stage Optimum	8	-	-	-

Design and energy optimization of the conventional sequences for the feed mixtures were carried out using the procedure previously described.

**Table 2. Optimum solvent to feed ratio for the (EDS)**

Sr. No.	Solvent /Feed	No. of Trays	Solvent Entry Stage	Feed Entry Stage	Reboiler Heat Duty (MJ)
1	3.0	35	7	24	5646
2	2.0	40	7	30	4562
3	1.33	50	8	35	3350
4	1.00	60	9	42	3094
5	0.9	70	10	50	2823

Typical optimization curves for the EDS, PSDS and HiPSDS are shown in Fig 3 to Fig 6 respectively, where the optimal value for the separation can be determined in order to guarantee the minimum energy consumptions.
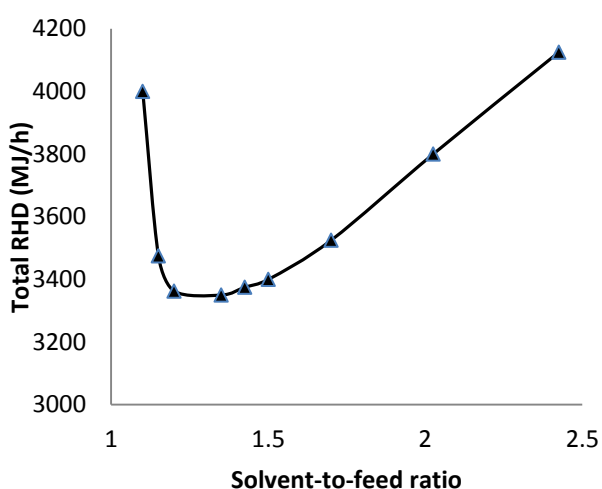

Figure 3. Total reboiler heat duty vs solvent to feed ratio in extractive distillation process

The optimization curves shows an interesting effect of the search variables on energy consumption. The design is sensitive, in terms of its energy consumption. An implication of this observation has to do with operational considerations. Tray arrangements and some important design variables for that sequence after the optimization has been carried out.
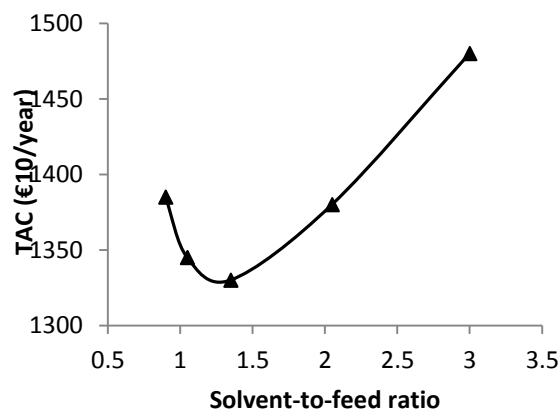
Figure 4. Total annual cost vs solvent to feed ratio in extractive distillation process

The results of the rigorous optimization are collected for the Extractive (EDS) and pressure swing distillation (PSDS) configurations, indicating the effect of solvent feed ratio (E/F) on energy consumption, economic evaluation, CO_2 emissions of the studied configurations. The results can be summarized as follows: i) increasing solvent feed ratio of the complex extractive distillation systems causes a reduction of energy savings in comparison with the conventional distillation sequence, and consequently the total annual cost will be increased; ii) the energy savings achieved by HiPSDS are in the considerable range in contrast to the conventional arrangement; iii) the second law efficiency of the pressure swing distillation is higher than that of the corresponding conventional extractive distillation option; iv) the reduction in global CO_2 emission, in heat integrated pressure swing distillation is considerable.
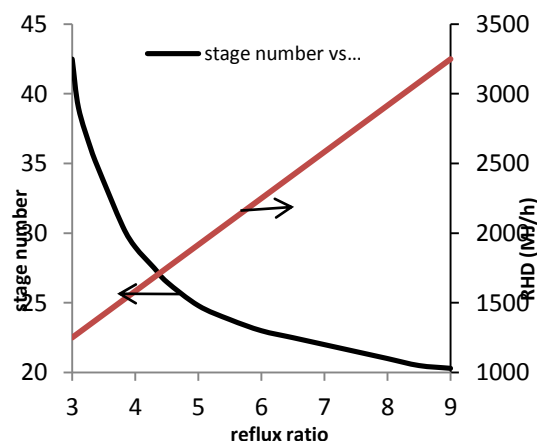
Figure 5. solvent recovery column case study in the Extractive Distillation Sequence.

The inefficiency of the conventional distillation sequences (associated with CO_2 emissions) has been reported as a consequence of remixing.
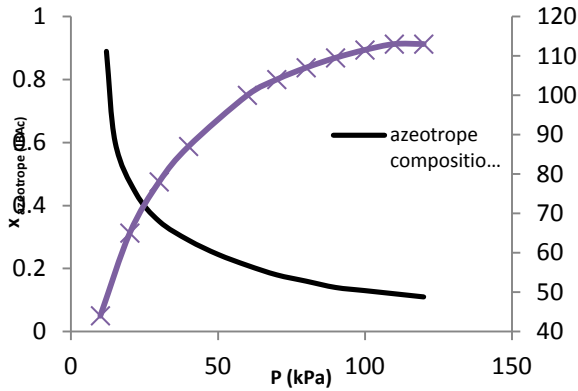
Figure 6. IBAc mole fraction and temparature of the azeotrope as a function of pressure.

Therefore, proper optimization should avoid such a remixing problem. The methodology proposed generates designs where the effect of remixing is eliminated.
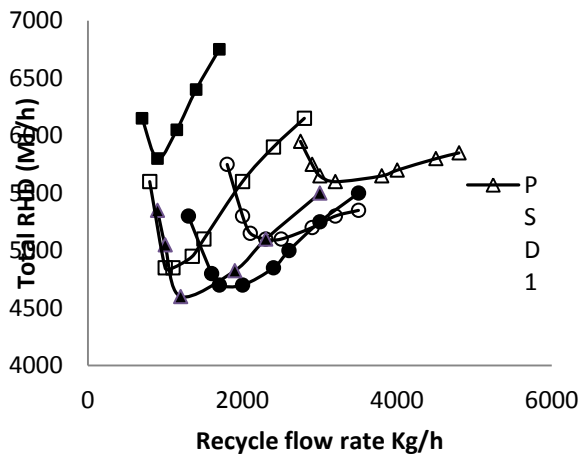

Figure 7. Total reboiler heat duty vs recycle flow rate in pressure-swing distillation process

In general, the results show that the optimization of the thermal link causes significant energy savings, Total Annual Cost (TAC) savings and reduction in CO_2 emissions and which improves the values of efficiencies.

Table 3. Optimum recycle flow rate for the (PSDS)

Sr. No.	HPC Distillate IBA	Recycle Flow Rate (kg/h)	RHD (HPC+LPC) (MJ)
PSD1	0.675	3300	5629
PSD2	0.700	2400	5079
PSD3	0.725	1900	4729
PSD4	0.75	1500	4594
PSD5	0.775	1100	4791
PSD6	0.8	850	5871

Table 4. Results of EDS, PSDS and HiPSDS

Type of Sequences	Energy Consumed (MJ)	TACx10^{-3}	Efficiency	CO_2 Emission (Ton/h)
EDS	3350	1329.95	17.3	1.93
PSDS	4594	990.89	18.09	2.7
HiPSDS	3216	876.99	18.7	1.62

8. Conclusion:

The design and optimization of the recycle PSDS and HiPSDS were studied and compared to those of a conventional extractive distillation sequence. A general energy efficient design procedure has been used that account for CO_2 emissions. The approach optimizes all process conditions in order to achieve energy savings and reductions in CO_2 emissions. Examples have shown that the design procedure can provide all of the operating parameters needed. Some trends were observed: PSDS presented energy and TAC savings over conventional schemes but GHG emissions are more as compared to the EDS. The present scheme presents a reduction in carbon dioxide emissions and energy savings. Regarding thermodynamic efficiency, in all cases, the introduction of thermal links increased its value. The results imply that the proposed heat integrated pressure swing distillation sequence (HiPSDS) can achieve significant energy savings and reduction of CO_2 emissions.

Nomenclature

b	Exergy function
h	Molar enthalpy
LW	lost work
n	Mole flow
Q	Reboiler heat duty
s	Molar entropy
TAC	Total annual cost
T_{FTB}	Flame temperature of the boiler flue gases
T_{stack}	Stack temperature
T_0	Temperature of the surroundings
T_s	Temperature of the system
$Wmin$	Minimum work for the separation
Ws	Shaft work
η	Second law efficiency
λ_{Proc}	The latent heat of steam delivered to the process
h_{Proc}	Enthalpy of steam delivered to the process

9. References

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