POLITECNICO DI TORINO

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Tesi di Laurea Magistrale

Study and optimization of separation process schemes for the production of bio-products from fermentation

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I.1 IFPEN

IFP ENERGIES NOUVELLES (IFPEN) è organismo di ricerca francese inquadrato come ente pubblico a carattere industriale e commerciale (EPIC) creato nel 1944. IFPEN è uno dei principali attori francesi nella ricerca e nella formazione nei settori dell'energia, dei trasporti e dell'ambiente. L'innovazione tecnologica è al centro della sua azione, articolata attorno a tre priorità strategiche: mobilità sostenibile, energie rinnovabili e idrocarburi responsabili, a basso impatto ambientale e a basso consumo energetico. Per essere un attore nella transizione energetica, IFPEN è fortemente coinvolta nello sviluppo di processi biotecnologici finalizzati alla produzione di biocarburanti e intermedi chimici ottenuti per via biochimica.

I.2 Produzione di IBEA

Il butanolo e l'isopropanolo sono attualmente prodotti per via petrolchimica, ma sono previsti sviluppi tecnologici per la produzione per via biotecnologica. La produzione di bio butanolo può essere effettuata anche per fermentazione (processo ABE: Acetone, Butanolo ed Etanolo). Il bio butanolo così prodotto è considerato un biocarburante alternativo. Il processo ABE utilizza un microrganismo puro del genere *Clostridium* ed è stato uno dei primi processi industriali su larga scala che sfrutta microrganismi per la produzione chimica, nonché il più grande processo di fermentazione in condizioni sterili. Mentre l'acetone era una volta considerato uno dei principali prodotti del processo ABE, ora è talvolta visto come un sottoprodotto a causa delle sue scarse proprietà come biocarburante. Poiché una miscela di isopropanolo, butanolo ed etanolo (IBE) è più interessante come biocarburante, si preferisce effettuare la riduzione dell'acetone in isopropanolo utilizzando diversi biocatalizzatori appartenenti al genere *Clostridium*. Il processo di produzione dell'IBEA si basa quindi sul processo di fermentazione ABE e utilizza ceppi del genere *Clostridium* in grado ridurre gran parte dell'acetone ad isopropanolo. Tuttavia, la concentrazione di alcol all'uscita del fermentatore è inferiore a 24 g/L, principalmente a causa dell'inibizione del butanolo. Sono state proposte diverse soluzioni per aumentare la concentrazione di IBE nel brodo di fermentazione. Tuttavia, sono necessari altri metodi di purificazione a valle del processo di fermentazione per ottenere IBE puro. Il sistema più utilizzato è la distillazione. Una volta rimosso l'acetone mediante una prima distillazione, la miscela IBE può essere utilizzata direttamente come biocarburante oppure i tre alcoli possono essere separati a seconda del loro utilizzo. Per quanto riguarda l'isopropanolo, questo è prodotto alla composizione azeotropica. Se è necessario ottenere isopropanolo puro, è necessario utilizzare dei processi di disidratazione per rompere l'azeotropo acqua/isopropanolo. I processi utilizzati sono generalmente la distillazione estrattiva, la pervaporazione o l’adsorbimento.

I.3 Obiettivi

La purificazione di IBEA viene convenzionalmente effettuata per distillazione, ma, date le concentrazioni molto basse nell’alimentazione, i costi di separazione possono essere molto elevati. L'obiettivo principale dela lavoro di Tesi è ottimizzare la sezione di separazione del processo, minimizzandone i costi. L’ottimizzazione è stata effettuata sullo schema di distillazione classico e su uno schema alternativo brevettato da IFPEN. Inoltre, è stato valutato l'impatto delle integrazioni energetiche su questi due processi. Un altro obiettivo è stato quello di studiare i diversi metodi di disidratazione dell'IPA. Infatti, entrambi i processi producono butanolo puro e isopropanolo all’azeotropo con un contenuto d’acqua di circa il 12% in peso. Infine, l'ultimo obiettivo è stato quello di studiare altri due processi (ELL e Diaz), che consentono la pre-concentrazione del brodo di fermentazione prima della distillazione.

II Ottimizzazione dei processi

In questa sezione verranno esaminati i diversi processi utilizzati per eseguire la separazione IBEA. Inoltre, per ogni processo verranno presentati anche i diversi processi di ottimizzazione e l'effetto di alcuni parametri sul costo di separazione. Per le simulazioni sono stati utilizzati la versione 10.2 di PROII e un metodo termodinamico sviluppato da IFPEN.

II.1 Processo di base

Il processo di base per la separazione dell'IBEA è quello mostrato nella ***Figura II.1.1***.

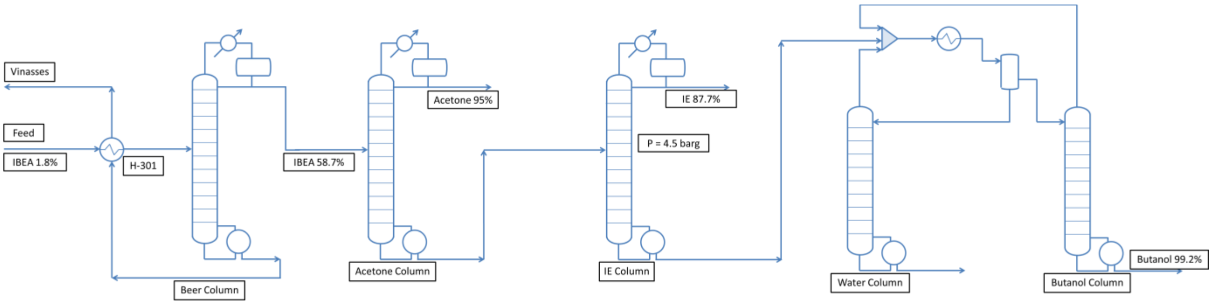


Figura II.1.1 Processo di base per la separazione dell'IBEA

Questo processo utilizza cinque colonne di distillazione per separare i diversi componenti. In particolare, le colonne utilizzate sono:

- **Colonna Birra (C-301)**: recupero di IBEA in alto ed eliminazione dell'acqua al fondo;
- **Colonna Acetone (C-401)**: permette l'eliminazione dell'acetone;
- **Colonna IE (C-501)**: recupero di isopropanolo ed etanolo nella parte superiore e recupero del butanolo al fondo della colonna;
- **Colonna Acqua (C-601) e Butanolo (C-602)**: utilizzate per rompere l'azeotropo acqua/butanolo e recuperare il butanolo puro al fondo della colonna butanolo.

In termini energetici, la colonna che consuma più energia è la colonna C-301. Per lo schema non ottimizzato, il consumo di questa colonna corrisponde all'83% del consumo totale. L'ottimizzazione mira a minimizzare il consumo energetico della C-301 preservando le prestazioni della colonna in termini di recupero IBEA.

II.1.1 Ottimizzazione del processo

Nella prima fase del lavoro si è ottimizzato il numero di stadi della colonna, nonché la posizione dell'alimentazione e la sua temperatura.

Lo schema di base non ottimizzato include un recupero del calore per la colonna C-301, che consiste nel riscaldare l'alimentazione utilizzando il prodotto di fondo della colonna. Questo viene fatto tramite lo scambiatore H-301 con una specifica HOCO (Hot Outlet - Cold Outlet) = 3°C. Poi, tramite un secondo scambiatore (H-303), la temperatura dell'alimentazione viene portata a 112°C. L'idea è quella di inserire l'alimentazione a una temperatura vicina a quella dello stadio di alimentazione.

Nella configurazione di base, la colonna C-301 ha 21 stadi. È stato eseguito uno studio di sensibilità per trovare il numero minimo di stadi necessari per la separazione. L'analisi ha portato ad un numero minimo di stadi pari a 6. Data la relazione:

$$2\, N_{min} < N_{opt} < 3\, N_{min} \tag{1}$$

è stato scelto di utilizzare una colonna C-301 con 15 stadi (2,5 x 6).

Lo step successivo è stato quello di valutare l'influenza della temperatura dell'alimentazione sul consumo energetico della colonna e dello scambiatore H-303. L'analisi di sensibilità è stata eseguita variando la temperatura di alimentazione da 75°C a 115°C. Aumentando la temperatura di mandata, aumentano anche il calore da sottrarre al condensatore e il calore da fornire allo scambiatore H-303. Il calore da fornire al ribollitore, invece, diminuisce. Tuttavia, la somma del calore da fornire al ribollitore e allo scambiatore H-303 aumenta. Infatti, sebbene il calore da fornire al ribollitore diminuisca, tale riduzione è minore rispetto all'aumento del calore da fornire allo scambiatore H-303. La scelta è stata quindi quella di rimuovere lo scambiatore H-303 e alimentare a circa 75°C, pari alla temperatura di uscita dello scambiatore H-301.

Successivamente è stata effettuata una valutazione economica per verificare se la rimozione dello scambiatore H-303 ha effetti positivi anche sul costo della separazione. L'analisi economica ha confermato la scelta fatta in precedenza.

Dopo l'ottimizzazione della colonna C-301, la stessa procedura è stata eseguita per la colonna acetone (C-401). Il primo step è stato trovare il numero minimo di stadi della colonna ottimizzando anche il piatto di alimentazione. Per la colonna acetone, essendo il numero minimo di stadi pari a 15, il numero di stadi teorici è 40 e l'alimentazione entra sullo stadio 12.

Anche per la C-401 è stato valutato l'effetto della temperatura dell'alimentazione sul consumo energetico della colonna (e di un eventuale scambiatore di calore, H-403). In questo caso l'analisi è stata condotta tra 35°C (temperatura del distillato della C-301) e 80°C (essendo 76°C la temperatura dell'alimentazione dopo il recupero termico del prodotto di fondo della C-401). Anche per la C-401 il calore da fornire al ribollitore diminuisce da 35°C a 80°C, ma la somma del calore da fornire al ribollitore e di quello da fornire allo scambiatore (H-403) aumenta. Successivamente è stata effettuata una valutazione economica per vedere se l'aggiunta di questo scambiatore ha effetti positivi anche sul costo di separazione. L'aggiunta di uno scambiatore di calore, però, causa un leggero aumento del costo di separazione. Si è quindi deciso di eliminare lo scambiatore H-403 e di alimentare a 35°C.

La stessa procedura di ottimizzazione è stata eseguita per la colonna IE (colonna C-501). Dopo l'ottimizzazione si è deciso di utilizzare una colonna con un numero di stadi pari a 50 alimentando allo stadio 14.

Per le colonne C-601 e C-602, entrambe senza condensatore, l'alimentazione è fornita allo stadio 1. L'ottimizzazione in questo caso è stata fatta solo sul numero di stadi. Dopo l'ottimizzazione si è deciso di utilizzare due colonne con un numero di stadi pari a 8. Un'altra possibile ottimizzazione dello schema è il recupero energetico tra la colonna C-501 e la colonna C-602. Il recupero di energia è possibile perché la temperatura del condensatore della colonna C-501 è superiore a quella del ribollitore della colonna C-602 così come i loro calori scambiati.

II.1.2 Influenza della temperatura di alimentazione

Un'altra possibile ottimizzazione dello schema di separazione consiste nel variare la specifica dello scambiatore H-301. Sullo schema di base, questa specifica è HOCO (Hot Outlet - Cold Outlet) = 3°C. Nel secondo scenario, questa specifica viene modificata in HICO (Hot Inlet - Cold Outlet) = 10°C. In questo modo, l'alimentazione entra nella C-301 a 109 °C. Queste due specifiche sono state scelte perché:

- HOCO pari a 3°C è una specifica conservativa e utilizza la ben nota tecnologia Shell & Tube.

- HICO pari a 10°C a priori coinvolge scambiatori di calore a piastre, tecnologia per la quale si hanno meno informazioni sia in termini di prestazioni sia di costi. Inoltre, per gli scambiatori di calore a piastre è necessario considerare il problema delle incrostazioni, che è più importante che per uno scambiatore di calore a fascio tubiero.

Un aumento della temperatura di alimentazione ha un effetto positivo sul consumo energetico della colonna. La ***Tabella II.1.1*** confronta il costo di separazione dei due scenari e dello schema di riferimento non ottimizzato (base 100).

Tabella II.1.1 Costo di separazione come somma di Capex e Opex per entrambi i casi: HOCO 3°C e HICO 10°C

	Reference HOCO 3	HOCO = 3°C	HICO = 10 °C
Separation Cost (normalized cost)	100	82.2	72.6
Capex	17.9	19.8	20.1
Opex (excl. Raw material)	82.1	62.4	52.5

Con questa nuova specifica c'è una significativa diminuzione del consumo di utilities. Tra queste, vi è una significativa diminuzione del quantitativo di vapore a bassa pressione richiesto dalla C-301, poiché l'energia richiesta per il ribollitore è notevolmente ridotta. Questa riduzione influisce direttamente sull'Opex. Quanto al Capex, questo aumenta leggermente. Con la nuova specifica, infatti, per effettuare il recupero energetico sono necessari nove scambiatori BEU posti in serie. In conclusione, rispetto al caso di riferimento, l'ottimizzazione dello schema con la specifica HOCO 3 ha consentito di ridurre il costo di separazione di circa il 17.8%. Utilizzando la specifica HICO 10, tuttavia, il costo della separazione è stato ridotto di circa il 27.4%. Per evitare di posizionare in serie nove scambiatori BEU è possibile utilizzare scambiatori a piastre che hanno il vantaggio di avere una superficie di scambio maggiore. Poiché la superficie di scambio totale richiesta è ancora troppo elevata, sono necessari due scambiatori a piastre posti in parallelo per ottenere il recupero di calore. In ***Tabella II.1.2*** viene presentato anche un caso in cui il coefficiente globale di scambio termico dello scambiatore a piastre è assunto essere pari a 2,5 volte maggiore di quello di uno scambiatore tubolare. In questo modo, se fosse possibile ottenere tale velocità di scambio termico, a parità di calore scambiato, si potrebbe avere una riduzione della superficie di scambio e sarebbe sufficiente un solo scambiatore a piastre per ottenere il recupero di calore.

Tabella II.1.2 Costo di separazione come somma di Capex e Opex per il caso HICO = 10: caso con 9 BEU in serie, caso con 2 scambiatori di calore a piastre in parallelo, caso con 1 scambiatore a piastre e coefficiente di scambio Ux2.5 (caso ottimista)

	BEU x9	Plates x2	Plate x1, Ux2.5
Separation Cost (normalized cost)	72.6	76.2	71.2
Capex	20.1	22.6	19.1
Opex (excl. Raw material)	52.5	53.6	52.1

La soluzione con 2 scambiatori a piastre, con un coefficiente di scambio termico (U) pari a quello di uno scambiatore tubolare, è più costosa rispetto al caso con 9 BEU in serie, sebbene sia migliore dal punto di vista pratico. Il caso con un coefficiente $U_2 = 2.5xU_1$ è il migliore dal punto di vista pratico e dal punto di vista dei costi di separazione. In questo caso, il costo della separazione è diminuito di circa il 28.8% rispetto al caso di riferimento.

II.1.3 Schema con compressore

Una soluzione per ridurre la quantità di energia richiesta dalla C-301 è comprimere i vapori in testa della colonna e utilizzarli per fornire il calore richiesto dal ribollitore. In questo modo, l'energia totale richiesta dalla colonna è fornita dal vapore di testa e dall'elettricità consumata dal compressore. Lo schema simulato utilizza un compressore con una pressione di uscita di 2.1 barg e una temperatura di 183°C.

Questo sistema permette di ridurre il consumo di vapore a bassa pressione necessario per fornire il calore richiesto dal ribollitore, ma il consumo di energia elettrica aumenta notevolmente. L'aumento dei consumi non incide in modo significativo sul costo della separazione, perché l'aumento dei consumi elettrici è bilanciato dalla diminuzione del vapore in termini di costi. Il fattore che rende questo schema poco attraente in termini di costo è l'elevato costo del compressore. Infatti, il costo di installazione del compressore e di tutte le apparecchiature ausiliare che devono essere aggiunte rispetto al caso senza compressore aumentano notevolmente il Capex di questo schema.

II.1.4 Integrazione energetica: caso 46

Per creare questo schema integrato energicamente, è stato utilizzato un programma di ottimizzazione energetica basato sulla metodologia PINCH. Questo caso, con le integrazioni energetiche, è stato denominato "Caso 46" (confidenziale). Questo schema utilizza classici scambiatori a fascio tubiero e permette di ottenere un costo di separazione equivalente a quelli del caso HICO = 10°C. I risultati sono presentati nella ***Tabella II.1.3*** in cui vengono confrontati 5 casi (4 HOCO 3 e 1 HICO 10): il caso non ottimizzato, il caso ottimizzato, lo schema con il compressore, il caso 46 e il caso HICO 10 ottimista.

Tabella II.1.3 Costo di separazione come somma di Capex e Opex: confronto tra il caso non ottimizzato, il caso ottimizzato, lo schema con il compressore, il caso 46 e il caso HICO 10 ottimista

	HOCO = 3 °C				HICO = 10 °C
	Non optimisé	BEU	Avec K	Case 46	Plate x1
Separation Cost (normalized cost)	100	82.2	104.9	72.1	71.2
Capex	17.9	19.8	35.6	17.2	19.1
Opex (excl. Raw material)	82.1	62.4	69.3	54.9	52.1

II.2 Schema Mikitenko

A differenza del processo di base, lo schema Mikitenko è composto solo da tre colonne. La particolarità di questo schema è tutto nella seconda colonna al cui interno, in una determinata zona, sono presenti due fasi liquide. Lo schema Mikitenko è presentato nella ***Figura II.2.1***.

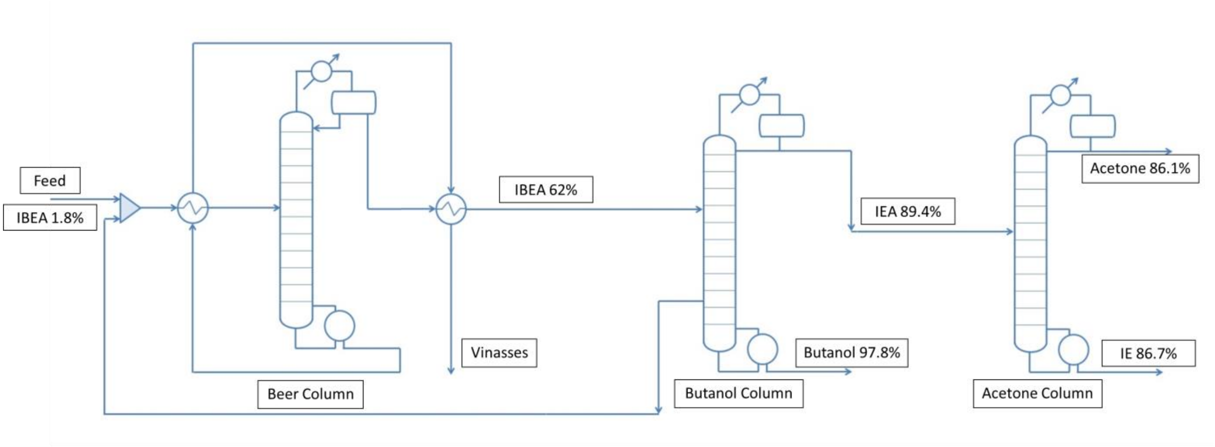


Figura II.2.1 Schema Mikitenko per la separazione di IBEA

In particolare, le colonne utilizzate sono:

- **Colonna Birra (C-301)**: recupero di IBEA in testa ed eliminazione dell'acqua al fondo;
- **Colonna Butanolo (C-401)**: recupero di isopropanolo ed etanolo in testa e recupero di butanolo disidratato al fondo della colonna;
- **Colonna Acetone (C-501)**: eliminazione dell'acetone dalla miscela di etanolo e isopropanolo.

In termini di energia, la colonna che consuma più energia è la C-301 (84% del consumo totale). L'ottimizzazione dello schema mira a ridurre al minimo il consumo energetico della C-301 mantenendo le prestazioni della colonna in termini di recupero IBEA.

II.2.1 Ottimizzazione dello schema

Il primo step per l'ottimizzazione della C-301 è stato trovare il numero minimo di stadi. La procedura è analoga a quella seguita per lo schema di base, che prevede anche l'ottimizzazione dello stadio di alimentazione. L'analisi ha portato ad un numero minimo di stadi pari a 4. Pertanto, il numero di stadi teorici scelto è 10 (2,5 x 4) e l'alimentazione entra sullo stadio 2.

Lo step successivo è stato quello di studiare l'influenza della temperatura di alimentazione sul consumo energetico della colonna nonché sull'IBEA perso nel gas in testa e sull'IBEA nel distillato. La temperatura è stata fatta variare da 75°C a 115°C con un passo di 5°C. All'aumentare della temperatura il calore da sottrare al condensatore aumenta, raddoppiando passando da 75°C a 105°C. Al contrario, il calore da fornire al ribollitore diminuisce all'aumentare della temperatura. Tuttavia, come per lo schema base, la somma del calore da fornire a ribollitore e preriscaldatore aumenta. La scelta è stata quindi di rimuovere il preriscaldatore e alimentare a circa 75°C, temperatura dell'alimentazione dopo il recupero energetico del prodotto di fondo della colonna.

Successivamente è stata ottimizzata la temperatura del condensatore. La temperatura è stata variata da 25°C a 70°C ed è stata studiata l'influenza della temperatura del condensatore sul consumo energetico della colonna nonché sull'IBEA perso nel gas in testa e sull'IBEA nel distillato. Il calore da fornire al ribollitore non ha una variazione significativa. Per il condensatore, ad ogni aumento di 5°C il calore da sottrarre diminuisce di circa lo 0.65%. Al contrario, la quantità di IBEA nel gas di testa aumenta notevolmente, circa il 35% ogni 5°C. Per quanto riguarda l'IBEA nel distillato, questo ha un comportamento opposto a quello dell'IBEA nel gas di testa, decrescente con l'aumentare della temperatura. Anche in questo caso però, la diminuzione non è significativa. Prendendo in considerazione questi risultati si è scelto di condensare i vapori di testa a 40°C.

Per il design della seconda colonna gli esempi di simulazione trovati in bibliografia sono stati presi come modelli. A partire dal diagramma ternario isopropanolo-butanolo-acqua (***Figura II.2.2***) è possibile descrivere ciò che avviene nella seconda colonna.

In questo diagramma possiamo vedere la presenza di due regioni di distillazione, separate da una linea tratteggiata che indica il confine che non può essere attraversato da una distillazione standard. L'alimentazione della seconda colonna contiene più del 50% in peso d'acqua e si trova nella regione 1 (a sinistra del confine di distillazione) del diagramma ternario. Partendo da questa alimentazione, per distillazione standard si otterrebbero vapori di isopropanolo (azeotropo) nella parte superiore e una miscela eterogenea di acqua e butanolo nella parte inferiore della colonna. Durante la distillazione si entra nella zona di equilibrio liquido-liquido con la conseguente formazione di due fasi liquide in equilibrio tra loro. Queste due fasi, al variare della temperatura, possono essere trovate in due campi distinti del diagramma ternario. Eliminando la fase acquosa, la fase ricca in butanolo si trova nella regione 2 (a destra del limite di distillazione) e permette di ottenere per distillazione un distillato composto da butanolo disidratato.

Secondo quanto detto, nella parte superiore la colonna è nella regione 1 del diagramma ternario. Successivamente la colonna passa al regime trifase (liquido-liquido-vapore) fino allo stadio di rimozione della fase acquosa. Infine, al di sotto di questo stadio, la colonna si trova nella regione 2 fino a raggiungere il fondo della colonna.

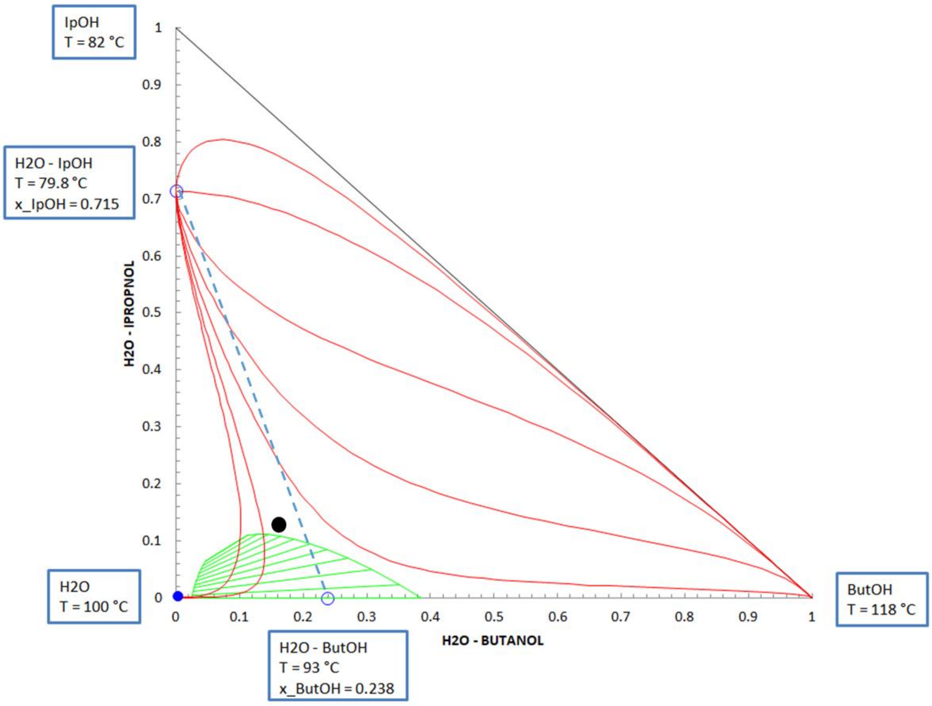


Figura II.2.2 Diagramma ternario Isopropanolo-Butanolo-Acqua

La configurazione scelta è una colonna con 30 stadi, alimentazione allo stadio 12 (condensatore in testa: stadio 1), equilibrio LLV tra lo stadio 12 e lo stadio 25, rimozione della fase acquosa allo stadio 25.

Per quanto riguarda la temperatura di alimentazione della colonna C-401, sono state prese in considerazione solo due temperature a causa dei problemi di convergenza dello schema. Le due temperature scelte sono 40°C (temperatura del distillato della colonna C-301) e 68.6°C, temperatura raggiunta dopo aver recuperato il calore residuo del prodotto di fondo della C-301 nello scambiatore E-304. L'aggiunta dello scambiatore E-304 ha come effetto la riduzione dell'Opex. Questa riduzione è maggiore rispetto all'aumento del Capex. L'effetto cumulato dell'aggiunta dello scambiatore E-304 è quindi una riduzione del costo di separazione. La scelta è stata quindi quella di aggiungere lo scambiatore.

Infine, l'acetone contenuto nel distillato della colonna C-401 viene rimosso attraverso la colonna C-501 o colonna acetone. In testa alla colonna C-501 si ottiene un distillato composto da acetone puro e al fondo una miscela azeotropica acqua-isopropanolo.

Il primo step per ottimizzare la colonna C-501 è stato trovare il numero minimo di stadi di colonna. L'analisi ha portato ad un numero minimo di stadi pari a 10, pertanto il numero di stadi teorici della colonna acetone è stato scelto pari a 25 (2,5 x 10).

Lo step successivo è stato quello di studiare l'influenza della temperatura dell'alimentazione sul consumo energetico della colonna. La temperatura è stata fatta variare da 40°C a 81°C. La scelta finale è stata quella di alimentare la C-501 a 81°C, pari alla temperatura di uscita del distillato dalla colonna C-401.

II.2.2 Influenza della temperatura di alimentazione

Anche per lo schema Mikitenko sono state confrontate due configurazioni per lo scambiatore E-301: la configurazione con la specifica HOCO 3 e la configurazione con la specifica HICO 10. Utilizzando la specifica HICO 10 l'alimentazione entra in colonna a 108.2°C.

La ***Tabella II.2.1*** confronta il costo di separazione dei due scenari e dello schema di riferimento non ottimizzato (base 100). Come nel caso di base, la specifica HICO 10 è più conveniente in termini di costi di separazione e consumo di utilities. Rispetto al caso di riferimento, l'ottimizzazione dello schema HOCO 3 ha consentito di ridurre il costo di separazione di circa il 19.1%. Con la specifica HICO 10, tuttavia, il costo di separazione è stato ridotto di circa il 26%.

Tabella II.2.1 Costo di separazione come somma di Capex e Opex per entrambi i casi: HOCO 3°C e HICO 10°C

	Reference HOCO 3	HOCO = 3°C	HICO = 10 °C
Separation Cost (normalized cost)	100.0	80.9	74.0
Capex	17.9	16.8	17.6
Opex (excl. Raw material)	82.1	64.1	56.4

Come nel caso base, è possibile evitare di mettere in serie 9 scambiatori BEU utilizzando 2 scambiatori a piastre in parallelo per effettuare il recupero di calore. In ***Tabella II.2.2*** viene presentato anche il caso con coefficiente globale di scambio termico 2.5 volte maggiore di quello di uno scambiatore tubolare.

Tabella II.2.2 Costo di separazione come somma di Capex e Opex per il caso HICO = 10: caso con 9 BEU in serie, caso con 2 scambiatori di calore a piastre in parallelo, caso con 1 scambiatore a piastre e coefficiente di scambio Ux2.5 (caso ottimista)

	BEU x9	Plates x2	Plate x1, Ux2.5
Separation Cost (normalized cost)	74.0	77.6	73.1
Capex	17.6	20.1	17.1
Opex (excl. Raw material)	56.4	57.5	56.0

Anche per lo schema Mikitenko il caso ottimista è il migliore dal punto di vista pratico e dei costi di separazione. Il costo di separazione è infatti inferiore di circa il 26.9% rispetto al caso di riferimento.

II.2.3 Schema con compressore

Anche per lo schema Mikitenko è stato simulato lo schema con la compressione dei vapori di testa della C-301. La pressione di uscita del compressore è di 2.1 barg come nel caso base e la temperatura di uscita del compressore è di 168°C. Anche in questo caso l'aggiunta del compressore per recuperare il calore dei vapori di testa si rivela svantaggiosa in termini di costo di separazione.

II.2.4 Integrazione energetica: caso FH

Come per il caso di base, per creare questo schema integrato energicamente è stato utilizzato un programma di ottimizzazione energetica basato sulla metodologia PINCH. Questo caso è stato denominato "Caso FH" (confidenziale). I risultati sono presentati nella ***Tabella II.2.3*** in cui vengono confrontati 5 casi (4 HOCO 3 e 1 HICO 10): il caso non ottimizzato, il caso ottimizzato, lo schema con il compressore, il caso FH e il caso HICO 10 ottimista.

Tabella II.2.3 Costo di separazione come somma di Capex e Opex: confronto tra il caso non ottimizzato, il caso ottimizzato, lo schema con il compressore, il caso 46 e il caso HICO 10 ottimista

	HOCO = 3 °C				HICO = 10 °C
	Non optimisé	BEU	Avec K	Case FH	Plate x1
Separation Cost (normalized cost)	80.9	74.0	100.4	65.7	73.1
Capex	16.8	17.6	29.6	11.7	17.1
Opex (excl. Raw material)	64.1	56.3	70.8	54.0	56.0

II.2.5 Influenza della concentrazione di IBEA nell'alimentazione

Con il sistema di produzione attualmente in uso la concentrazione di IBEA in uscita dal fermentatore e inviato alla colonna di birra è di circa 19.6 g/L. Utilizzando altri sistemi di produzione o diversi ceppi di batteri è possibile variare la concentrazione in uscita dal fermentatore. Per osservare l'influenza della concentrazione sullo schema di distillazione sono state effettuate diverse simulazioni per i due casi ottimizzati (caso 46 e caso FH) variando la concentrazione all'ingresso della C-301 e osservando la variazione del consumo energetico della colonna. La concentrazione è stata variata tra 10 g/L e 75 g/L.

È stata effettuata anche una valutazione economica per osservare l'influenza della concentrazione di IBEA sul costo di separazione. La ***Figura II.2.3*** mostra un confronto tra i due schemi.

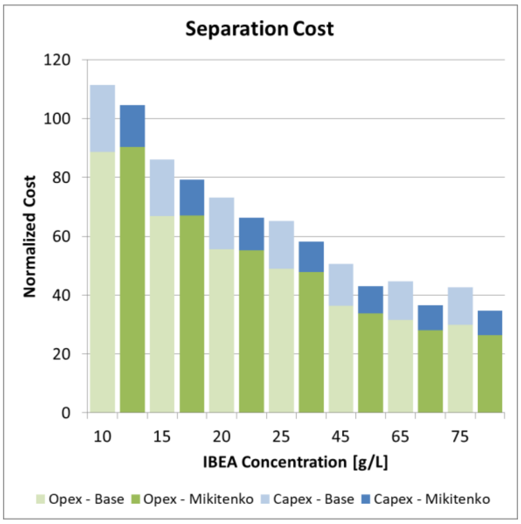


Figura II.2.3 Influenza della concentrazione di IBEA sul costo di separazione dei due schemi

Si può osservare che aumentando la concentrazione di IBEA in ingresso nella C-301, per entrambi i casi, il suo consumo di energia diminuisce. Si osserva infatti una netta diminuzione dell'Opex all'aumentare della concentrazione. Alimentare la C-301 con un IBEA più concentrato riduce il costo di separazione. Inoltre, si può notare che lo schema Mikitenko sia più conveniente dello schema di base a tutte le concentrazioni.

II.2.6 Effetto della qualità delle "vinacce" sul costo di separazione

Un altro fattore che può incidere sul costo di separazione è la quantità di IBEA presente nelle vinacce. Con vinacce si intende il prodotto di fondo della C-301. Non essendo nota la quantità massima di alcol accettata per il trattamento delle acque reflue è stato condotto uno studio che evidenzia come la quantità di IBEA nelle acque reflue influisce sul costo di separazione. Per lo studio sono state considerate tre concentrazioni di IBEA nelle vinacce: 100, 200 e 300 ppm in peso. Il caso FH è stato utilizzato per questo studio.

In termini di utilities si registra una diminuzione del consumo di vapore a bassa pressione e dell'acqua di raffreddamento. La diminuzione del vapore porta ad una riduzione dell'Opex. Per quanto riguarda il Capex, non ci sono grandi variazioni. In generale, si riscontra una riduzione del costo di separazione di circa il 7% passando da 100 ppm a 300 ppm nelle vinacce.

Inoltre, potrebbe anche essere presa in considerazione la possibilità di riciclare le vinacce. Il riciclo delle vinacce potrebbe avere un effetto positivo sul trattamento delle acque reflue e sulla perdita di IBEA. D'altra parte, è necessario le concentrazioni nelle vinacce riciclate non superino i limiti di tossicità dei microrganismi nel fermentatore.

II.3 ELL

Per ridurre il consumo energetico necessario per la purificazione di IBEA è possibile utilizzare un sistema ibrido di estrazione – distillazione. Le prestazioni del processo di estrazione – distillazione dipendono molto dalla scelta del solvente. I diversi solventi possibili sono stati scelti in base a criteri diversi come alta capacità, alta selettività, bassa viscosità, diversa densità dell'acqua, disponibilità in commercio e a basso costo.

Tra i vari solventi presenti in letteratura, sono stati scelti i seguenti per simulare una colonna di estrazione liquido-liquido in cui dall’alto viene introdotto il prodotto in uscita dal fermentatore e dal fondo viene inserito il solvente:

- Solvente A (confidenziale)
- 2-etil-1-esanolo
- Trioleina
- 2-butil-1-ottanolo
- Solvente B (confidenziale)
- Solvente C (confidenziale)
- Alcol oleilico

Per simulare e confrontare le prestazioni che si ottengono utilizzando i vari solventi, sulla base dei dati presenti in letteratura, si è deciso di inserire i due flussi a 80°C. Come primo parametro di confronto è stato considerato il rapporto tra la quantità di solvente necessaria per eseguire l'estrazione liquido-liquido e l'alimentazione in uscita dal fermentatore. La quantità di solvente è stata valutata in modo da avere una concentrazione di IBEA nella fase acquosa (vinacce) di 100 ppm. Osservando il dato, a causa dell'elevata portata richiesta, si è deciso quindi di non utilizzare Trioleina per effettuare l'estrazione. Come secondo parametro è stata valutata la quantità di acqua nella fase organica che esce dall'estrattore. La fase organica viene successivamente inviata ad una colonna di distillazione per il recupero del solvente. La quantità di acqua in fase organica corrisponde quindi alla quantità di acqua presente insieme all'IBEA nel prodotto della colonna di distillazione. È stata quindi calcolata la percentuale di acqua presente nel prodotto di distillazione (come rapporto tra H_2O e somma tra H_2O e IBEA). Questo rapporto è stato calcolato per poter confrontare lo schema di estrazione liquido – liquido con lo schema di base. La percentuale di acqua nel prodotto della colonna di birra dello schema di base è di circa il 40%.

L'implementazione di un sistema ibrido di estrazione-distillazione ha lo scopo di diminuire il fabbisogno energetico di separazione a condizione che si ottenga un prodotto con le stesse caratteristiche o con caratteristiche migliori in termini di percentuale di acqua. Gli unici due solventi che permettono di ottenere un prodotto con meno del 40% di acqua sono il Solvente A e la Trioleina (che abbiamo precedentemente escluso). Si è deciso di utilizzare il solvente A per effettuare il processo di estrazione in quanto questo solvente, sebbene non abbia il più basso dei rapporti S/F, permette di ottenere un prodotto con una quantità di acqua molto inferiore a quella del prodotto ottenuto con lo schema base. Lo schema ibrido di estrazione-distillazione simulato utilizzando il solvente A come solvente è mostrato in ***Figure 2.3.2***.

Nella ***Figure 2.3.2*** possiamo vedere come l'alimentazione entra dalla testa della colonna in controcorrente al solvente inserito dal fondo della colonna. La fase acquosa (vinacce) viene eliminata dal fondo della colonna mentre la fase organica in uscita dalla testa della colonna viene inviata ad una colonna di distillazione che produce IBEA nella parte superiore e recupera il solvente al fondo. Il solvente recuperato al fondo della colonna viene utilizzato per preriscaldare l'alimentazione prima di entrare nella colonna di estrazione.

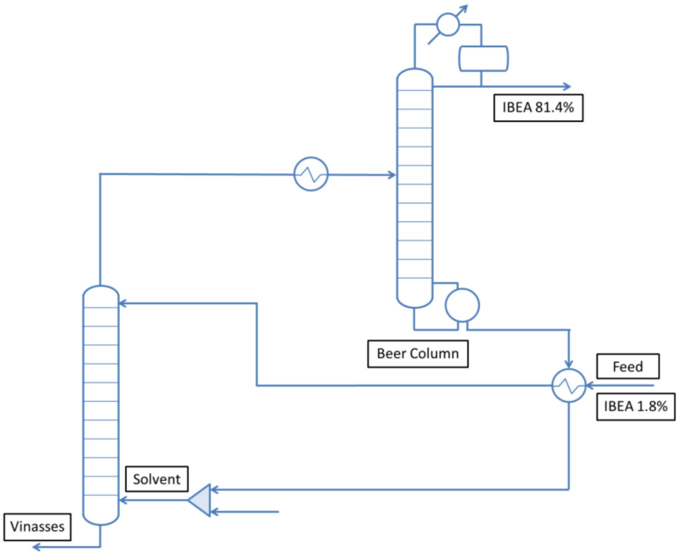


Figura II.3.1 Processo ibrido Estrazione – Distillazione

La quantità di solvente persa e la quantità di acqua che viene trasportata con il solvente dipendono dalla solubilità dell'acqua nel solvente e del solvente in acqua. I valori ottenuti con il metodo termodinamico utilizzato per la simulazione sono stati confrontati con quelli presenti in letteratura. I risultati di questo confronto sono riportati nella ***Tabella II.3.1***.

Tabella II.3.1 Solubilità del solvente in acqua e dell'acqua nel solvente a 25 e 80 °C

	UNIFAC 25 °C	Measure 25 °C	Model 25 °C	Measure 80 °C	Model 80 °C
Water in solvent (mol frac)	0.0011	0.0031	0.0024	0.0074	0.0104
Solvent in water (mol frac)	4e-6	7.8e-6	7.1e-6	-	1.9e-5

La colonna di assorbimento simulata lavora a 80°C circa. Dalla ***Tabella II.3.1*** è possibile notare che il modello ha previsto un contenuto d'acqua nel solvente in uscita dalla colonna di assorbimento superiore a quello che potrebbe essere calcolato dai dati misurati, di circa il 30%. Questi dati dovrebbero essere studiati in seguito in quanto, se fossero disponibili dati più accurati, si potrebbe ottenere un contenuto di acqua ancora più basso nel flusso IBEA concentrato. Inoltre, anche il contenuto di solvente in acqua è un dato importante. Infatti, le vinacce potrebbero essere riciclate al fermentatore, al di sotto dei limiti di concentrazione considerati tossici dai microrganismi. La tossicità del solvente A ai livelli mostrati nella ***Tabella II.3.1*** dovrebbe essere studiata in seguito.

Considerando lo schema ELL come uno schema di concentrazione IBEA, un aspetto importante dello schema diventa quindi la quantità di acqua presente nel prodotto in testa alla colonna di distillazione. La quantità di acqua presente nell'IBEA prodotto dipende dalla qualità delle vinacce. Infatti, all'aumentare della concentrazione di IBEA nelle vinacce, diminuisce la percentuale di acqua nel prodotto di testa della colonna.

Infine, è stata effettuata una valutazione economica dello schema simulato. Prima di effettuare la valutazione economica è stato necessario verificare la fattibilità dell'estrazione in termini di proprietà dei due fluidi. In particolare, è stato verificato che:

- differenza di densità > 50 kg/m^3
- differenza di viscosità < 500 cP
- differenza tra tensioni interfacciali > 2 mN/m

Le proprietà dei fluidi, riportate in ***Tabella II.3.2*** soddisfano queste specifiche.

Tabella II.3.2 Proprietà dell'alimentazione e del solvente

	Density	Viscosity	Interfacial tension
	kg/m^3	cP	mN/m
Feed	938.6	0.357	61.83
Solvent	818.9	0.372	22.67

I risultati della valutazione economica dello schema ELL sono presentati in ***Tabella II.3.3***. Per la valutazione totale del costo di separazione dell'IBEA, e per poter fare un confronto con gli schemi precedenti, è necessario aggiungere le colonne per l'eliminazione dell'acetone e per la separazione del butanolo dall'isopropanolo e dall'etanolo. La valutazione del costo totale di separazione non verrà effettuata in questo lavoro di Tesi. Il confronto verrà effettuato tra lo schema ELL e la C-301 dello schema di base poiché per entrambi lo scopo è concentrare l'IBEA. Va ricordato a questo punto che la C-301 dello schema di base concentra l'alimentazione a circa il 40% in peso di acqua, mentre l'ELL a circa il 9.6–18.6% in peso.

Tabella II.3.3 Costo di separazione come somma di Capex e Opex al variare della qualità delle vinacce

Vinasses quality (ppm wt)	100	200	300	Basic scheme 100 ppm
Separation Cost (normalized cost)	92.9	80.0	78.6	51.8
Capex	31.9	29.7	29.5	10.1
Opex (excl. Raw material)	61.0	50.3	49.1	41.6

Dalla ***Tabella II.3.3*** si può notare l'effetto della qualità delle vinacce sul costo di separazione. Infine, confrontando questi risultati con lo schema di base è possibile notare che, se consideriamo lo schema ELL come un metodo di concentrazione di IBEA, la quantità di acqua in uscita dalla colonna di distillazione è inferiore ma il costo di separazione di questo schema è circa due volte quello della C-301. Pertanto, per verificare che lo schema ELL sia più vantaggioso della singola colonna di birra è necessario effettuare una valutazione dello schema completo.

II.4 Diaz

Un altro possibile schema per la concentrazione di IBEA è una combinazione di distillazione estrattiva e azeotropica. In questo caso il butanolo presente nell'alimentazione viene utilizzato come agente di separazione. Lo schema di distillazione (da ora chiamato schema Diaz dal nome dell'autore dell'articolo in cui è stato proposto) prevede due colonne di distillazione. L'alimentazione viene introdotta nella prima colonna dopo essere stata preriscaldata dalle vinacce. A causa dell'immiscibilità tra acqua e butanolo su alcuni piatti della colonna 1 sono presenti due fasi liquide, una ricca di acqua e una ricca di butanolo. La fase ricca di butanolo viene quindi estratta e inviata sul primo piatto della colonna 2. Dalla testa della colonna 1 si produce un distillato composto principalmente da acqua e isopropanolo (ed etanolo) con composizione azeotropica che viene alimentato alla colonna 2. Nella colonna 2, utilizzando il butanolo estratto dalla prima colonna come agente di separazione è possibile ottenere al fondo un flusso costituito da IBEA concentrato. Con 100 ppm in peso di IBEA nelle vinacce si ottiene come prodotto un'IBEA a circa l'89%. Pertanto, lo schema Diaz, come lo schema ELL, può essere considerato uno schema di concentrazione IBEA. Lo schema è presentato nella ***Figura II.4.1***.

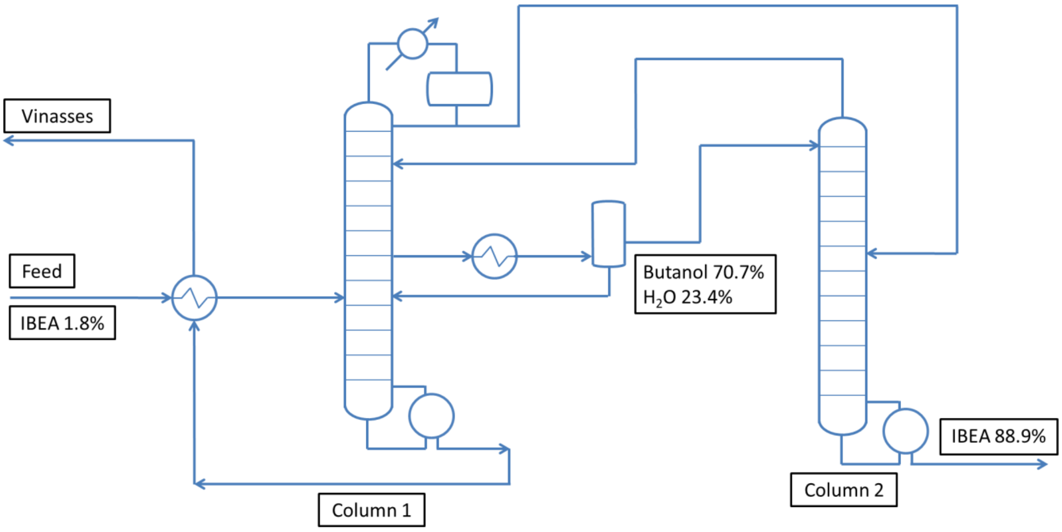


Figura II.4.1 Schema Diaz: concentrazione di IBEA usando butanolo come agente di separazione

II.4.1 Influenza della qualità delle vinacce sulla qualità di IBEA

Considerando lo schema Diaz come uno schema di concentrazione IBEA, un aspetto importante dello schema diventa quindi la quantità di acqua presente nel prodotto finale. In particolare, la quantità di acqua diminuisce all'aumentare dell'IBEA nelle vinacce. La ***Figura II.4.2*** mostra la variazione della concentrazione del prodotto ottenuto al variare della qualità delle vinacce. Inoltre, viene effettuato anche un confronto tra la C-301 dello schema di base, lo schema ELL e lo schema Diaz.

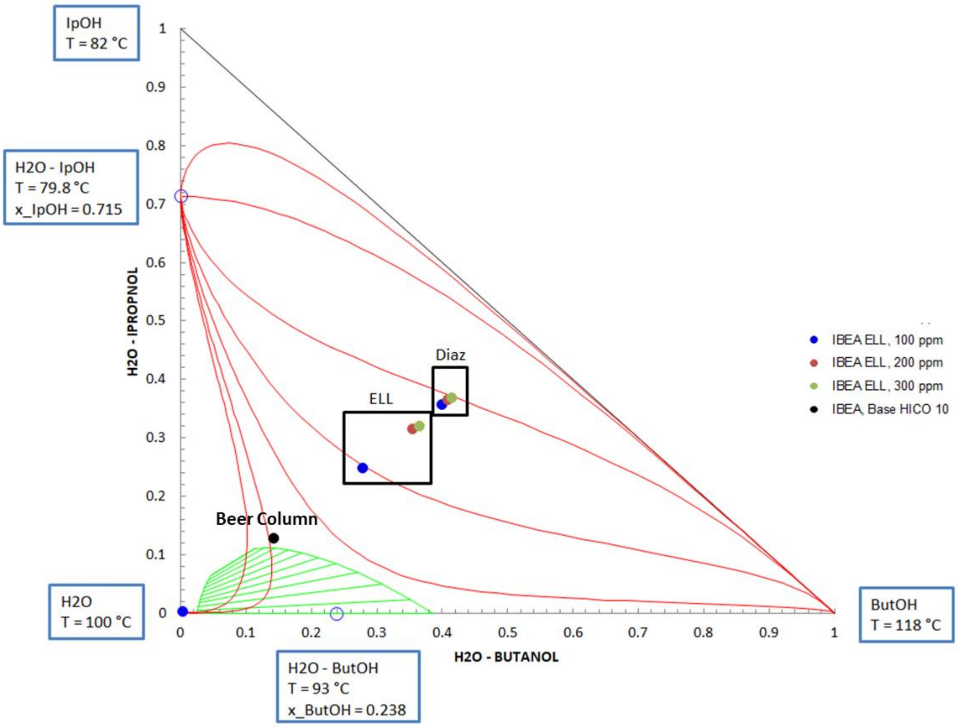


Figura II.4.2 Diagramma ternario acqua-isopropanolo-butanolo: influenza della qualità delle vinacce su IBEA prodotto

Il diagramma evidenzia come lo schema Diaz consenta di ottenere un prodotto più concentrato in IBEA. È anche possibile notare che l'effetto della qualità delle vinacce sulla concentrazione del prodotto finale è meno importante per lo schema Diaz che per lo schema ELL.

II.4.2 Costo di separazione dello schema Diaz

Infine, è stata effettuata una valutazione economica dello schema in esame. I risultati della valutazione economica del sistema Diaz sono presentati in***Tabella II.4.1***. Come per lo schema ELL, per poter fare un confronto con lo schema base completo e lo schema Mikitenko è necessario aggiungere le colonne per l'eliminazione dell'acetone e per la separazione del butanolo da isopropanolo ed etanolo. La valutazione completa dei costi di separazione degli schemi non verrà effettuata in questo lavoro di Tesi. Il confronto verrà effettuato tra lo schema Diaz e la colonna birra dello schema di base poiché entrambi hanno lo scopo di concentrare l'IBEA.

Tabella II.4.1 Costo di separazione come somma di Capex e Opex al variare della qualità delle vinacce

Vinasses quality (ppm wt)	100	200	300	Base HICO 10 Ux2.5
Separation Cost (normalized cost)	48.1	47.5	47.4	46.8
Capex	7.2	7.2	7.2	9.1
Opex (excl. Raw material)	40.8	40.3	40.1	37.8

La ***Tabella II.4.1*** mostra che per lo schema Diaz l'effetto della qualità delle vinacce sul costo di separazione è trascurabile. Si registra infatti una diminuzione di circa l'1% passando da 100 a 300 ppm di IBEA nelle vinacce. Inoltre, a parità di IBEA nelle vinacce (100 ppm) il costo di separazione dello schema Diaz è solo il 2.6% maggiore di quello del regime di base. Tuttavia, lo schema Diaz consente di ottenere un prodotto più concentrato rispetto al caso base. Pertanto, per vedere se lo schema Diaz è più vantaggioso della singola colonna di birra è necessario valutare lo schema completo.

III Disidratazione dell’isopropanolo

Lo schema base e lo schema Mikitenko ci permettono di separare l’alimentazione proveniente dal fermentatore ottenendo un flusso di vinacce contenente principalmente acqua, un flusso contenente principalmente acetone, uno di butanolo e uno di isopropanolo ed etanolo. Quest'ultimo flusso, a causa degli azeotropi acqua-etanolo e acqua-isopropanolo, contiene una quantità di acqua non trascurabile. Per questo motivo è prevista una fase di disidratazione per questo flusso. Cinque processi di disidratazione sono stati considerati:

- Pressure Swing Distillation
- Same Pressure Distillation
- Distillazione azeotropica con Cicloesano/Benzene
- Pervaporazione
- Adsorbimento

III.1 Pressure Swing Distillation/Same Pressure Distillation

Sebbene entrambi i metodi siano adatti per la disidratazione di isopropanolo ed etanolo, solo la PSD è stata considerata la disidratazione dei due alcool. La SPD potrebbe essere studiata in seguito.

Per verificare la fattibilità della disidratazione del nostro flusso, è stato disegnato il diagramma ternario (composizione molare) Etanolo-Acqua-Isopropanolo come mostrato in ***Figura III.1.1***. Sul diagramma è possibile notare gli azeotropi alle diverse pressioni (0,05 bar, 1 bar e 10 bar). Il diagramma mostra anche la presenza di due regioni di distillazione distinte divise da un confine di distillazione che collega l'azeotropo acqua-etanolo con l'azeotropo acqua-isopropanolo. La Regione 1 è definita come quella a destra di questo confine e la Regione 2 quella a sinistra.

La separazione mediante lo schema Pressure Swing Distillation (PSD) prevede l'uso di tre colonne di distillazione che lavorano a pressioni differenti, in particolare 0.05, 1 e 10 bar. Infatti, la separazione è possibile poiché la composizione dell'azeotropo acqua-isopropanolo a 1 bar è diversa da quella a 10 bar. Solo lavorando a due pressioni differenti è possibile superare il confine di distillazione e ottenere isopropanolo puro. Il primo passo per la disidratazione è l'eliminazione dell'etanolo. La colonna per eliminare l'etanolo lavora a una pressione di 0.05 bar e sfrutta il fatto che a questa pressione l'azeotropo acqua-etanolo contiene una frazione molare di etanolo di 0.997, come mostrato in ***Figura III.1.1***. Il prodotto di fondo della prima colonna viene miscelato con il prodotto di testa della terza colonna e viene inviato alla seconda colonna. In questo modo si ottiene al fondo della seconda colonna una corrente composta principalmente da acqua e in testa una corrente composta da un azeotropo isopropanolo-acqua a 1 bar. Questo distillato diventa l’alimentazione della terza colonna che funziona a 10 bar. A 10 bar l'azeotropo acqua-isopropanolo è più ricco di acqua rispetto all'azeotropo a 1 bar. Ciò permette ottenere al fondo della terza colonna un flusso composto principalmente da isopropanolo.

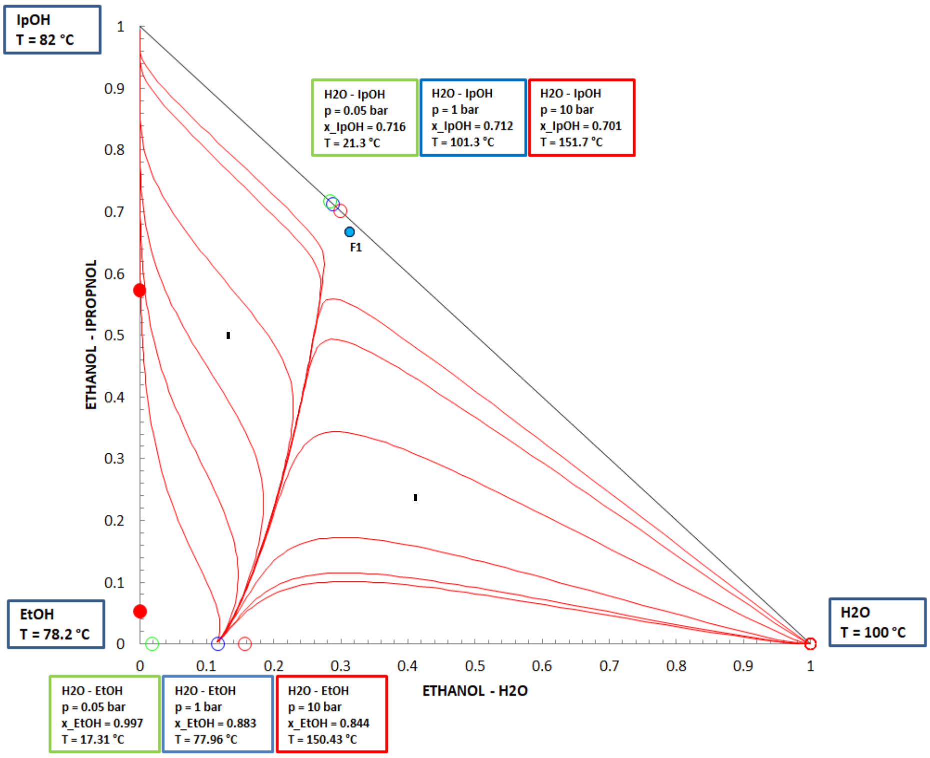


Figura III.1.1 Diagramma ternario Etanolo-Acqua-Isopropanolo (composizione molare)

Lo schema simulato è mostrato in ***Figura III.1.2***.

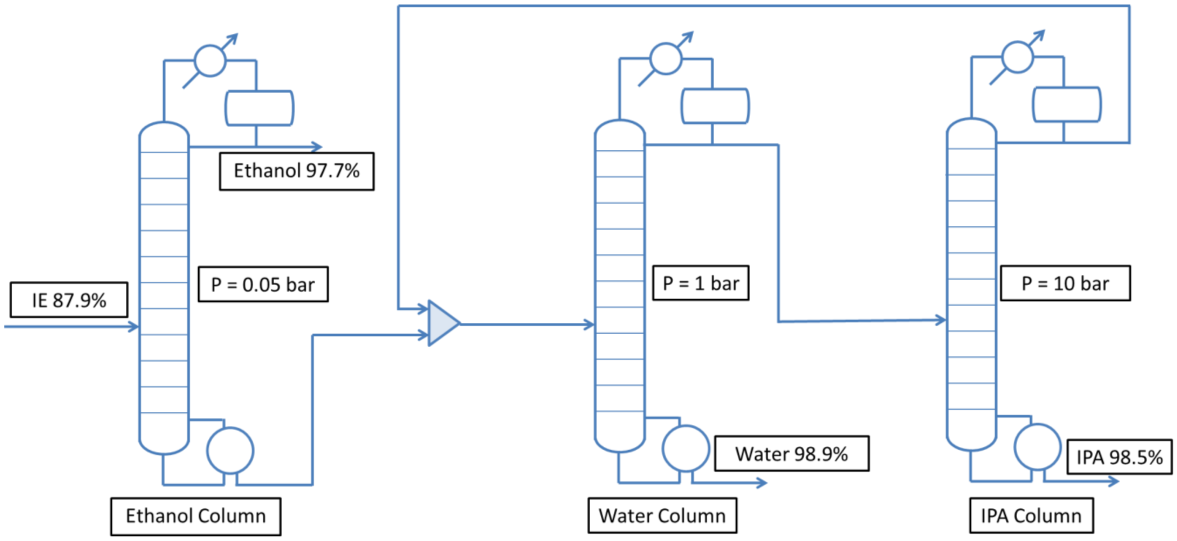


Figura III.1.2 Schema Pressure Swing Distillation simulato

Sulla colonna etanolo è stata effettuata un'ottimizzazione in termini di numero di stadi e posizione dell'alimentazione. Per effettuare questa separazione, la colonna necessita di un numero minimo di stadi pari a 60. Il numero di stadi teorici è stato quindi scelto pari a 120. A 0.05 bar e con la composizione dell'azeotropo, la temperatura del distillato della colonna etanolo è di 17.31°C. Nel caso simulato, la temperatura del distillato ottenuto è di 17.35 °C. Per condensare i vapori nel condensatore si è deciso di utilizzare acqua glicolata a 4°C. Per fornire il calore al ribollitore si è deciso di recuperare parte del calore dal condensatore della seconda colonna.

Il numero di stadi delle due colonne utilizzate per rompere l’azeotropo acqua-isopropanolo, così come la posizione dell’alimentazione, non sono stati ottimizzati. Il numero di stadi per entrambe le colonne è pari a 50, come trovato in letteratura.[13] Tuttavia, è stata realizzata un'integrazione energetica tra le due colonne. La temperatura e il calore di ribollitore e condensatore rispettivamente della seconda e della terza colonna sono tali da rendere possibile questa integrazione energetica.

La ***Tabella III.1.1*** mostra i risultati della valutazione economica dello schema PDS. I risultati in tabella si riferiscono alla produzione totale di IBEA (5 t/h) e alla produzione di isopropanolo (1.85 t/h). I risultati in tabella mostrano come questo processo di disidratazione sia un processo oneroso sia in termini di Opex che in termini di Capex. Infatti, il consumo delle utilities è elevato e questo ricade direttamente sull'Opex. Inoltre, sono necessarie 3 colonne di distillazione. Confrontando il risultato relativo alla produzione di IBEA, il processo di disidratazione con PSD è più oneroso del processo di separazione dell'alcol stesso al quale questo costo deve essere aggiunto.

Tabella III.1.1 Costo dello schema PSD come somma di Capex e Opex: costo riferito alla produzione di IBEA e di isopropanolo

	PSD/IBEA	PSD/IPA
Separation Cost (normalized cost)	109.4	288.0
Capex	25.2	66.4
Opex (excl. Raw material)	84.2	221.6

III.2 Distillazione azeotropica con Cicloesano/Benzene

Il secondo metodo per disidratare l'isopropanolo è la distillazione azeotropica. L’agente di separazione aggiunto alla miscela azeotropica acqua-isopropanolo è il benzene. Lo schema di distillazione azeotropica simulato è mostrato nella ***Figura III.2.1***.

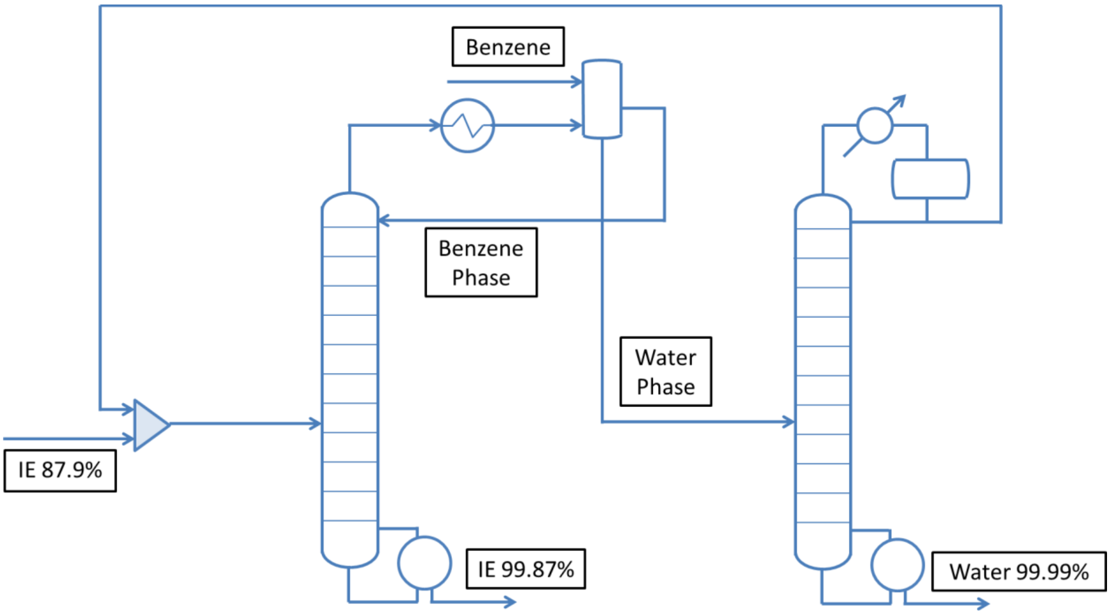


Figura III.2.1 Schema simulato della distillazione azeotropica con benzene come agente di separazione

Il sistema acqua-isopropanolo-benzene presenta a pressione atmosferica 3 azeotropi binari tra cui l'etero azeotropo acqua-benzene e un etero azeotropo ternario. Acqua-isopropanolo e isopropanolo-benzene sono completamente miscibili in fase liquida mentre la miscela acqua-benzene è completamente immiscibile. La totale immiscibilità della miscela acqua-benzene genera un'area relativamente ampia di parziale immiscibilità all'interno di un diagramma ternario e l'etero-azeotropo ternario ha una composizione che si trova in questa zona di parziale immiscibilità. Se si alimenta in una prima colonna una miscela acqua-isopropanolo alla quale si aggiunge benzene, si ottiene isopropanolo puro dal fondo della colonna e l'etero azeotropo ternario dalla testa. Dopo la condensazione, l'etero azeotropo si separa in due fasi liquide: una fase ricca di acqua e una fase ricca di benzene. La fase ricca in benzene viene inviata alla prima colonna. La fase ricca di acqua viene inviata ad una seconda colonna che produce acqua al fondo e un etero azeotropo ternario come distillato che viene riciclato alla prima colonna.

Pertanto, il benzene ha la funzione di far apparire un etero azeotropo ternario a bassa temperatura di ebollizione e di creare un'ampia zona di smiscelazione nella fase liquida in modo da aggirare l'azeotropo isopropanolo-acqua. A causa dei problemi di tossicità del benzene, lo stesso tipo di operazione è stata eseguita con il cicloesano.

La ***Tabella III.2.1*** mostra i risultati del costo della distillazione azeotropica con benzene e con cicloesano. I risultati in tabella si riferiscono alla produzione totale di IBEA (5 t/h) e a quella di isopropanolo (1.85 t/h).

Tabella III.2.1 Costo della distillazione azeotropica come somma di Capex e Opex: benzene e cicloesano

	Benzene/IBEA	Benzene/IPA	CH/IBEA	CH/IPA
Separation Cost (normalized cost)	11.1	30.0	8.9	24.0
Capex	3.8	10.3	3.5	9.5
Opex (excl. Raw material)	7.3	19.7	5.4	14.5

A differenza dello schema di disidratazione PSD, la distillazione azeotropica risulta più conveniente, con un costo di separazione pari a 1/10 di quello del processo PSD. Si ricorda che questo costo deve essere sommato a quello dello schema di separazione dell'IBEA (caso di base o Mikitenko).

III.3 Pervaporazione

Le tecnologie a membrana sono recentemente emerse come un'ulteriore categoria di processi di separazione. Queste tecnologie di separazione offrono numerosi vantaggi rispetto ai processi esistenti, come alta selettività, basso consumo energetico, rapporto costo/prestazioni moderato e design compatto e modulare. Negli ultimi anni, la pervaporazione si è affermata come una delle tecnologie a membrana più promettenti per un'ampia gamma di applicazioni: dalla disidratazione di composti organici al recupero di composti organici dall'acqua e separazione di miscele organiche. Essendo una tecnologia non ancora ben consolidata, la pervaporazione come processo singolo deve spesso competere con processi convenzionali come distillazione, estrazione liquido-liquido, adsorbimento e strippaggio, che sono affidabili e il cui costo può essere facilmente calcolato.

La pervaporazione è un processo in cui le specie trasferite passano alla fase vapore ma, a differenza della semplice evaporazione che avviene nella distillazione, la membrana funge da terzo corpo solido. A causa della membrana, si ha una dissoluzione irregolare della specie sulla faccia a monte a contatto con il liquido. Il trasferimento di materia nella pervaporazione si basa su un meccanismo a tre fasi.

1. La membrana densa si comporta come uno strato di solvente che dissolve selettivamente la miscela liquida adiacente.
2. Le specie assorbite nel film denso si diffondono sotto l'influenza del gradiente di attività locale che esiste per ogni specie e in ogni punto della membrana.
3. Desorbimento, a pressione ridotta, delle molecole che hanno raggiunto la faccia a valle. In condizioni operative normali, quest'ultimo processo è molto più veloce dei precedenti ed è noto che non gioca un ruolo nella selettività di trasferimento o nel controllo del flusso di trasferimento.

Uno dei vantaggi del processo di pervaporazione è la selettività di trasferimento e l'energia richiesta. Le membrane per evaporazione sono sviluppate per applicazioni molto specifiche e la loro selettività è generalmente molto elevata. Quando la pervaporazione viene eseguita come un processo di purificazione, l'elevata selettività delle membrane si traduce nella vaporizzazione di una frazione molto limitata della carica, il che implica un notevole risparmio di costi rispetto all'energia richiesta dalla distillazione. Inoltre, la pervaporazione può essere molto selettiva nelle aree di composizione in cui un processo di separazione convenzionale non è più selettivo (caso di composizioni azeotropiche o pseudo-azeotropiche). Questa tecnica si presenta quindi come metodo di separazione alternativo e complementare alla distillazione. Tra le possibili associazioni, infatti, la distillazione è l'operazione unitaria più spesso accoppiata alla pervaporazione. Ad esempio, nella distillazione azeotropica, un processo ibrido di distillazione-pervaporazione consente di effettuare la separazione evitando la necessità di un terzo componente che contamina il prodotto finale e il costo aggiuntivo dell'utilizzo di tre colonne accoppiate.

In letteratura sono presenti diversi processi ibridi distillazione-pervaporazione per la disidratazione dell’isopropanolo.

III.4 Adsorbimento

Il processo di disidratazione per adsorbimento non viene tipicamente utilizzato per l'intervallo di disidratazione richiesto per la rimozione dell'acqua dall'azeotropo acqua-isopropanolo. Inoltre, non sono presenti in letteratura processi per la disidratazione dell'isopropanolo mediante adsorbimento. Tuttavia, questa tecnica è ampiamente utilizzata per la disidratazione dell'azeotropo acqua-etanolo. Per questo motivo la tecnica di disidratazione per adsorbimento è stata presa in considerazione per un eventuale sviluppo futuro di un processo di disidratazione dell’azeotropo isopropanolo-acqua.

IV Conclusioni e prospettive future

L'ottimizzazione sia dello schema di distillazione classico che dello schema Mikitenko ha permesso di ridurre il costo di separazione dei due schemi. In particolare, mediante l'ottimizzazione dello scambiatore alimentazione/effluente e della sua tecnologia il costo di separazione dello schema classico è stato ridotto di circa il 28.8%. Tuttavia, la tecnologia a fascio tubiero si è rivelata non ottimale dal punto di vista pratico, date le aree ad alto scambio coinvolte. In questo caso, gli scambiatori a piastre si dimostrano una tecnologia migliore. Occorre quindi uno studio più approfondito su questa tecnologia, per il suo dimensionamento e per essere sicuri del suo utilizzo per questo tipo di applicazione. Tuttavia, lo schema migliore è lo schema Mikitenko ottimizzato attraverso il programma di integrazione energetica che consente una riduzione dei costi di separazione del 34.3% rispetto al caso di riferimento, pur utilizzando la classica tecnologia di scambiatori a fascio tubiero.

Inoltre, è stato evidenziato l'effetto della qualità delle vinacce sul costo di separazione. Sarà necessario verificare la possibilità di avere una maggiore concentrazione di IBEA nelle vinacce. Ciononostante, un aumento dell'IBEA nelle vinacce porta a una perdita di produzione nell'IBEA. In letteratura si parla anche della possibilità di riciclare parte delle vinacce nel fermentatore senza trattarle. Ciò consentirebbe quindi di ottenere un vantaggio in termini di trattamento dell'acqua e in termini di perdita di produzione. D'altra parte, è necessario che le specie nelle vinacce non superino i limiti di tossicità dei microrganismi nel fermentatore. Uno studio sulla quantità di vinacce riciclabili potrebbe essere oggetto di futuri studi per l'ottimizzazione dello schema produttivo IBEA.

Anche la concentrazione di IBEA nell'alimentazione di distillazione non ha un effetto trascurabile sul costo di separazione. Tuttavia, è necessario considerare un perimetro più ampio per poter ottimizzare lo schema. Infatti, se l'aumento della concentrazione di IBEA nell’alimentazione consente una diminuzione del costo di separazione, non è noto se tale diminuzione compensi l'aumento del costo per ottenere IBEA più concentrata dal fermentatore.

In questo studio sono stati presentati due schemi alternativi per la concentrazione di IBEA. Per quanto riguarda lo schema ELL, questo si è rivelato non vantaggioso rispetto alla colonna della birra. Tuttavia, ulteriori ottimizzazioni possono essere effettuate su questo schema. Ad esempio, si potrebbe condurre uno studio sulla temperatura di alimentazione dell’alimentazione e del solvente. Inoltre, un dimensionamento più accurato della colonna di assorbimento e l’utilizzo di una tecnologia diversa di colonna possono essere presi in considerazione per un eventuale studio futuro.

Infine, sia lo schema ELL che lo schema Diaz hanno portato alla produzione di un IBEA più concentrato. Attualmente, lo schema classico e lo schema Mikitenko prevedono la separazione degli alcool e la successiva eliminazione dell'acqua dall'azeotropo isopropanolo-acqua. Date le basse concentrazioni di acqua nei flussi prodotti dagli schemi ELL e Diaz, potrebbe essere interessante verificare la possibilità di eliminare l'acqua prima di procedere con la separazione dei vari alcool. Ciò richiede quindi uno studio più approfondito sulle tecniche di disidratazione. In particolare, è necessario studiare tecniche di disidratazione come l'adsorbimento e la pervaporazione. Quest'ultimo è presentato come la tecnica di disidratazione più promettente. Tuttavia, sono disponibili pochi dati per il dimensionamento e la valutazione di questa tecnologia.

1 Context

1.1 IFPEN

IFP ENERGIES NOUVELLES (IFPEN) is a public industrial and commercial establishment (Epic) created in 1944. IFPEN is a major player in research and training in the fields of energy, transport, and environment. From research to industry field, technological innovation is at the heart of its action, articulated around three strategic priorities:

- sustainable mobility
- new energies
- responsible hydrocarbons

In the context of sustainable mobility, the main challenges are to take into account the evolution of modes of travel, respond to the challenges of energy efficiency in transport, and diversify energy sources. IFPEN puts its expertise at its service, through its Carnot institute IFPEN Transports Energy, and offers innovations that can be exploited by industry, competitive in economic, energy, and environmental terms, and for the benefit of the community and citizens. Three themes are explored: electric mobility (from hybrid to fully electric vehicles), connected mobility, with the development of services and applications, and mobility with low environmental impact, with the improvement of heat engines and the optimization of the use of fuels.

In the context of new energies, the fight against climate change and the transformation of the energy sector towards a mix of sustainable, carbon-free, and cost-controlled energies require technological innovations. IFPEN is supporting this change by developing processes for the production of advanced biofuels, bio-based products as well as processes for recycling plastics. IFPEN is also working on solutions for CO_2 capture and storage, exploitation of marine energies, and energy storage.

Finally, in the context of responsible hydrocarbons, to reduce the environmental footprint and reduce energy consumption, IFPEN is developing for industry eco-efficient and flexible processes for the production of fuels and chemical intermediates meeting the most demanding standards. To better exploit the reserves, IFPEN also offers modeling tools and cutting-edge technologies, always more efficient for the exploration and production of hydrocarbons.

As part of the general interest mission entrusted by the public authorities, IFPEN focuses its efforts on:

- providing solutions to the societal challenges of energy and the climate, by promoting the transition to sustainable mobility and the emergence of a more diversified energy mix;
- the creation of wealth and jobs, by supporting French and European economic activity and the competitiveness of associated industrial sectors. IFPEN's ambition is to contribute to the development of green industrial sectors and sustainable mobility, accelerating the identification of opportunities in NTE (NEW ENVIRONMENTAL

TECHNOLOGIES). In this regard, diversification into industrial partnerships, support for innovation for SMEs (small and medium-sized enterprises) and startups, and the development of the branches of the IFPEN group are underway.

As a major player in training, the IFP School is an integral part of IFPEN, and as such prepares future generations to face these challenges.

In the context of the energy transition, IFP School and IFP Training closely support industries in their needs by providing highly qualified personnel. IFP School offers young graduate engineers additional training in the energy and sustainable mobility professions and each year more than 500 students graduate from all over the world. IFP Training, a subsidiary of IFPEN, for its part offers professional training to almost 15000 employees in the sector every year, allowing them to improve their competitiveness.

1.2 Introduction

In the context of the strategic priority of new energies, IFPEN has a strong will to be an active part of the Energy Transition.

To be a player in the energy transition, IFPEN is strongly involved in the development of bio-based and biotechnological processes that aim to produce biofuels and bio-based chemical intermediates.

1.2.1 IBEA Production

Butanol and isopropanol are currently produced by the petrochemical route, but technological developments are expected including biotechnological pathways competing with the IBIS process (IBIS = **I**sopropanol and **B**utanol B**i**o **S**ources, IFPEN's biotechnological process for isopropanol and n-butanol production, currently under development).

Butanol produced by petrochemicals has a production of around 4-6 million tons. The production of bio-butanol can also be carried out by fermentation (ABE production: **A**cetone, n-**B**utanol, and **E**thanol). The bio-butanol thus produced is considered an alternative biofuel. The ABE production process using a pure isolated *Clostridium*-type microorganism was one of the first large-scale industrial microbial processes for chemical production, as well as the largest fermentation process under sterile conditions. [1]

Initially, acetone was the main compound of interest for its use in the production of cordite during World War 1 and its use in the production of other chemicals. Over time, butanol became the most desired product as it could be used as a solvent. Moreover, it can also be used as biofuel: due to the large consumption of oil and its trend of rising prices, as well as its impact on the environment, the use of biofuels to partially replace fossil fuels has gained great attention throughout the world. Among these, bio-butanol plays an important role since it can be used directly as a liquid fuel. Compared to ethanol, butanol has many chemical and physical characteristics that are particularly attractive for the application as a biofuel: it is not miscible with water and, therefore, is not corrosive; it has a lower vapor pressure, and higher energy content of almost 50% compared to ethanol. It can also be mixed with gasoline in any ratio without the need to modify vehicle engines and can be transported and stored in the existing infrastructure of the piping and tank system.

While acetone was once considered one of the major products of the ABE process, it is now sometimes considered an undesirable by-product due to its low properties as a biofuel. The reduction of acetone into isopropanol is possible using different biocatalysts belonging to the genus *Clostridium*. The production process of IBEA is therefore based on the ABE fermentation process (Acetone/n-Butanol/Ethanol) and uses strains of the genus *Clostridium* capable of fermenting simple sugars and reducing a large part of the acetone into isopropanol.

An alcoholic mixture of isopropanol, butanol, and ethanol (IBE) is a more attractive biofuel than ABE due to the better properties of isopropanol. Nonetheless, the alcohol concentration in the fermentation broth achieved with these biocatalysts is less than 24 g/L, mainly due to the inhibition of butanol. Several solutions have been proposed to increase the concentration of IBE in the fermentation broth by reducing the toxicity of butanol towards the microorganism. These methods are mainly: integrated reactors with pervaporation, gas stripping, liquid-liquid extraction, or adsorption. However, further purification methods are required downstream of the fermentation process to obtain IBE. The most used system to purify IBE leaving the fermenter is to subject this stream to distillation. Unfortunately, due to the additional binary azeotrope (isopropanol-water), recovery of IBE is more difficult than that of ABE.

After distillation to purify IBEA, acetone is also eliminated, considered as a by-product, or used for other purposes. Once the acetone has been eliminated, the IBE mixture can be directly used or the three alcohols can be separated according to their use.[2] By separating the two main alcohols (I and B) it is possible to use n-butanol as a biofuel, solvent, or chemical intermediate. As for isopropanol, this is produced with an azeotropic composition. This can be directly used (azeotropic water/isopropanol + ethanol) and sent to a transformation process in propylene to create polypropylene-based monomers (without having to remove the percentage of ethanol present in the flow). Alternatively, by eliminating the water it is possible to obtain pure bio-isopropanol. To break up the water/isopropanol (and ethanol) azeotrope, dehydration is carried out generally through extractive distillation, pervaporation, or molecular sieves.

1.2.2 Butanol market

The butanol market was estimated at $ 4 billion in 2017. It is also considered a fast-growing market and is currently driven by Asia and the Middle East due to strong general demand for solvents and butyl acrylate (an additive used in the paint/solvent industry but also in oil fields). n-Butanol, in addition to being used as a biofuel, is used as a solvent in paints, varnishes, natural or synthetic resins, for coating textiles. It also acts as an extractor of natural products: oils, gums, waxes, perfumes, alkaloids, antibiotics, vitamins, hormones, etc. Finally, it is an intermediate in organic synthesis, in particular for the manufacture of butyl esters such as butyl acetate (produced today by acid catalysis of n-butanol and acetic acid of petrochemical origin). Historically, it is in China that the production of n-butanol by biotechnology has been significant, but the number of operating units still operated to date is very low.

1.2.3 Isopropanol market

The isopropanol market, worth $ 1.8 billion in 2017, is considered a strong growth market. In the food and pharmaceutical sectors, it is used in particular for the extraction and purification of various natural products (alkaloids, flavors, gums, oils, proteins, vitamins, etc.). It is also present in the formulations of several products for domestic use, such as floor detergents, waxes, insecticides, window cleaners, automobile window defrosters, or even disinfectants. In cosmetics, it is added to mass-market products. It is also used as a raw material for the production of acetone and its derivatives, glycerin, isopropylamine (pesticides), and as a reaction medium for the production of pharmaceutical ingredients of carboxymethyl cellulose. In the medical field, isopropyl alcohol is used as an antiseptic and disinfectant, mainly in the form of a mixture of 70% isopropyl alcohol and 30% water. It is also found in the tincture of iodine, solutions for local anesthesia, with over 200 different uses. Finally, isopropanol has long shown its interest as an additive in fuels.

1.3 Objectives

Butanol produced by *Clostridium*-type strains is toxic to microorganisms, typically between 7 and 15 g/L. This greatly limits the final alcohol concentration in the fermentation broth (approximately 10 to 30 g/L of IBE).

The water/IBEA separation is conventionally carried out by distillation but, given the very low concentrations of the feed, the separation costs can be very high.

The main objective of this Thesis is to optimize the separation section of the process, minimizing separation costs.Three strategies have been investigated:

- Optimizing the classic distillation scheme (base case)
- Evaluating an alternative scheme, patented by IFPEN (Mikitenko)
- Evaluating the impact of innovative energy integrations on these two cases

The two schemes (basic scheme and Mikitenko scheme) have pure butanol and an azeotrope IPA (+ethanol)/H_2O with a content of about 12% wt of water as products. The obtained IPA stream is suitable for the production of propylene. On the other hand, if it is desired to produce an IPA solvent at a higher purity, this azeotrope must be dehydrated.

Another objective of this Thesis was to study the different methods to dehydrate IPA.

Finally, another objective of the internship was to study two other processes (ELL and Diaz), which allow us to pre-concentrate the fermentation broth before distillation.

It should be noted that many articles are present in the literature, in the ABE/IBE field, on techniques known as ISPR (In Situ Product Recovery).[3][4][5] These are technologies whose objective is to eliminate butanol from the fermentation broth, which is toxic to microorganisms during fermentation. For example, Gas Stripping or two-phase fermentation in the presence of a biocompatible solvent in the fermenter are two types of techniques for removing butanol from the fermentation broth. In this way, it is possible to increase the final concentration of the fermentation broth. However, these are expensive techniques and there is no evidence that the cost of ISPR techniques is offset by the decrease in separation costs.

However, the separation of the fermentation broth obtained with ISPR techniques is not one of the objectives of this Thesis.

2 Schemes and optimization

In the second part of this Thesis we will examine the various schemes used to perform the IBEA separation. Also, the various optimization processes and the effect of some parameters, such as the IBEA feed concentration, on the process energy consumption will be presented for each scheme.

For simulation purposes, PROII (version 10.2) was used. An in-house thermodynamic method, developed by IFPEN was used for calculations.

2.1 Basic scheme

The basic scheme proposed for the separation of IBEA is the one shown in *Figure **2.1.1***.

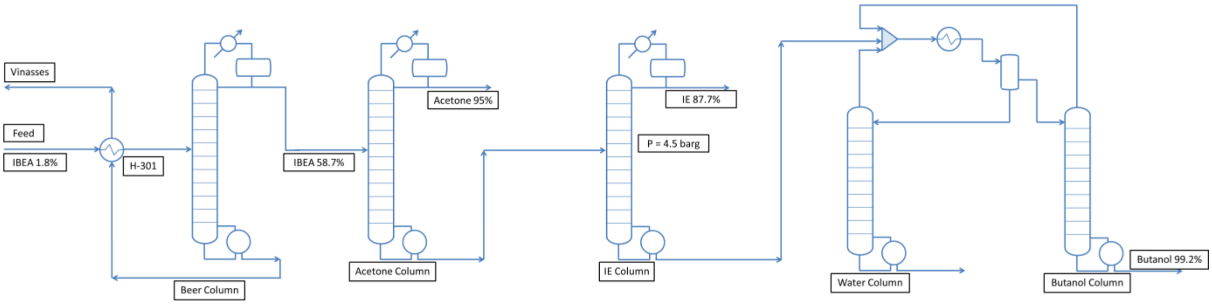


Figure 2.1.1 Basic scheme for the IBEA separation

This scheme involves five distillation columns to perform the separation of the various components.

In particular, the columns used are:

- **Beer column (C-301)**: for the recovery of IBEA at the top of the column and elimination of water at the bottom of the column;
- **Acetone column (C-401)**: it allows the elimination of acetone;
- **Column IE (C-501)**: with this column it is possible to separate the isopropanol and ethanol at the top of the column, from the butanol that is recovered at the bottom of the column;
- **Water (C-601) and Butanol (C-602) column**: the last two columns are used to break the water/butanol azeotrope and recover the butanol at the bottom of the butanol column.

In terms of performance of the columns and quality of the product obtained, the specifications of the 5 columns are the followings:

- **Beer column (C-301):** IBEA in the bottom product is less than 100 ppm;
- **Acetone column (C-401):** the maximum amount of acetone in the overhead product of the next column is equal to 1000 ppm wt.
- **Column IE (C-501):** the recovery of butanol at the bottom of the column is equal to 99.9% and the recovery of isopropanol and ethanol at the top of the Column is

99.99%. It should be noted that at the top of the C-501 column a mixture of isopropanol and water with the azeotrope composition is recovered. The ethanol content in this mixture is considered an impurity.

- **Water (C-601) and Butanol (C-602) column:** the maximum amount of butanol in the bottom product of the Water column is equal to 0.01% wt and the maximum amount of water in the bottom product of the butanol column is equal to 1000 ppm wt.

These specifications remain valid in terms of overall process performance to allow a comparison of the various schemes, even if the following schemes involve a different number of columns.

In terms of energy, the most energy-consuming column is the beer column. *Table* ***2.1.1*** shows the energy required by the reboiler of each column and C-301's preheater (H-303) to perform the separation and the duty of the beer column's feed pre-heater. This Table refers to the non-optimized scheme.

Table 2.1.1 Reboilers duty for the non-optimized scheme for 40 000 t/year of IBEA production

Column	Duty reboiler [MW]	Duty reboiler [MJ/kg IBEA]
C-301	12.4	8.9
H-303	10.9	7.8
C-401	0.8	0.6
C-501	2.3	1.7
C-601	0.4	0.3
C-602	1.2	0.9

The optimization of the scheme aims to reduce the energy consumption of the beer column as much as possible while preserving the performance of the column in terms of IBEA recovery.

The pressure drops losses taken into consideration for the optimization of the scheme are listed in *Table* ***2.1.2***.

Table 2.1.2 Heat exchanger's pressure drops production

Pre-heater – hot side	[bar]	0.3
Pre-heater – cold side	[bar]	0.3
Reboiler – cold side	[bar]	0.3
Trim cooler – hot side	[bar]	0.3
Air cooler – hot side	[bar]	0.3

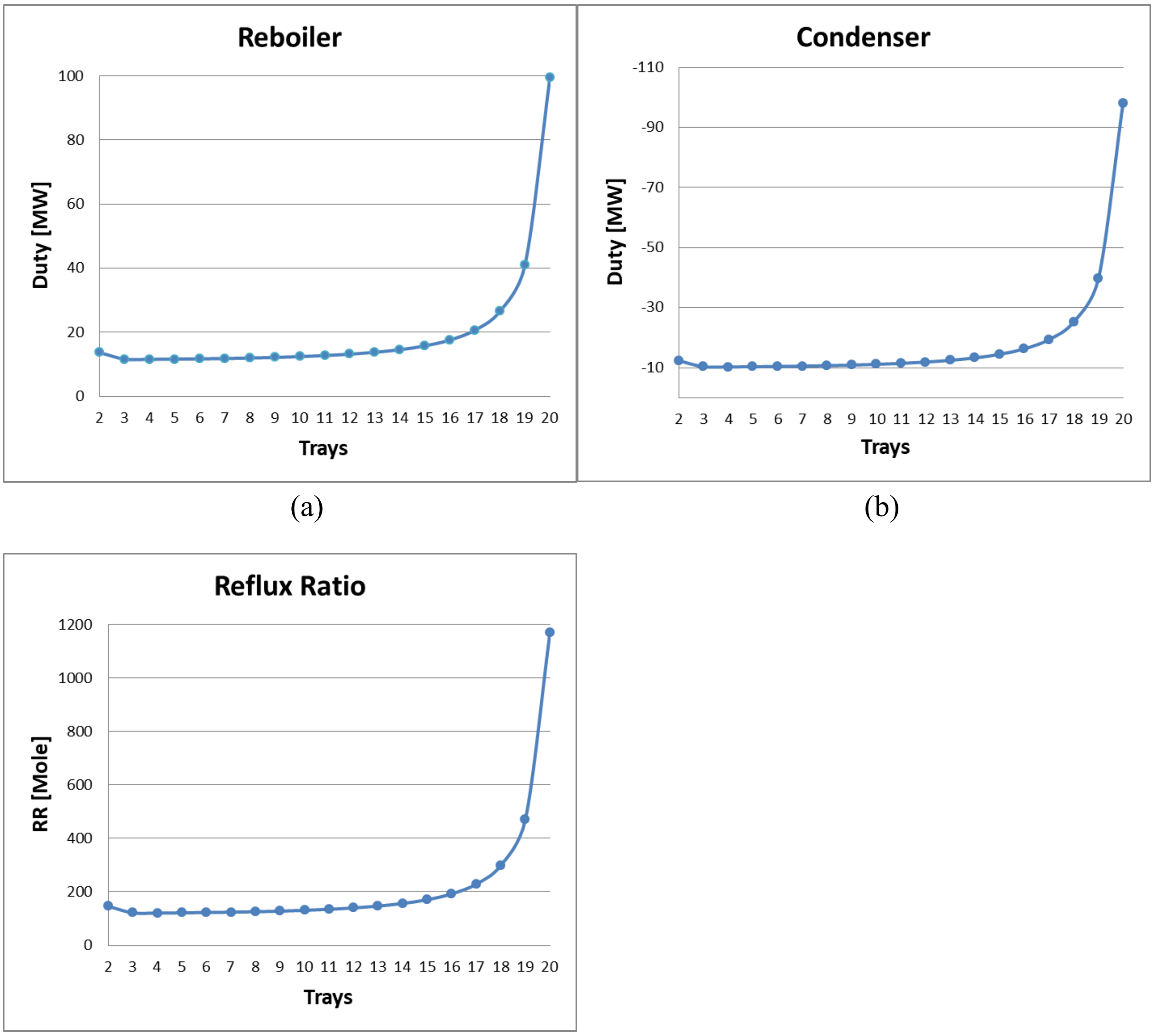
2.1.1 Scheme optimization

2.1.1.1 Scheme optimization: C-301 feed tray

The first step of the optimization of the scheme aims to optimize the number of stages of the column, as well as the feed position and the column feed temperature.

The non-optimized basic scheme includes a heat recovery, consisting of heating the feed using the bottom product of the column. This is done through the H-301 exchanger with a specification of HOCO (Hot Outlet - Cold Outlet) = 3°C. Subsequently, a second exchanger (H-303) is used to bring the feed temperature to 112°C. The idea was to bring the feed to a temperature close to one of the feed plate of the Beer Column.

In the basic configuration, the column has 21 stages, a partial condenser, and a kettle reboiler. The first step was to optimize the feed position to reduce energy consumption. The feed plate has been varied from 2 to 20 and the results obtained are shown in *Figure* ***2.1.2***.



(a)

(b)

(c)

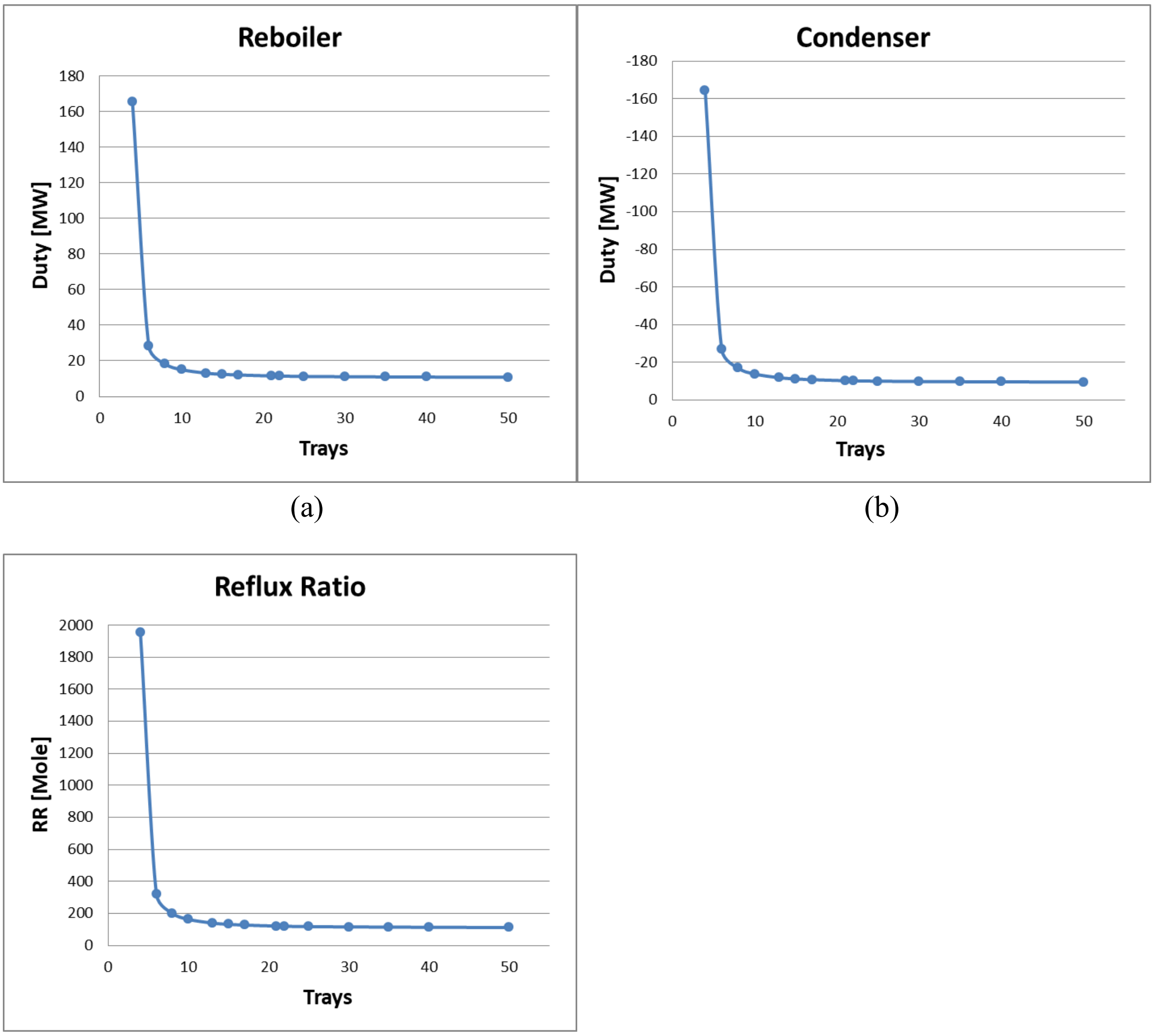
Figure 2.1.2 Optimization of the feed position. Variation of reboiler duty, condenser duty, and reflux ratio varying the tray position: (a) reboiler duty, (b) condenser duty, (c) reflux ratio

In this way, it was possible to optimize the position of the feed by bringing it to plate 4.

2.1.1.2 Scheme optimization: C-301 number of stages

An analysis was then conducted on the energy consumption of the column as the number of stages is varied. Furthermore, at each variation in the number of stages, the optimization of the feeding plate was carried out. Through this analysis, it was possible to find the minimum number of stages necessary for separation.

The analysis led to a minimum number of stages equal to 6. The following figure (*Figure* ***2.1.3***) shows the results of the analysis in terms of energy consumption at the reboiler, at the condenser, and in terms of the reflux ratio.



(a) (b)

(c)

Figure 2.1.3 Optimization of the number of trays. Variation of reboiler duty, condenser duty, and reflux ratio varying the number of trays: (a) reboiler duty, (b) condenser duty, (c) reflux ratio

Given the set of solutions technically feasible, the selection of the optimal configuration is based on an economic comparison. The total cost of the installation includes the depreciation cost (Capex) and the operating cost (Opex). The sum Capex + Opex characterizing the total cost of the process passes through a minimum defining the reflux ratio and the optimum number of stages (*Figure **2.1.4***).

Experience has made it possible to locate, in common cases, the position of this optimum with the limit conditions of distillation. In particular:

(1) $$1.05\, rf_{min} < rf_{opt} < 1.2\, rf_{min}$$

(2) $$2\, N_{min} < N_{opt} < 3\, N_{min}$$

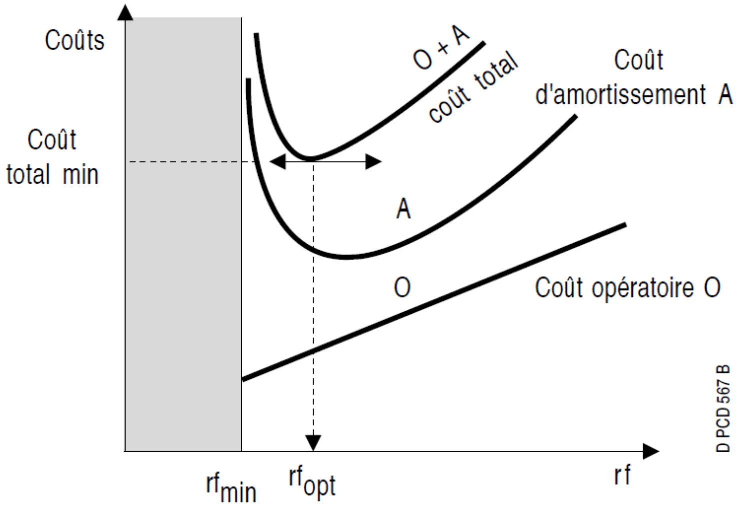


Figure 2.1.4 Distillation costs as a function of reflux ratio

The number of stages chosen for the beer column was therefore equal to 15 (2.5 x 6).

2.1.1.3 Scheme optimization: C-301 feed temperature

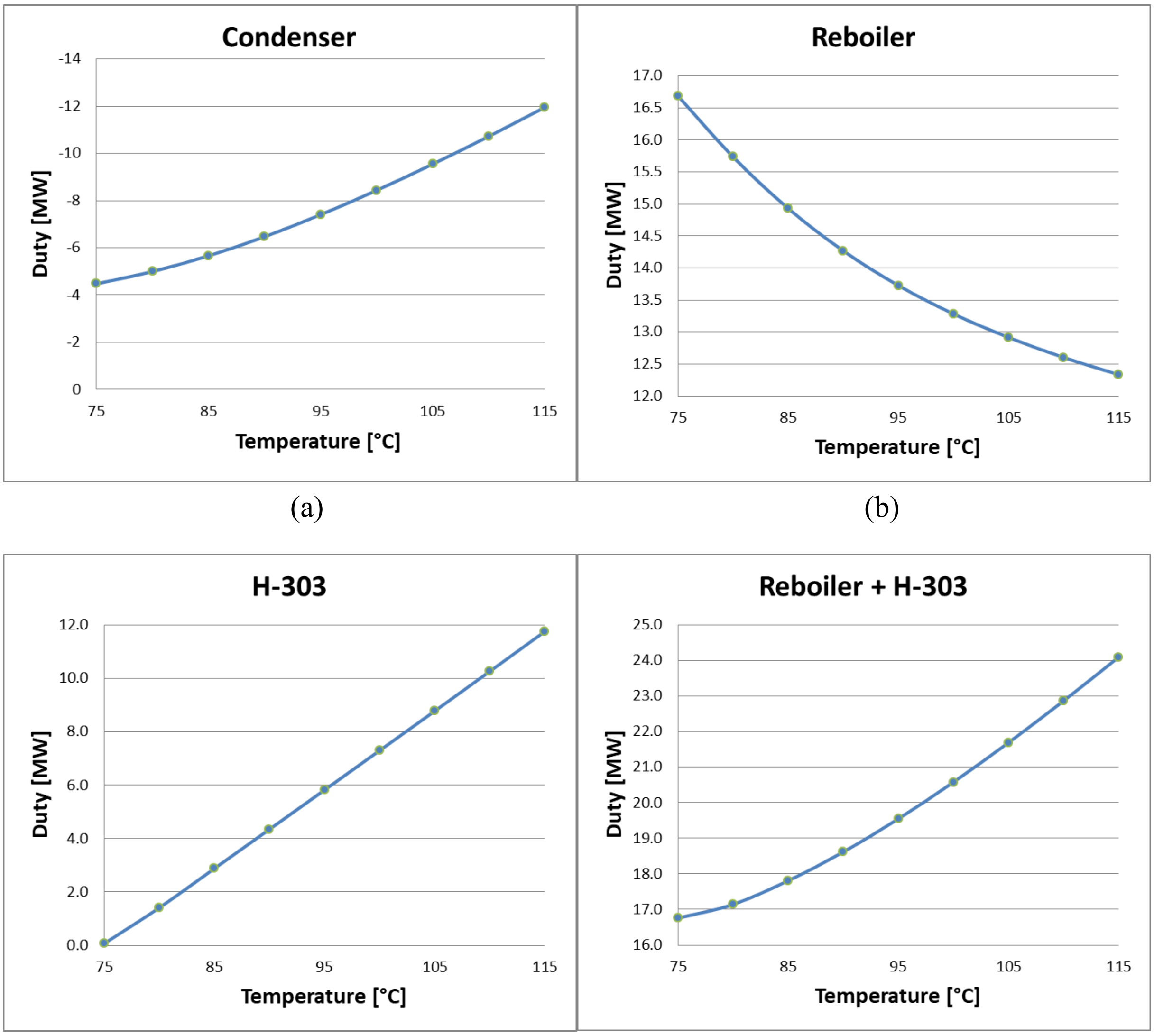
Once the optimal number of stages of the column was found, the next step was to find the influence of the feed temperature on the energy consumption of the column (condenser and reboiler) and the H-303 exchanger.

A sensitivity analysis was carried out in this case, by varying the feed temperature from 75°C to 115°C, with a step of 5°C. The two extremes have been chosen to simulate the temperature of 75°C, equal to the temperature of the feed after being preheated in the H-301 exchanger, and 115°C to be close to the 112°C temperature of the basic scheme and to see what happens when you go above this temperature.

The results are presented in *Figure* ***2.1.5***.

As expected, as the supply temperature increases, the heat to be removed from the condenser and the heat to be supplied to the H-303 exchanger also increase. The heat to be supplied to the reboiler, on the other hand, decreases progressively from 75 to 115°C.

From *Figure* ***2.1.5*** *(d)*, however, we can see how as the supply temperature increases, the sum of the heat to be supplied to the column reboiler and the exchanger increases. The heat to be supplied to the reboiler decreases as the feed temperature increases, but this decrease is slower and to a lesser extent than the increase in the heat to be supplied to the H-303 exchanger. Passing from 75 to 115°C the heat at the reboiler goes from about 16.7 MW to about 12.3 MW with a decrease of 26%. The heat to be supplied to the exchanger instead increases from 0 MW to about 12 MW. The choice was therefore to remove the H-303 exchanger and let the feed enter at about 75°C, equal to the outlet temperature of the H-301 feed-effluent exchanger.



(a) (b)

(c) (d)

Figure 2.1.5 Sensitivity analysis: influence of the feed temperature. (a) Condenser duty, (b) Reboiler duty, (c) H-303 duty, and (d) sum of reboiler and H-303 duty

Subsequently, an economic analysis was carried out to see if the removal of the H-303 exchanger also has positive effects on the cost of separation.

To make this economic evaluation, only the part of the scheme that includes the first beer column was taken into consideration.

For the analysis, an IBEA production of 5 t/h was considered. For the price of the utilities, and IFPEN in-house price data was chosen as shown in *Table **2.1.3***.

Table 2.1.3 IFPEN in-house price data for the utility price

	Price	
Electricity NWE	*Confidential Data*	€/kWh
LPS NWE		€/t
MPS NWE		€/t
CW NWE		€/t

After carrying out the two simulations with and without the H-303 exchanger required to bring the feed temperature to 115°C, the consumption of the utilities was first evaluated using an IFPEN in-house tool. The consumption of utilities in the two cases is shown in *Table **2.1.4***.

Table 2.1.4 Utility consumption with and without H-303

		Without H-303	With H-303
Electricity NWE	kWh/h	267.7	379.3
LPS NWE	t/h	28.4	41.5
CW NWE	t/h	171.3	180.1

Furthermore, using an IFPEN in-house tool it was possible to evaluate the ISBL (Inside Battery Limit) related to the two configurations. Finally, by reporting the value of the ISBL and the consumption of utilities on an IFPEN in-house tool, it was possible to evaluate the separation cost of this first part of the IBEA separation scheme. The economic parameters are taken into consideration on an IFPEN in-house tool to make the economic evaluation are shown in *Table **2.1.5***. The values in blue were calculated directly by the program.

Table 2.1.5 Economic parameters for economic analysis. Fixed Costs

Total Capital Requirement			
ISBL	Process Units	MM €	
OSBL	Storages	MM €	25%
	Utilities	MM €	25%
	Buildings	MM €	5%
	Infrastructure	MM €	6%
	Engineering	MM €	25%
	Contingencies	MM €	25%
Total Fixed (installed) Cost		MM €	211%
	Direct Owner's Costs	MM €	5%
	Indirect Owner's Costs	MM €	10%
Working Capital	Networking capital	MM €	37%
Total Investment		MM €	263%
	Interest on the construction loan	MM €	Calc.
	Escalation Cost	MM €	4%
Total Capital Requirement		MM €	286%
Fixed Costs			
Fixed Charges			
	Maintenance	MM €	3%
	Insurance	MM €	2%
	Overheads	MM €	1%
	TOTAL Fixed Charges	MM €	

The estimated separation costs (C-301 only), consisting of Capex and Opex, are shown in *Table **2.1.6***:

Table 2.1.6 Separation cost as the sum of Capex and Opex with and without H-303

Normalized cost	Without H-303	With H-303
Separation Cost (C-301 only)	59.7	83.8
Capex	11.0	13.9
Opex (excl. Raw material)	48.7	69.9

As can be seen from *Table **2.1.4***, with a feed temperature of 115 °C the consumption of utilities is greater. In fact, in addition to a large increase in LPS already predicted by the analysis of the temperature effect, there is also an increase in utilities such as cooling water and electricity to be supplied to the condenser, which is also foreseen by the previous analysis. . These two effects are reflected in an increase in the Opex of the scheme as can be seen in *Table **2.1.6***. Furthermore, adding the H-303 exchanger also increases the Capex. Although at 115 °C the size of the column is smaller and therefore with a lower cost, the total cost increases as it is necessary to add an exchanger (H-303), and the size of the condenser increases.

2.1.1.4 Scheme optimization: C-401 feed tray and number of stages

After optimizing the beer column (C-301 column) the same procedure was done for the acetone column (C-401 column). The first step in optimizing the C-401 column was to find the minimum number of column stages. The procedure performed is similar to the previous one which also provides for the optimization of the feed plate. The graphs obtained for this column are similar to the previous ones as can be seen from the curve relating to the reflux ratio as a function of the number of stages shown in *Figure **2.1.6***.

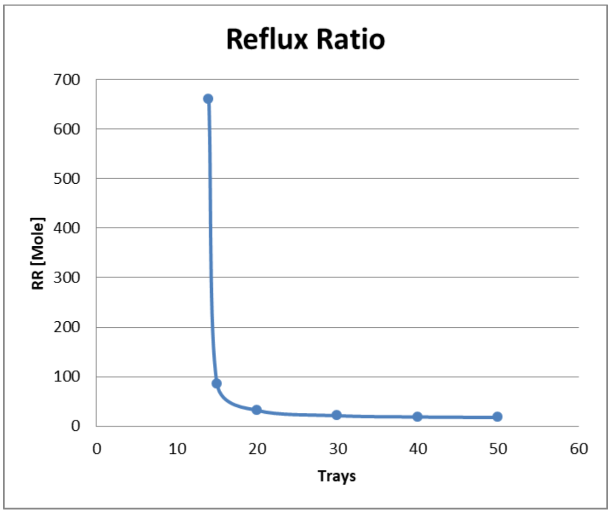


Figure 2.1.6 Optimization of the number of trays for the column C-401. Reflux ratio as a function of the number of trays

For the acetone column, since the minimum number of stages is 15, it has been chosen to operate with 40 stages feeding the column to stage 12.

2.1.1.5 Scheme optimization: C-401 feed temperature

A sensitivity analysis on the effect of the feed temperature on the energy consumption of the column (and of a possible heat exchanger, H-403) was also carried out for the acetone column. In this case, the analysis was carried out between 35°C (temperature of the distillate coming from the condenser of the column C-301) and 80°C, being 76° C the temperature of the feed recovering the heat of the bottom product of the column C-401.

Also for the acetone column, the heat to be supplied to the reboiler decreases passing from 35°C to 80°C (*Figure* ***2.1.7*** *(a)*), but the sum of the heat to be supplied to the reboiler and that to be supplied to the exchanger (H-403) increases (*Figure* ***2.1.7*** *(b)*).

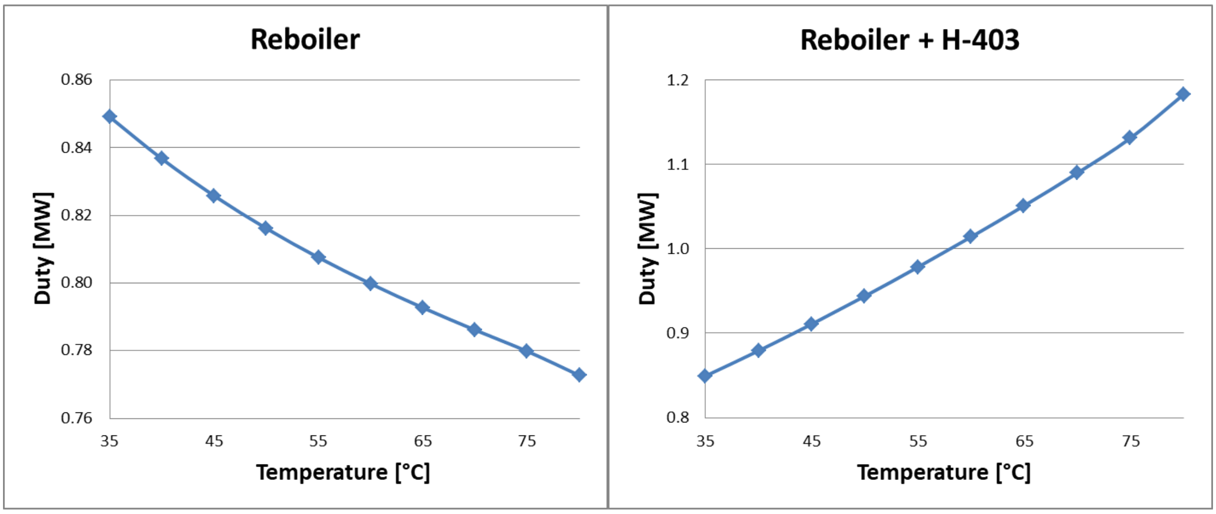


Figure 2.1.7 Figure 2.5 Sensitivity analysis: influence of the feed temperature. (a) Reboiler duty, (b) Sum of reboiler and H-403 duty

Nevertheless, given the possibility of reaching 76 °C with a feed-effluent heat recovery between the bottom of the column and the feed, at first, it was decided to install an exchanger to carry out this heat recovery. *Figure* ***2.1.8*** shows the location of the H-403 exchanger.

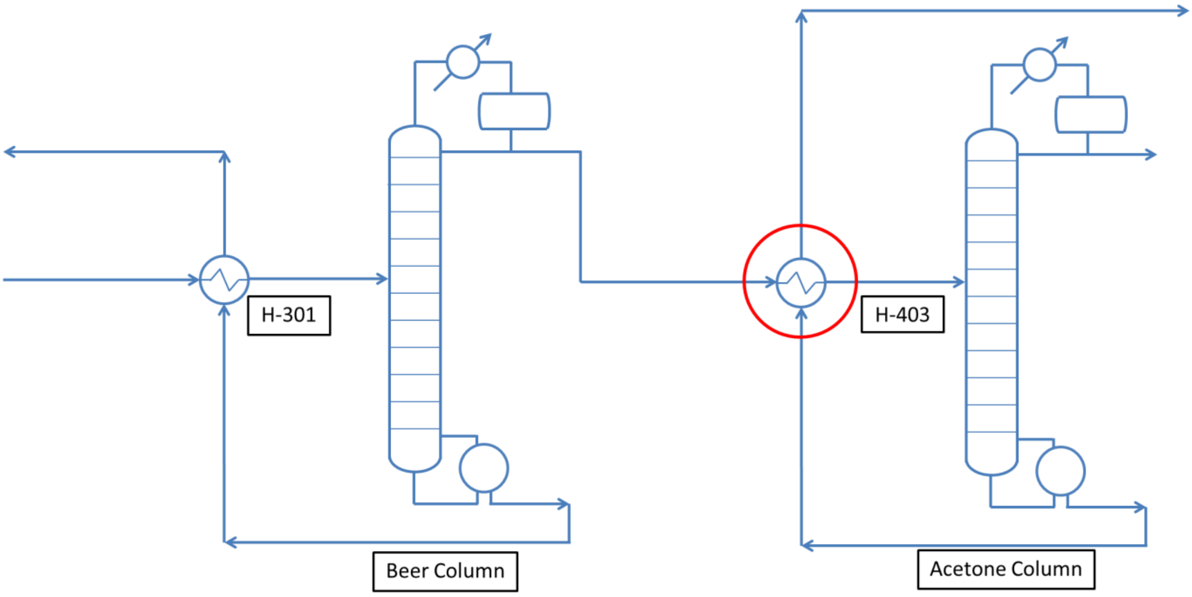


Figure 2.1.8 Adding of a feed-effluent heat exchanger to pre-heat the C-401 feed

Subsequently, an economic analysis was carried out to see if the addition of this exchanger also has positive effects on the cost of separation. To make this economic evaluation, only the part of the scheme that includes the first two columns was taken into consideration, namely the Beer Column (C-301) and the Acetone Column (C-401). After carrying out the two simulations with and without the H-403 exchanger required for heat recovery, the consumption of the utilities was evaluated. The consumption of utilities in the two cases is shown in *Table* ***2.1.7***:

Table 2.1.7 Utility consumption with and without the heat recovery

		No H-403	H-403
Electricity NWE	kWh/h	275.2	287.3
LPS NWE	t/h	29.8	29.7
CW NWE	t/h	172.5	173.3

The estimated separation costs, consisting of Capex and Opex, are shown in *Table **2.1.8***:

Table 2.1.8 Separation cost as the sum of Capex and Opex with and without the heat recovery

Normalized cost	No H-403	H-403
Separation Cost (C-301 + C-401)	65.5	65.9
Capex	13.6	14.0
Opex (excl. Raw material)	51.9	52.0

The addition of a heat exchanger for the recovery of the bottom product heat has the effect of an increase, even if slight, in the production cost. Unlike the case without heat recovery, it is possible to note that with the addition of the exchanger, the LPS to be supplied to the C-401 reboiler decreases but, by increasing the heat to be removed from the condenser, the consumption of cooling water and electricity consumed by the air condensers. This is reflected in an increase in Opex. Furthermore, the increase in heat to be removed from the condensers has an effect on their size which, together with the cost of H-403 which is absent in the case without recovery, leads to an increase in Capex.

It was therefore decided to eliminate the H-403 exchanger and to operate with the feed at the temperature leaving the beer column (about 35°C).

2.1.1.6 Scheme optimization: C-501, C-601, and C-602

The same optimization procedure was performed for the IE column (column C-501). After the optimization, it was decided to operate with 50 stages by feeding the Column to stage 14.

As for the feed temperature, the presence or absence of the H-403 exchanger before the acetone column has an impact on the feed temperature of the C-501 column. In fact, in the case without H-403, the temperature of the C-501 feed is about 102°C while in the other case it is about 71°C. An economic evaluation was carried out by examining only the part of the scheme including the 3 columns. The results are reported in *Table **2.1.9*** and ***Table 2.1.10***.

Table 2.1.9 Utility consumption with and without the heat recovery: influence on C-501

		No H-403	H-403
Electricity NWE	kWh/h	312.0	314.0
LPS NWE	t/h	29.8	29.7
MPS NWE	t/h	4.2	4.4
CW NWE	t/h	173.7	174.5

Table 2.1.10 Separation cost as the sum of Capex and Opex with and without the heat recovery: influence on C-501

Normalized cost	No H-403	H-403
Separation Cost (C-301 + C-401 + C-501)	77.2	77.6
Capex	17.0	17.2
Opex (excl. Raw material)	60.1	60.4

The addition of the H-403 exchanger increases the cost of separation of the scheme also including the IE column. In addition to the effects already discussed on the C-401 column, the preponderant effect for the C-501 column is the increase in the heat to be supplied to the reboiler. The request for MPS is greater if the supply temperature was 71°C. The choice, therefore, remains not to use the H-403 exchanger for the recovery of the bottom heat of the acetone column.

For columns C-601 and C-602, both without a condenser, the feed is supplied to plate 1. The optimization, in this case, was performed only on the number of stages. After optimization, it was decided in this case to operate with 8 stages.

Another possible optimization of the scheme is the energy recovery between Column C-501 and Column C-602.

Energy recovery is possible as the temperature of the C-501's condenser is higher than that of the C-602's reboiler as well as their duties, as shown in *Table **2.1.11***.

Table 2.1.11 Temperature and duties of C-501 condenser and C-602 reboiler

	C-501 Condenser	C-602 Reboiler
T [°C]	130	120
Duty [MW]	2.0	1.3

The gain in terms of utilities and separation costs is presented in *Table **2.1.12*** and ***Table 2.1.13***.

Table 2.1.12 Utility consumption with and without the heat recovery: heat recovery between C-501 condenser and C-602 reboiler

		No Heat Recovery	Heat Recovery
Electricity NWE	kWh/h	345.4	331.7
LPS NWE	t/h	32.5	30.4
MPS NWE	t/h	4.2	4.2
CW NWE	t/h	195.9	195.9

Table 2.1.13 Separation cost as the sum of Capex and Opex with and without the heat recovery: heat recovery between C-501 condenser and C-602 reboiler

Normalized cost	No Heat Recovery	Heat Recovery
Separation Cost	86.4	82.6
Capex	20.5	20.1
Opex (excl. Raw material)	65.9	62.5

In terms of utilities, it is possible to note that there is a decrease in electricity cost and LPS which therefore positively affects the value of the Opex. Indeed, by carrying out this energy integration, all the heat to be supplied to the C-602 column comes from the overhead stream of the C-501. The 1.3 MW required by the C-602 is then supplied by the C-501 column without having to use LPS.

As for electricity, this decreases because much of the condensation heat is removed through energy integration and only a small part remains to be removed using an air condenser.

The value of the Capex also decreases because thanks to the energy integration the heat exchange is carried out in a heat exchanger, less expensive than a Kettle reboiler, and a smaller air condenser is required to completely condense the vapors of the C-501 column.

The scheme with energy recovery is shown in *Figure **2.1.9*** and the heat exchanger used for this purpose is highlighted inside the red circle.

In the basic scheme, the distillate of the C-501 column is cooled from 124°C to 40°C using an aero condenser to bring it to the temperature of 50°C and a trim condenser to reach 40°C. In the scheme presented in *Figure **2.1.9*** the cooling from 124°C to 40°C is done directly with the trim condenser (green circle).

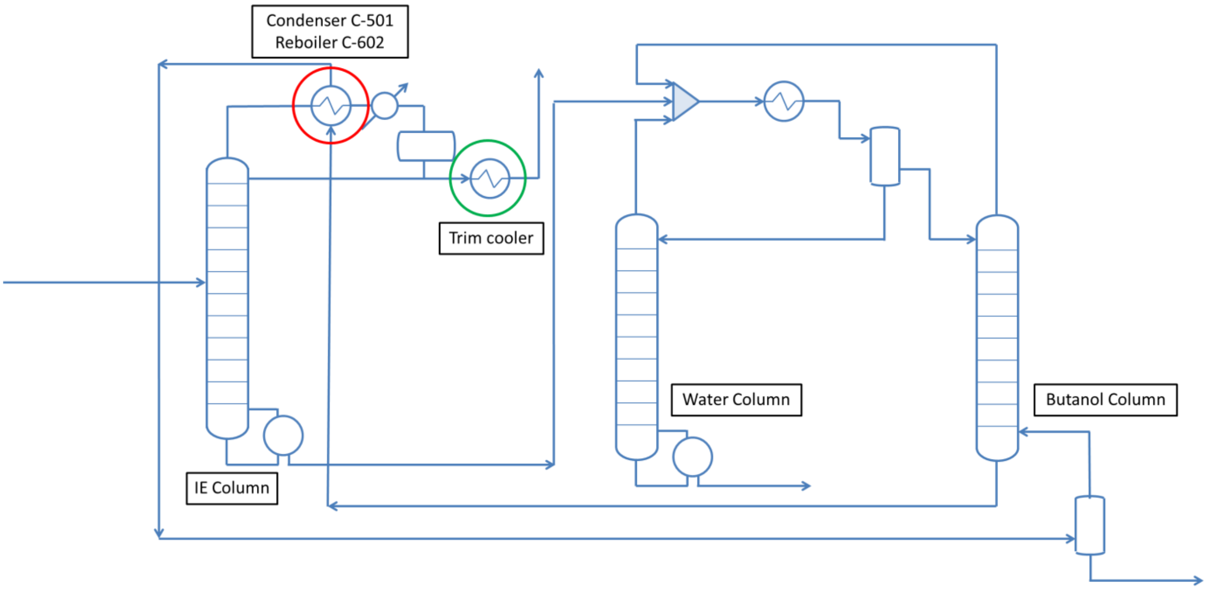


Figure 2.1.9 Optimization scheme with heat recovery between C-501 condenser and C-602 reboiler

The results are reported in *Table **2.1.14*** and ***Table 2.1.15***.

Table 2.1.14 Utility consumption with and without the aero condenser

		Aero + Trim	Trim
Electricity NWE	kWh/h	331.7	327.7
LPS NWE	t/h	30.4	30.4
MPS NWE	t/h	4.2	4.2
CW NWE	t/h	195.9	205.8

Table 2.1.15 Separation cost as the sum of Capex and Opex with and without the aero condenser

Normalized cost	Aero + Trim	Trim
Separation Cost	82.6	82.2
Capex	20.1	19.8
Opex (excl. Raw material)	62.5	62.4

Eliminating the condenser has the advantage of reducing costs due to the installation of an additional exchanger with a consequent decrease in Capex. Furthermore, it can be seen that there is a decrease in electricity consumption and an increase in water consumption which, however, has a slightly lower cost, with a consequent reduction in Opex. The elimination of the condenser therefore has the effect of reducing the separation cost of separation.

2.1.2 Feed temperature influence (HOCO, HICO)

Another possible optimization of the separation scheme is to vary the target on the H-301 recovery exchanger. On the basic scheme, this specification is HOCO (Hot Outlet - Cold Outlet) = 3°C. In the second scenario, this specification is changed to HICO (Hot Inlet - Cold Outlet) = 10°C. In this way, the feed is supplied to the Beer Column at a temperature of 109°C. These two specifications were chosen because:

- HOCO 3 corresponds to a conservative specification and uses a well-known shell and tube technology.
- HICO 10 implies a priori plate heat exchangers (although in theory, we can do this with many shells and tubes in series, in practice we will not), a technology for which we have less information as well for performances' specifications and price data. Furthermore, for plate heat exchangers it is necessary to consider the problem of fouling, more relevant than for a shell and tube heat exchanger.

As seen above, an increase in the feed temperature has a positive effect on the energy consumption of the column. *Table* ***2.1.16*** and ***Table 2.1.17*** compare the two cases with HOCO = 3°C and HICO = 10°C in terms of utility consumption and cost of separation. Furthermore, ***Table 2.1.17*** also shows the separation cost of the non-optimized starting reference scheme.

Table 2.1.16 Utility consumption for the two cases HOCO=3°C and HICO=10°C

		HOCO = 3°C	HICO = 10 °C
Electricity NWE	kWh/h	327.7	253.8
LPS NWE	t/h	30.4	24.0
MPS NWE	t/h	4.2	4.2
CW NWE	t/h	205.8	128.9

Table 2.1.17 Separation cost as the sum of Capex and Opex for the two cases: HOCO=3°C and HICO=10°C

Normalized cost	Reference HOCO 3	HOCO = 3°C	HICO = 10 °C
Separation Cost	100.0	82.2	72.6
Capex	17.9	19.8	20.1
Opex (excl. Raw material)	82.1	62.4	52.5

From the Tables, it can be deduced that with this new specification there is a significant decrease in utilities requirement. The HICO specification = 10°C allows, first of all, to eliminate the aero condenser to cool the bottom product of the column leaving the H-301 exchanger as this stream is already at a temperature of 43.2°C. A simple trim cooler is therefore needed to bring this stream to 40°C. Furthermore, with this specification there is a significant decrease in the LPS required by the beer column, as the energy required for the reboiler is significantly reduced, as already seen. This reduction in utilities can also be observed in the Opex item of ***Table 2.1.17***. As for the Capex, this is slightly increasing although there is the elimination of the condenser and a reduction in the size of the reboiler. In fact, with the new specification there is an increase in the size of the condenser of the beer column, but above all, to carry out the exchange required by the H-301 exchanger 9 BEU exchangers placed in series are required. In conclusion, compared to the reference case, the optimization of the scheme with the HOCO 3 specification allowed to reduce the separation cost by about 17.8%. Using the HICO 10 specification, however, the separation cost was reduced by approximately 27.4%.

2.1.2.1 Plates exchangers for HICO = 10°C

To avoid placing 9 BEU exchangers in series, an alternative is to use plate exchangers which have the advantage of having a larger exchange surface. Since the total required exchange surface is still too high, two plate exchangers placed in parallel are necessary to carry out the heat recovery.

A more optimistic case is also presented in *Table **2.1.18***. In this case, the global heat exchange coefficient of the plate exchanger is 2.5 times greater than that of a tubular exchanger. This precise value was chosen after consultation with a heat exchanger expert. In this way, with the same heat exchange, with a higher exchange coefficient, there is a reduction of the exchange surface and therefore only one exchanger is required to carry out the heat recovery. The results in terms of separation costs are shown below.

Table 2.1.18 Separation cost as the sum of Capex and Opex for the case HICO = 10 °C: the case with 9 BEU in series, the case with 2 plates exchangers in parallel, the case with 1 plate and exchange coefficient Ux2.5 (optimistic case)

Normalized cost	BEU x9	Plates x2	Plate x1, Ux2.5
Separation Cost	72.6	76.2	71.2
Capex	20.1	22.6	19.1
Opex (excl. Raw material)	52.5	53.6	52.1

The solution with 2 plate exchangers with heat exchange coefficient (U) equal to that of a tubular exchanger, is more expensive than the case with 9 BEU in series, although it is better from a practical point of view. The optimistic case, on the other hand, with a coefficient $U_2 = 2.5xU_1$ is the best from a practical and separation cost point of view. In this case, the separation cost decreased by approximately 28.8% compared to the reference case.

It should be noted that for the optimistic case only the heat exchange coefficient U was changed, while the specification HICO = 10°C and the installation factor for the calculation of the Erected cost of the exchanger remained unchanged since the latter is already much lower than that of a BEU (2.07 for BEU and 1.15 for plates exchangers).

Finally, another very optimistic case was simulated: HICO 3 with $U_2 = 2.5xU_1$. However, this case was not reported in the Thesis as it was less advantageous than the optimistic case. In the optimistic case, there is a feed/vinasses heat recovery of 21.6 MW and with the HICO 10 specification, the LMTD is about 8.7°C. The necessary exchange area is about 1900 m^2 and this makes it possible to exchange using a single plate exchanger. In the very optimistic case, the heat recovery is 23.7 MW and with the HICO 3 specification, the LMTD is about 1°C. The necessary exchange area is approximately 17 500 m^2 which seems unrealistic.

2.1.3 Scheme with compressor

One solution to reduce the amount of energy required by the column is to compress the column overhead vapor and use it to provide the heat required by the reboiler. In this way, the total energy required by the beer column is supplied by the overhead vapor and the electricity consumed by the compressor. The modified scheme is shown in *Figure* ***2.1.10***, in which the compressor in the red circle operates with an outlet pressure of the overhead vapors of 2.1 barg and an outlet temperature of 183°C.

From *Figure* ***2.1.10*** it is possible to see how, in addition to the compressor, it was necessary to add other heat exchangers. In particular, two heat exchangers have been added, compared to the optimized case, on the feed. In addition to the H-301 exchanger between the feed and the bottom of the column, another exchanger was added to recover the heat of the overhead vapors after they supplied their heat to the reboiler. Finally, a third exchanger was added to this line to bring the feed to 125°C. Below this temperature and with the compressor at 2.1 barg, energy integration to the reboiler would not be possible. With a feed at temperatures below 125°C, the heat required by the reboiler would be far greater than the heat that can be provided by the overhead vapors at 2.1 barg. Therefore, although it is not necessary to supply steam to the column reboiler, an important amount of steam must be supplied to the exchanger just before the column inlet to allow the separation and heat integration. The results obtained with this configuration are reported in *Table* ***2.1.19*** and ***Table 2.1.20***.

Table 2.1.19 Utility consumption with and without the compressor

		Without K	With K
Electricity NWE	kWh/h	327.7	1820.8
LPS NWE	t/h	30.4	27.0
MPS NWE	t/h	4.2	4.20
CW NWE	t/h	205.8	237.9

Table 2.1.20 Separation cost as the sum of Capex and Opex with and without the compressor

Normalized cost	Without K	With K
Separation Cost	82.2	104.9
Capex	19.8	35.6
Opex (excl. Raw material)	62.4	69.3

The data shown in the Tables point put how, although this system allows reducing the consumption of LPS necessary to supply the heat required by the reboiler, the consumption of electricity increases considerably. The increase in the consumption of utilities is not very significant on the cost of separation since, although electricity increases a lot, its cost is negligible compared to that of steam. The increase in electricity consumption and the decrease in steam consumption are almost balanced.

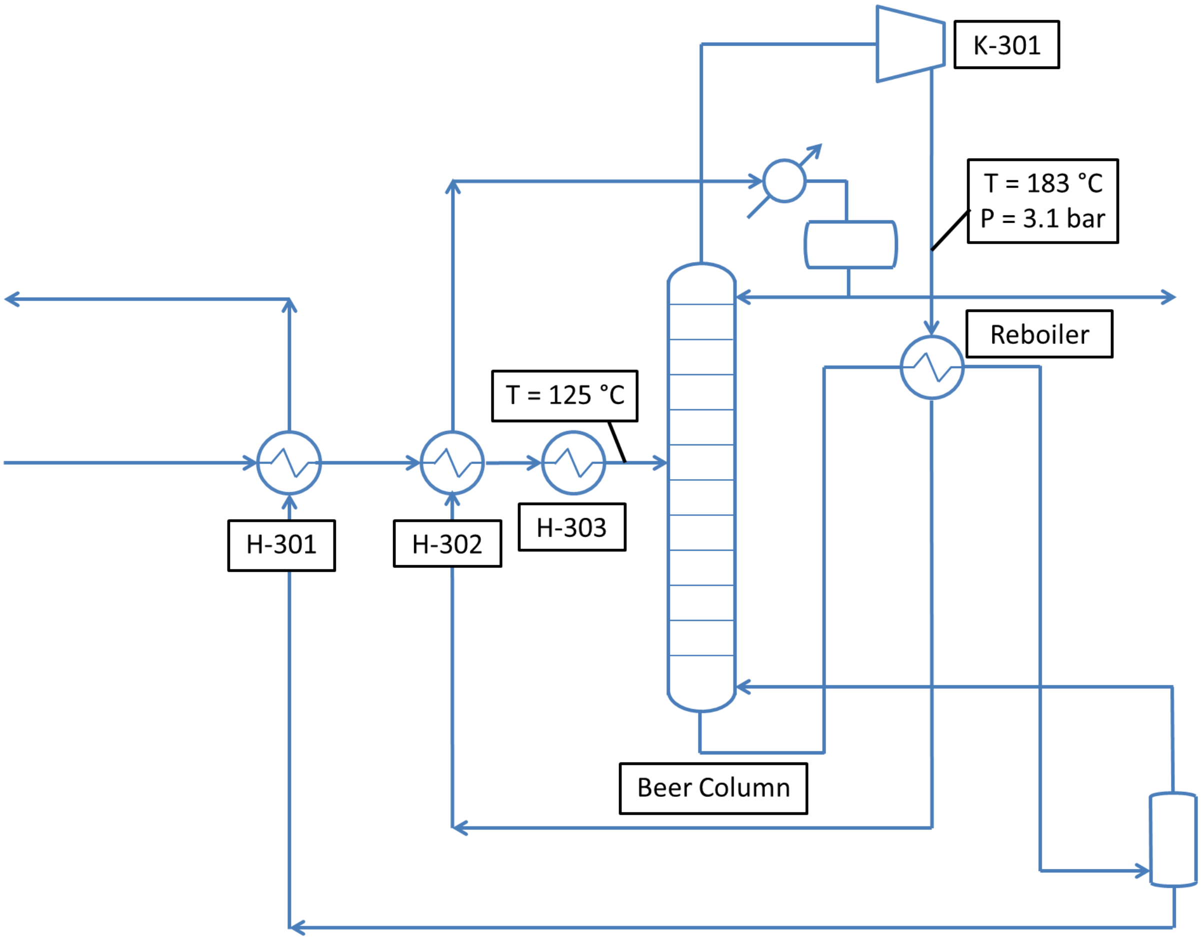


Figure 2.1.10 Basic schema: C-301 with compressor

The biggest problems with this scheme with the compressor are the investments and costs for the installation of the compressor and of all the equipment that had to be added compared to the case without a compressor.

2.1.4 Comparison with the case 46

An in-house energy optimization tool, based on the PINCH methodology was used and resulted in a new energy integrated process scheme, called "*Case 46*" (confidential). This scheme uses classical shell and tube exchangers and allows an equivalent separation cost to the ones of the HICO=10°C cases.

Figure 2.1.11 Case 46: Optimized heat exchanger network – Confidential Data

Figure 2.1.12 Case 46: Optimized scheme – Confidential Data

Table ***2.1.21*** and ***Table 2.1.22*** compare 5 cases: the optimized case (HOCO = 3°C), the case 46 with two different conditions on the cooling water out temperature, and the optimized case with the HICO specification = 10°C. It was decided to use 40°C as the outlet temperature of the cooling water as this temperature was proposed by the energy optimization tool. Furthermore, by using a lower temperature than that of the reference case (45°C) it is possible to reduce the exchange surface required to carry out the cooling, therefore the number of shells required.

Table 2.1.21 Utilities consumption: comparison between optimized case with HOCO = 3 °C, the case 46 (Tout,w = 45 °C and Tout,w = 40 °C) and the optimized case with HICO = 10 °C: 2 plates and 9 BEU

		Case HOCO = 3 °C	Case 46 Trim 45 °C	Case 46 Trim 40 °C	Case HICO = 10 °C
Electricity NWE	kWh/h	327.7	251.9	251.9	253.80
LPS NWE	t/h	30.4	25.8	25.8	24.00
MPS NWE	t/h	4.2	4.2	4.2	4.2
CW NWE	t/h	205.8	340.5	456.5	128.9

Table 2.1.22 Separation cost as sum of Capex and Opex: comparison between optimized case with HOCO=3°C, the case 46 (Tout,w=45°C and Tout,w=40°C) and the optimized cases with HICO=10°C: 2 plates and 9 BEU

Normalized cost	HOCO = 3 °C	Case 46 Trim 45 °C	Case 46 Trim 40 °C	BEU x9	Plate x1, Ux2.5
Separation Cost	82.2	72.5	72.1	72.6	71.2
Capex	19.8	17.7	17.2	20.1	19.1
Opex (excl. Raw material)	62.4	54.8	54.9	52.5	52.1

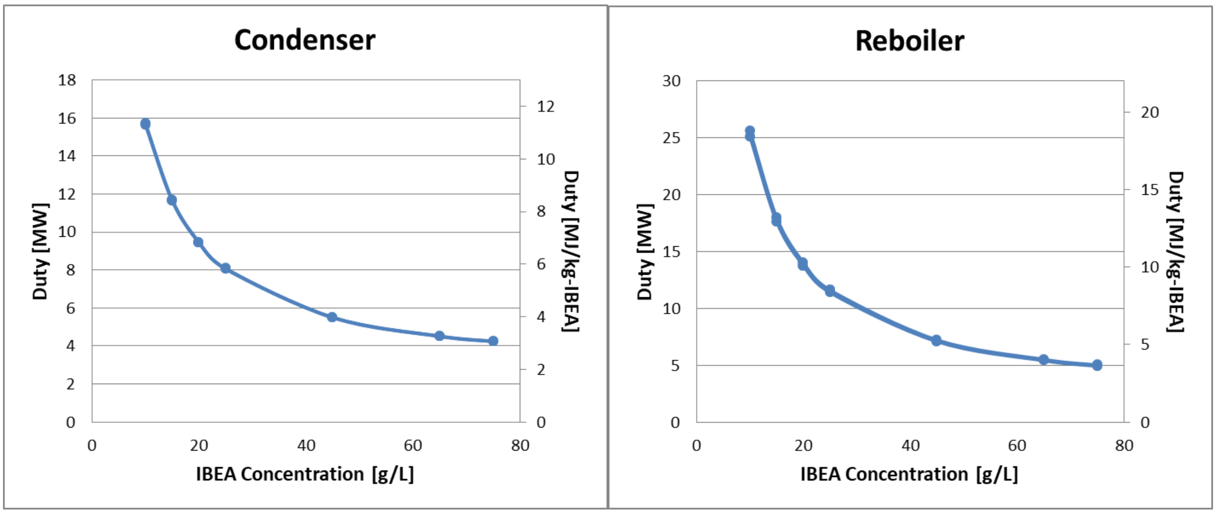
In general, there is a decrease in Opex due to a reduction in LPS which has a much higher cost than that of water, offsetting the cost of increased water consumption. The reduction in LPS and electricity are indicative of a lower duty both of the reboiler and of the aero condensers. This, therefore, affects the size of these two pieces of equipment which decreases, leading to a lower Capex (although the total number of equipment in case 46 is greater than in the base case). The decrease in Capex is also because, with an outlet temperature of the cooling water of 40°C, the number of shells for the trim coolers decreases. This effect can be directly seen looking at Capex, whose value is decreasing between Case 46 with Trim = 45°C and Case 46 with Trim = 40°C.

Comparing case 46 with the base case HICO = 10°C with 9 BEU exchangers, it can be seen that case HICO = 10°C is better in terms of utility consumption and this is reflected in the Opex of this scheme. As for the Capex, however, the case HICO = 10°C is less favorable, due to the presence of 9 BEU exchangers in series necessary to reach the specification. However, looking at the sum of Opex and Capex, the case 46's separation cost is lower. On the contrary, case 46 is less advantageous than the case HICO = 10°C optimistic. Although this solution has a higher Capex due to the presence of a plate heat exchanger, the Opex is lower thanks to a greater recovery of feed/vinasses heat. In fact, for case 46 the separation cost is approximately 27.9% lower compared to the reference case, while for the HICO = 10°C optimistic is 28.8 % lower.

2.1.5 IBEA feed concentration influence

With the production system currently used the concentration of IBEA in the stream leaving the reactor and sent to the beer column is about 19.6 g/L. Using other production systems or different strains of bacteria it is possible to vary the concentration of the beer column feed.

This variation certainly affects the separation pattern. To observe the influence of the concentration, several simulations were carried out by varying the concentration at the entrance to the beer column and observing the change in energy required by the column. The scheme of case 46 was considered to perform the simulation. The concentration was varied between 10 g/L and 60 g/L. The results in terms of the energy required by the column are shown in *Figure* ***2.1.13***.



(a) (b)

Figure 2.1.13 Influence of IBEA Concentration on C-301 energy consumption. (a) Condenser duty, (b) Reboiler duty

As can be seen from the figures, as the IBEA concentration in the C-301 column increases, the heat to be removed from the condenser decreases, as does the heat to be supplied to the reboiler.

In particular, focusing on the decrease in the heat to be supplied to the reboiler, the energy consumption of the column goes from approximately 26 MW to approximately 5 MW with a decrease of approximately 80%. This decrease is reflected in the consumption of LPS steam to be supplied to the beer column which is reduced from 45.5 t/h to 10.7 t/h and on the exchange surface of the reboiler which is reduced from 1350 m² to 265 m². There is therefore a strong decrease in steam consumption (one of the factors that most influence Opex because of its high cost) and the exchange surface of the reboiler with a consequent decrease in Capex.

The increase in the concentration of IBEA entering the distillation scheme therefore has a positive influence on the separation cost.

2.1.5.1 Separation cost vs. IBEA feed concentration

An economic evaluation was carried out to observe the influence of the IBEA concentration in the feed on the separation cost.

Figure ***2.1.14*** shows the variation in the separation cost as the sum of Opex and Capex.

As can be seen from *Figure* ***2.1.14***, the part that most affects the cost of separation is given by the Opex. In fact, for a concentration of IBEA of 10 g/L, Opex corresponds to 78% of the total cost, passing to 70% for a concentration of 75 g/L.

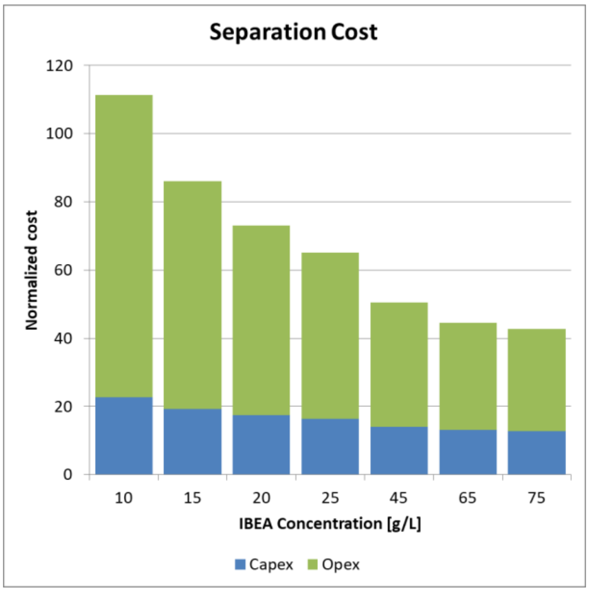


Figure 2.1.14 Influence of IBEA Concentration on the separation cost

It is possible to notice a decrease in both Opex and Capex as the concentration of IBEA in the feed increases. The decrease is greater for Opex and that is closely linked to the decrease in utility consumption. Furthermore, the decrease in separation cost is more important passing from 10 to 15 g/L. The influence of concentration becomes less and less important by moving to higher concentrations. Passing from 10 to 15 g/L there is a decrease in the separation cost of 23%, while from 65 to 75 g/L the decrease in the separation cost is only 4%.

Concentrations above 25 - 30 g/L can hardly be achieved without ISPR techniques, it is not sure so far that the cost of ISPR processes can be balanced by the reduction of Separation Cost.

The study was not carried above 75 g/L. Indeed, if IBEA is over approximately 175 g/L the feed shows liquid-liquid equilibrium and other distillation schemes must be used.[6]

2.1.6 Acid path

In the feed entering the scheme, there are, in addition to water and IBEA, also fermentation by-products such as organic acids. In particular, the organic acids we find in the feed are acetic acid and butyric acid. In this paragraph, we will briefly analyze how the acids produced during fermentation are distributed between the various columns and, therefore, between the various products of the separation scheme. The scheme is taken into consideration in the basic scheme with HOCO = 3°C.

Looking individually column by column, *Table* ***2.1.23*** to ***Table 2.1.26*** shows how acids are distributed during separation. The intermediate flows between the two columns are shown in red.

Table ***2.1.23*** shows that most of the acid contained in the feed comes out in the stream EAU_OUT_1, the bottom product of the first column. Only 0.74% of acetic acid and 3.35% of butyric acid end up in the distillate (DIST1) and pass to the acetone column. In the off-gas stream, on the other hand, a negligible part of these acids is lost. From ***Table 2.1.24*** and ***Table***

2.1.25 we can instead see that all the acid entering the column comes out at the bottom of both columns.

The BOT3 stream that comes out of Column IE is sent to the two columns (water and butanol). The acetic acid is divided between the two columns and 48.3% comes out at the bottom of the water column and 51.7% from the butanol column. Butyric acid, on the other hand, ends up 97% at the bottom of the butanol column and only 3% in the water column.

Table 2.1.23 Acid distribution: beer column

		FEED1	EAU_OUT_1	OFFGAS1	DIST1
Acetic	kg/h	452.9	449.5	8.5 E-04	3.3
Butyric	kg/h	453.3	438.1	6.5 E-04	15.2

Table 2.1.24 Acid distribution: acetone column

		DIST1	OFFGAS2	DIST2	BOT2
Acetic	kg/h	3.3	3.1 E-14	6.5 E-12	3.3
Butyric	kg/h	15.2	1.5 E-24	5.3 E-21	15.2

Table 2.1.25 Acid distribution: IE column

		BOT2	DIST3	BOT3
Acetic	kg/h	3.3	1.5 E-10	3.3
Butyric	kg/h	15.2	6.7 E-13	15.2

Table 2.1.26 Acid distribution: water column and butanol column

		BOT3	BOT4	BUT_OUT
Acetic	kg/h	3.3	1.6	1.7
Butyric	kg/h	15.2	0.5	14.7

Finally, *Table* ***2.1.27*** summarizes the acid path showing the acid distribution in the overall separation scheme.

Table 2.1.27 Acid distribution: separation scheme

		FEED1	EAU_OUT_1	BOT4	BUT_OUT
Acetic	kg/h	452.9	99.2 %	0.4 %	0.4 %
Butyric	kg/h	453.3	96.7 %	0.1 %	3.2 %

2.2 Mikitenko

The scheme presented previously provides one beer column, one column for the separation of acetone, one to recover ethanol and isopropanol, and two columns for the separation of the water-butanol azeotrope. The Mikitenko scheme consists only of one beer column and a second column to separate the butanol from the other components.[7] These are finally sent to a third column which separates isopropanol and ethanol from acetone. The peculiarity of this scheme is all in the second column. This column provides a three-phase area (two liquid and one vapor) on some trays. The distillate from the first column is sent to the second column and is composed of concentrated IBEA. In this stream, the concentration by weight of IBEA can even exceed 50%. The aqueous phase is subtracted from the three-phase zone and is recycled and mixed with the feed of the first Column. The Mikitenko scheme is presented in *Figure* ***2.2.1***.

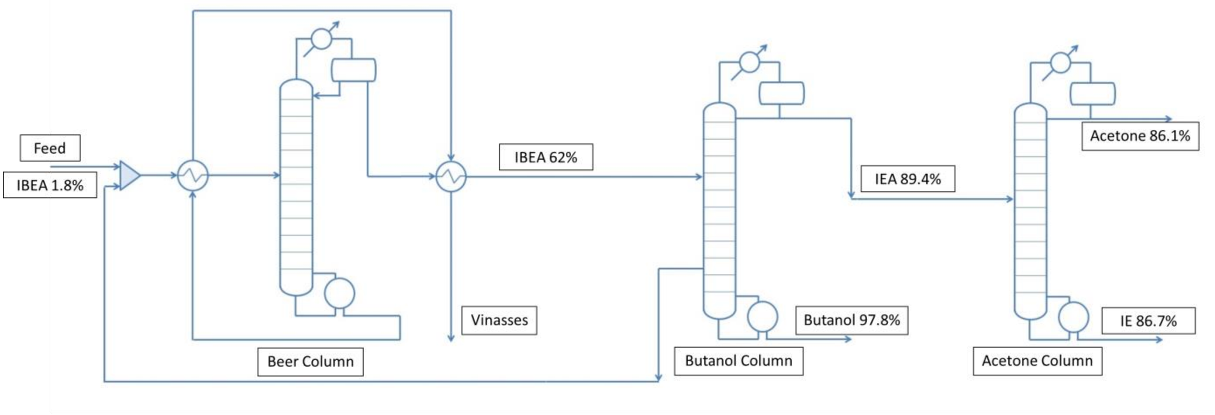


Figure 2.2.1 Mikitenko scheme for the IBEA separation

In particular, the columns used are:

- **Beer column (C-301)**: for the recovery of IBEA at the top of the column and the elimination of water at the bottom of the column;
- **Butanol column (C-401)**: with this column it is possible to separate the isopropanol and ethanol at the top of the column from the dry butanol that is recovered at the bottom of the column;
- **Acetone column (C-501)**: it allows the elimination of acetone from the ethanol and isopropanol mixture;

In terms of performance of the columns and quality of the product obtained, the specifications of the 5 columns are:

- **Beer column (C-301):** IBEA in the bottom product less than 100 ppm;
- **Butanol column (C-401)**: recovery of butanol at the bottom of the column of 99.99% and butanol concentration at the bottom of the column higher than 98 % wt;
- **Acetone column (C-501)**: recovery of isopropanol and ethanol at the bottom of the Column of 99.8% and maximum amount of acetone in the bottom product equal to 1000 ppm wt.

In terms of energy, the most energy-consuming column is the beer column. *Table **2.2.1*** shows the energy required by the reboiler of each column to perform the separation and the duty of the beer column's feed pre-heater. This table does not refer to the optimized final scheme.

Table 2.2.1 Reboilers duty for 40 000 t/year of IBEA production

Column	Duty reboiler [MW]	Duty reboiler [MJ/kg IBEA]
C-301	17.0	12.3
C-401	3.0	2.2
C-501	0.3	0.2

The optimization of the scheme aims to reduce the energy consumption of the beer column as much as possible while preserving the performance of the column in terms of IBEA recovery. The pressure drops taken into consideration for the optimization of the scheme are listed in *Table **2.2.2***.

Table 2.2.2 Heat exchanger's pressure drops

Pre-heater – hot side	[bar]	0.3
Pre-heater – cold side	[bar]	0.3
Reboiler – cold side	[bar]	0.3
Trim cooler – hot side	[bar]	0.3
Air cooler – hot side	[bar]	0.3

2.2.1 Scheme optimization

2.2.1.1 Scheme optimization: C-301 feed tray and number of stages

The first step in optimizing the C-301 column was to find the minimum number of column stages. The procedure performed is similar to the previous one which also provides for the optimization of the feed plate. An analysis was then conducted on the energy consumption of the column as the number of stages varied. The analysis led to a minimum number of stages equal to 4. The following figure (*Figure **2.2.2***) shows the results of the analysis in terms of energy consumption at the reboiler.

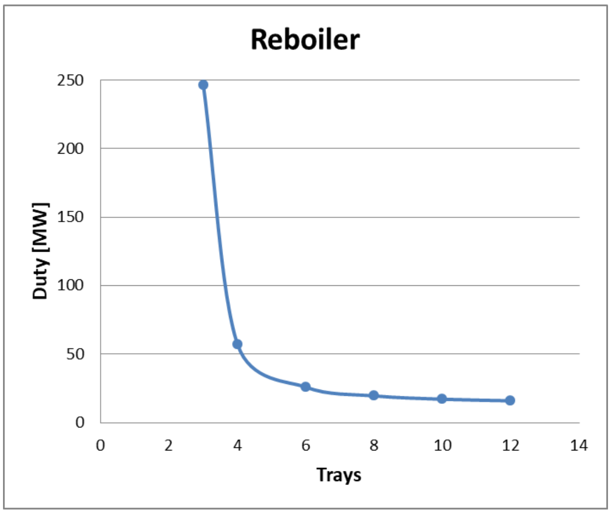
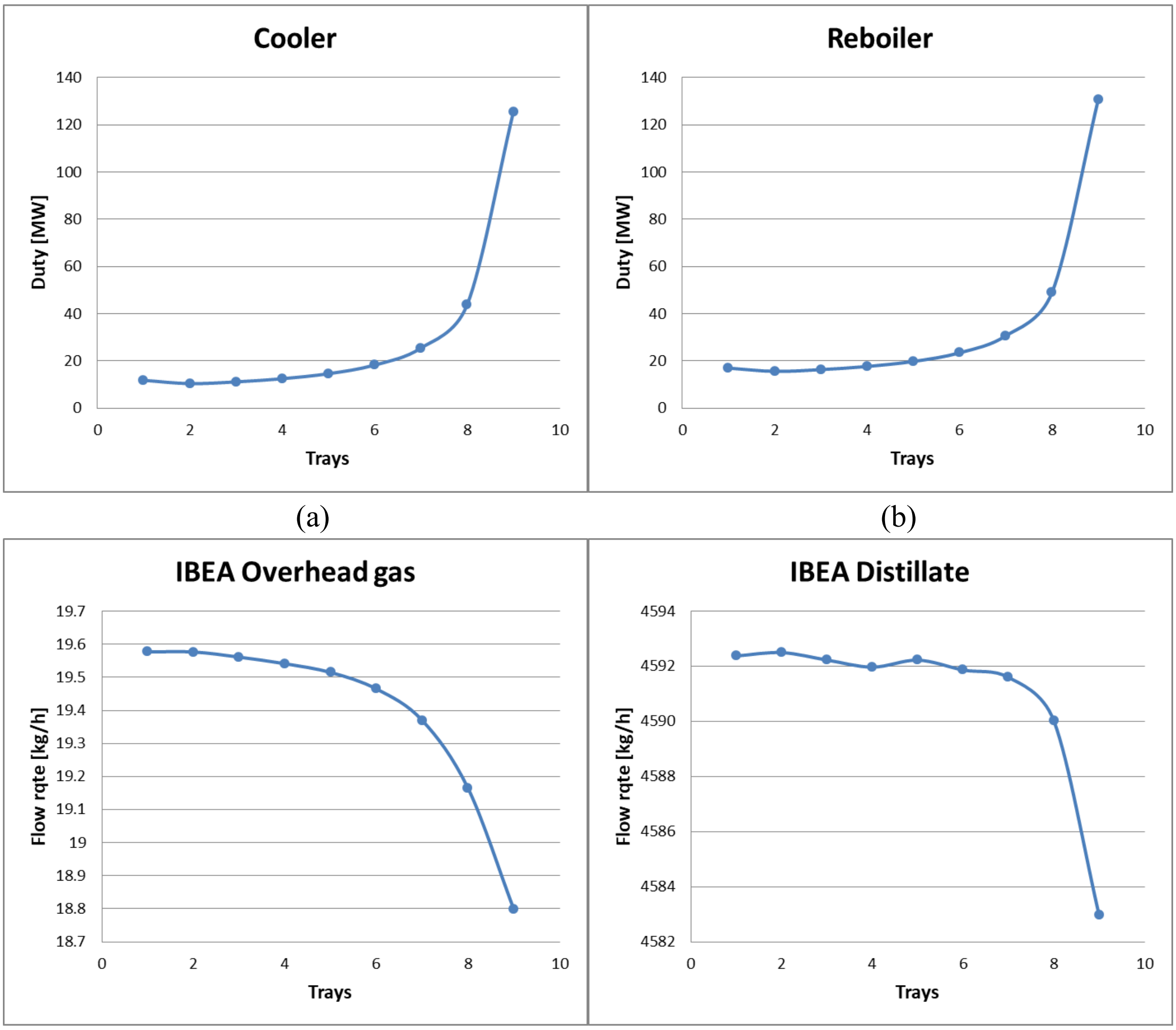


Figure 2.2.2 Optimization of the number of trays. Variation of reboiler duty varying the number of trays

The number of stages chosen for the operation of the beer column was equal to 10 (2.5 x 4).

As for the feeding plate, a more accurate analysis was carried out for the case with 10 trays. *Figure **2.2.3*** shows the results in terms of reboiler duty, cooler duty (absolute values), IBEA flow in the gas overhead, and IBEA flow in the distillate. It has been chosen to feed the column to plate 2. By inserting the feed to plate 2, the duties of the cooler and of the reboiler are lower, with consequent savings in terms of utilities and investments both for the cooler (aero-condenser and trim condenser) and for the reboiler. This choice also has the advantage of allowing to obtain a high flow of IBEA in the distillate, although in this way there is a greater loss of IBEA in the overhead gas. The IBEA loss decrease in the overhead gas going from plate 1 to plate 9 is only 4% while the reboiler duty when feeding to plate 9 is 8 times that of plate 1. Therefore the predominant factor in this choice was the duty of the reboiler and cooler.



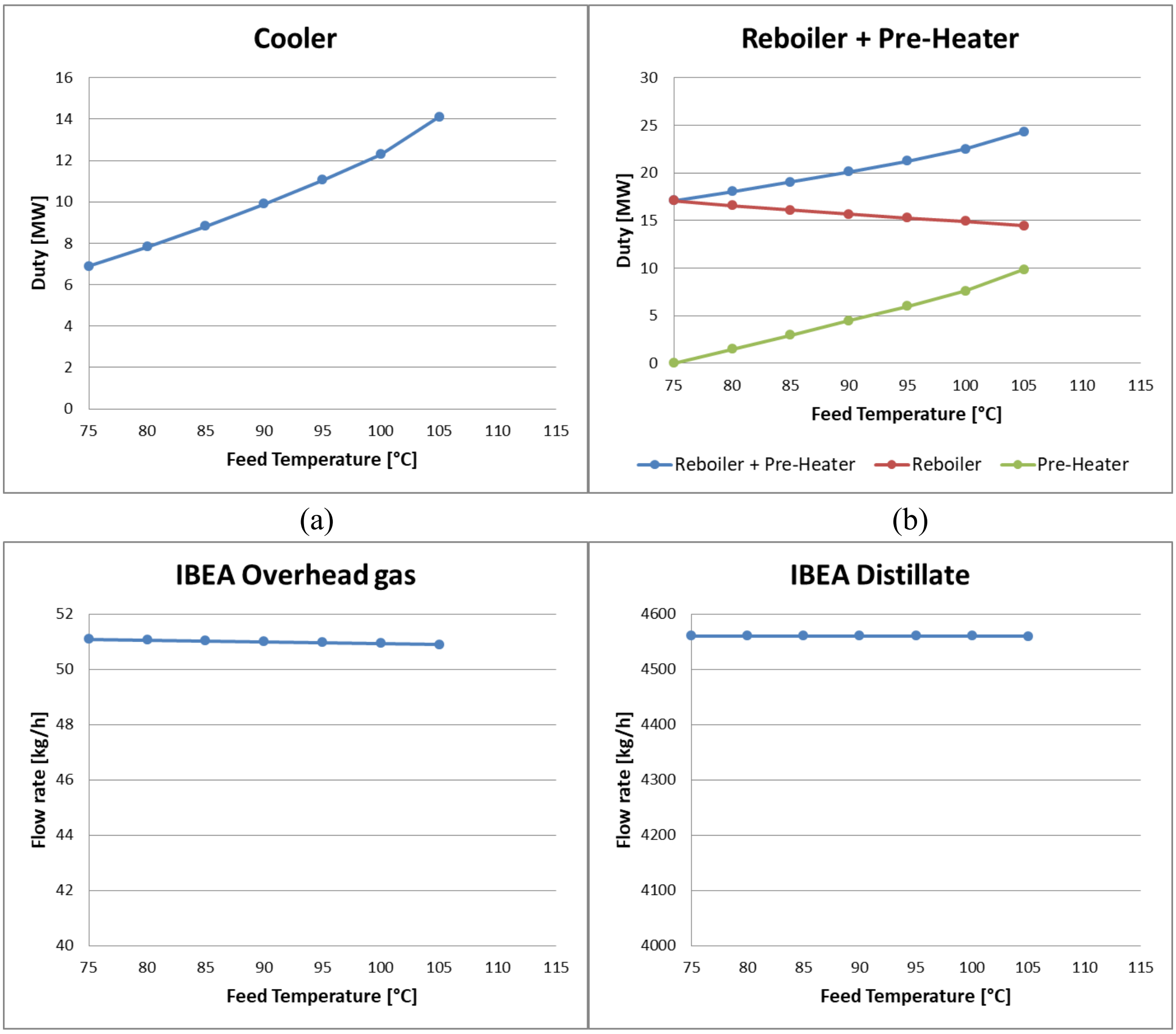
(a) (b)

(c) (d)

Figure 2.2.3 Optimization of the feed position. Variation of reboiler duty, cooler duty, IBEA flow rate in the overhead gas, and IBEA flow rate in the distillate varying the tray position: (a) cooler duty, (b) reboiler duty, (c) IBEA overhead gas, (d) IBEA distillate

2.2.1.2 Scheme optimization: C-301 feed temperature

Once the optimal number of stages and the feed tray were found, the next step was to find the influence of the feed temperature on the energy consumption of the column (cooler and reboiler) as well as on the IBEA flow rate in the overhead gas and the distillate. A sensitivity analysis was carried out in this case, by varying the feed temperature from 75°C to 115°C with a step of 5°C. The two extremes have been chosen for the same reasons as the basic scheme. The results are presented in *Figure **2.2.4***.



(a) (b)

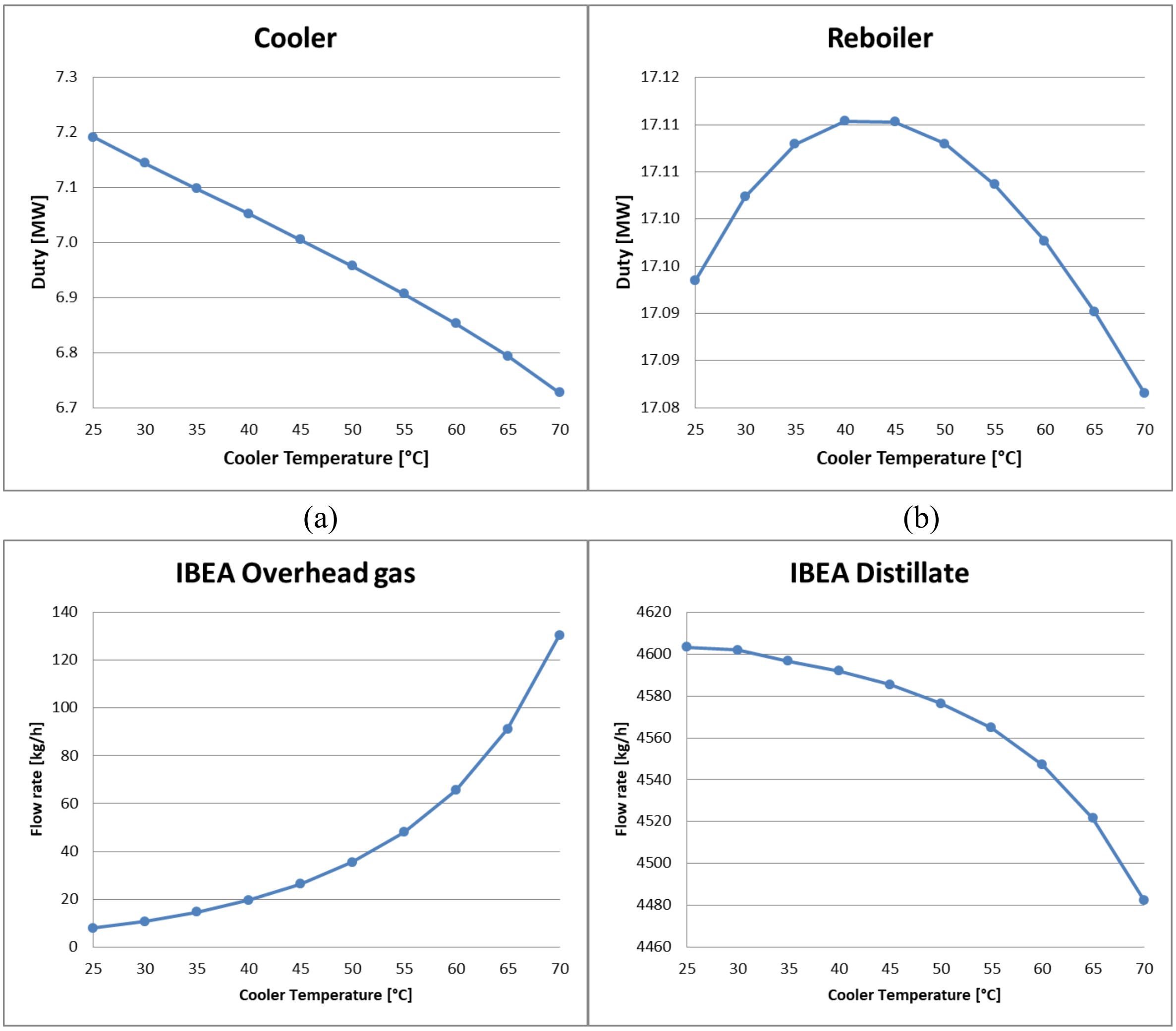
(c) (d)

Figure 2.2.4 Optimization of the feed temperature Variation of reboiler duty, cooler duty, IBEA flow rate in the overhead gas, and IBEA flow rate in the distillate varying the feed temperature: (a) cooler duty, (b) reboiler, pre-heater, reboiler + pre-heater duty, (c) IBEA overhead gas, (d) IBEA distillate

Although the analysis was from 75 to 115°C it was decided to present the results from 75 to 105°C because at 110°C the feed becomes all vapour. Entering the column with a vapour-state feed has not a big impact on the quantity of IBEA in the overhead gas and in the distillate. However it has a huge impact on the cooler and the pre-heater whose duty becomes more than 10 times their duty at 105°C. So, the results at 110 and 115°C where not considered. Nonetheless, from *Figure **2.2.4*** it is possible to see how as the temperature increases, the duty of the cooler increases by doubling, passing from a feed at 75°C to a feed at 105°C. Furthermore, as for the basic scheme, the reboiler duty decreases as the feed temperature increases. However, the duty on the pre-heater is increasing. Also in this case, as for the basic scheme, the cumulative effect of reboiler and pre-heater consists of an increase in duty as the temperature increases. As for the IBEA flow in the distillate, the variation is minimal, passing from a maximum of about 4561.3 to a minimum of 4560.6 kg/h. The flow of IBEA in the overhead gas also decreases in a not very significant way. Also in this case the choice was therefore made based on the preponderant effect of the reboiler and cooler duty. It was chosen to feed at about 75°C, feed temperatures after being pre-heated by the bottom product of the Column.

2.2.1.3 Scheme optimization: C-301 cooler temperature

The next step was to optimize the cooler temperature. An analysis was carried out by varying the cooler temperature from 25°C to 70°C. In this way, it was possible to see the influence of the cooler temperature on reboiler duty, cooler duty, IBEA in the distillate, and the gas overhead. The results are presented in *Figure* ***2.2.5***.



(a) (b)

(c) (d)

Figure 2.2.5 Optimization of the cooler temperature Variation of reboiler duty, cooler duty, IBEA flow rate in the overhead gas, and IBEA flow rate in the distillate varying the cooler temperature: (a) cooler duty, (b) reboiler duty, (c) IBEA overhead gas, (d) IBEA distillate

First of all, we can see how the reboiler duty variation is not very significant. Its effect will not be taken into consideration when choosing the cooler temperature. As for the duty of the cooler, as we might have expected, we notice how this increases as the temperature of the cooler decreases. For every 5°C temperature increase, the cooler duty decreases by about 0.65%. On the contrary, the amount of IBEA in the overhead gas increases significantly, going from about 10 kg/h to about 130 kg/h. Its increase is about 35% every 5°C. As for IBEA in the distillate, this has an opposite behavior to that of the IBEA in the overhead gas, decreasing with increasing temperature. Also in this case, however, as for the cooler, the decrease is not significant. Taking into consideration all the parameters discussed and considering to use a cooler composed of an aero condenser and a trim condenser that uses water at 30°C, it was chosen to operate with a temperature of 40°C.

2.2.1.4 Scheme optimization: C-401

For the second column design, the simulation examples were found in the bibliography and were taken as models.[7][8] Unlike our case, these two publications study the separation of an ABE mixture (acetone, butanol, ethanol). *Pucci et al.* describe the problem starting from the construction of the acetone-butanol-water ternary diagram, highlighting the presence of a liquid-liquid equilibrium zone (***Figure 2.2.6***).[8]

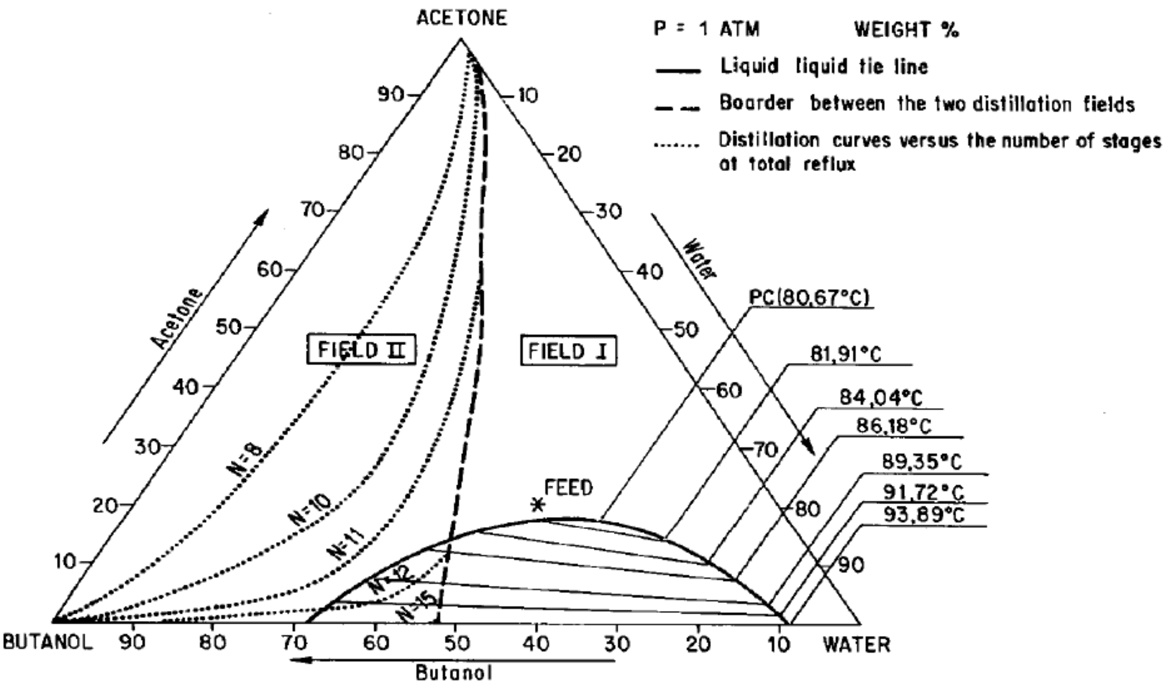


Figure 2.2.6 Acetone-butanol-water ternary diagram [5]

In this diagram we can see the presence of two distillation regions, in particular, FIELD I and FIELD II separated by a dotted line indicating the boundary that cannot be crossed by a standard distillation. As mentioned above, the distillate from the first column and fed to the second column contains more than 50% wt. water and is located in Field I of the ternary diagram. In this way, by standard distillation, it would supply acetone vapors at the top and a heterogeneous mixture of water and butanol at the bottom of the column. During the distillation, the liquid-liquid equilibrium zone is entered with the consequent formation of two saturated liquid phases in equilibrium with each other. These two phases, as the temperature varies, can be found in two distinct fields of the ternary diagram. By eliminating the aqueous phase, the organic phase in FIELD II leads to obtaining a distillate composed of dehydrated butanol.

According to what has been said, in the upper part the column is in FIELD I of the ternary diagram. Subsequently, the column passes to the three-phase regime (liquid-liquid-vapor) up to the plate for removing the aqueous phase. Finally, below this plate, the column is in FIELD II until it reaches the bottom of the column.

As shown in ***Figure 2.2.6*** the column needs at least 12 stages (at total reflux) to enter the liquid-liquid equilibrium region. The configuration chosen by Pucci et al. is a column with 30 stages, feed at stage 13 (overhead condenser: stage 1), and removal of the aqueous phase at stage 23.

Following this configuration, it was possible to find the configuration for the separation of IBEA. This configuration includes a column with 30 stages (overhead condenser or stage 1 and reboiler or stage 30), feed at stage 12, LLV equilibrium between stage 12 and stage 25, removal of the aqueous phase at stage 25 (*Figure **2.2.7***).

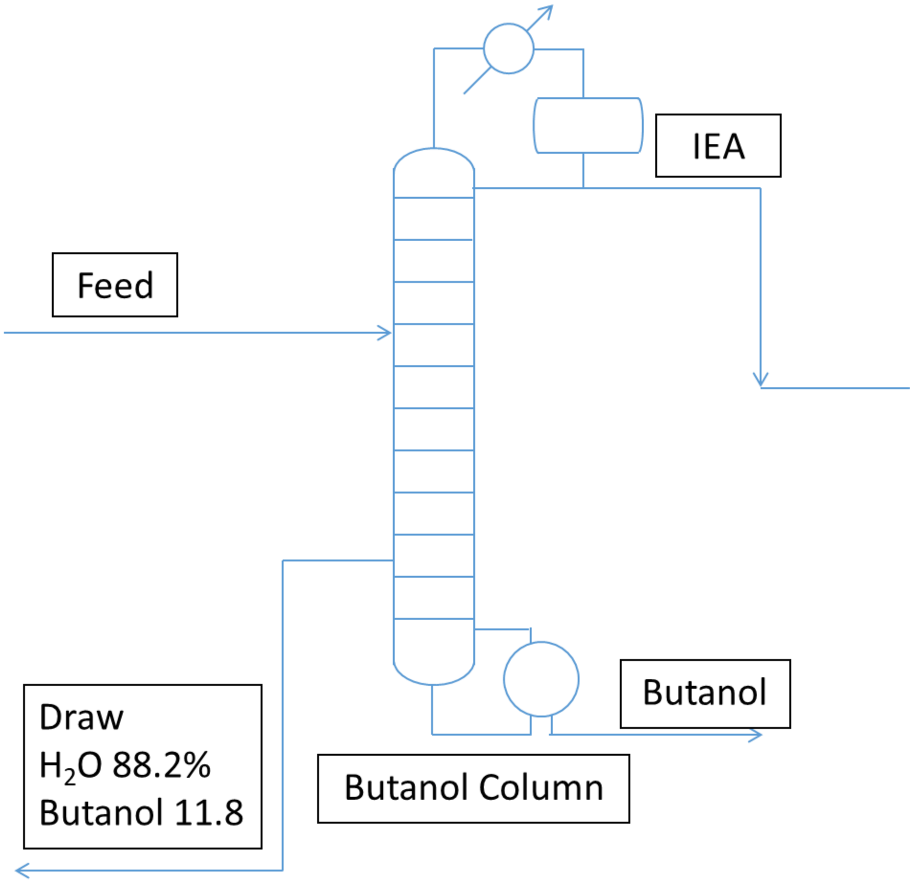


Figure 2.2.7 Butanol column (C-401) for IBEA separation.

The ternary diagram in *Figure **2.2.8*** (expressed in molar fractions) refers to the scheme in *Figure **2.2.7***. On the diagram, it is possible to notice the two azeotropes (water-butanol and water-isopropanol), the equilibrium zone LL (in green), the total reflux distillation curves (in red), the feed and the distillation path of column C -401 simulated using ProII.

The figure clearly shows how from stage 1 to 11 the column is in FIELD I of the ternary diagram, obtaining at the top of the column a distillate with a composition that is close to that of the water-isopropanol azeotrope. Remember that the distillate also contains ethanol, acetone, and in small concentrations butanol. Starting from stage 12 the column enters the biphasic zone with a separation of the two liquid phases. The points shown in the graph refer to the average composition of the two liquid phases. After stage 25 with the removal of the aqueous phase, the column enters the FIELD II of the ternary diagram with the production of dehydrated butanol at the bottom of the column.

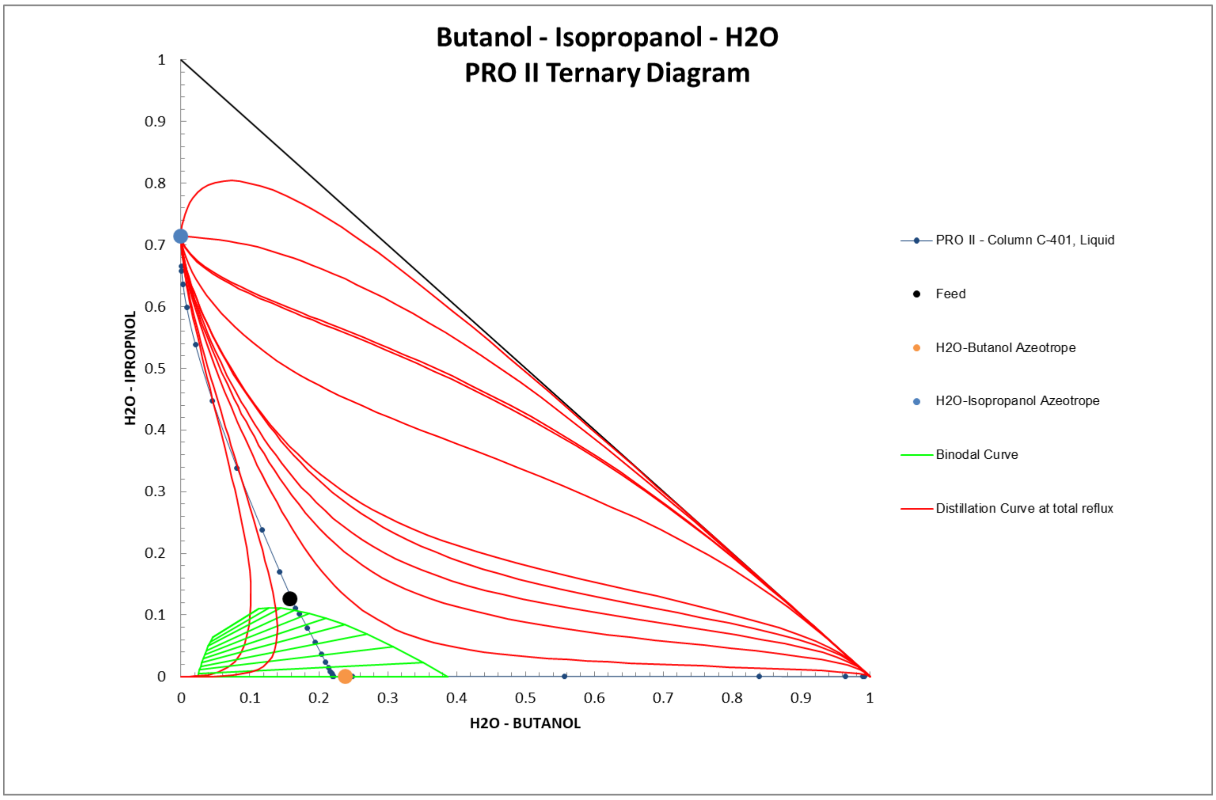


Figure 2.2.8 Butanol – Isopropanol – Water ternary diagram with ProII C-401 distillation path

2.2.1.5 Scheme optimization: C-401

As for the feed temperature of Column C-401, only two temperatures were taken into consideration due to the convergence problems of the scheme. In the first case, the feed temperature is 40 °C equal to the distillate temperature of Column C-301. In the second case, the temperature is 68.6 °C. This temperature is reached by the E-304 heat exchanger which recovers the residual heat of the C-301 bottom product after it has transferred some of its heat to E-301.

The results in terms of utilities and cost of separation are shown in *Table* ***2.2.3*** and ***Table 2.2.4***

.

Table 2.2.3 Utility consumption: comparison between the case without E-304 and with E-304

		Without E-304	With E-304
Electricity NWE	kWh/h	329.0	322.9
LPS NWE	t/h	34.8	34.4
CW NWE	t/h	191.3	191.3

Table 2.2.4 Separation cost as the sum of Capex and Opex: comparison between the case without E-304 and with E-304

Normalized cost	Without E-304	With E-304
Separation Cost (C-301 + C-401)	76.6	76.4
Capex	15.9	16.2
Opex (excl. Raw material)	60.7	60.2

From *Table **2.2.3*** we can see how the addition of the E-304 exchanger to recover the residual heat of the bottom product of the C-301 column allows us to reduce the consumption of electricity. Recovering part of the heat from the bottom product of C-301 decreases the duty of the aero-condenser used to bring its temperature to 50°C. Furthermore, if the feed of the C-401 is at 68.6°C the duty of the C-401 reboiler decreases with a consequent decrease in the consumption of LPS. The decrease in electricity consumption and steam consumption is directly reflected on the Opex (***Table 2.2.4***) and the separation cost. The Capex decreases by eliminating the E-304 exchanger but the increase in Opex is higher, causing an increase in the final separation cost. Therefore, the choice was to insert the E-304 exchanger to recover part of the residual heat of the bottom product of C-301. The specification of the E-304 exchanger is HOCO = 3°C.

2.2.1.6 Scheme optimization: C-501 feed tray and number of stages

To remove the acetone contained in the distillate of column C-401 it is necessary to add a third column. Column C-501, or column acetone, has the purpose of obtaining at the bottom of the column a water-isopropanol mixture at a concentration similar to that of the azeotrope (with a small percentage of ethanol) and to eliminate all the acetone at the top of the column.

The first step in optimizing the C-501 column was to find the minimum number of column stages. The procedure performed also allows the optimization of the feed plate (*Figure **2.2.9***).

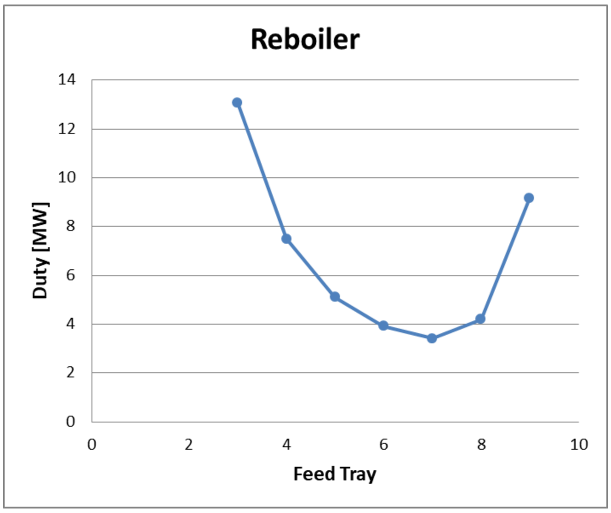


Figure 2.2.9 Optimization of the feed position for the column C-501. Reboiler duty as a function of the feed tray

An analysis was then conducted on the energy consumption of the column as the number of stages varies. The analysis led to a minimum number of stages equal to 10.

The following figure (*Figure* ***2.2.10***) shows the results of the analysis in terms of energy consumption at the reboiler.

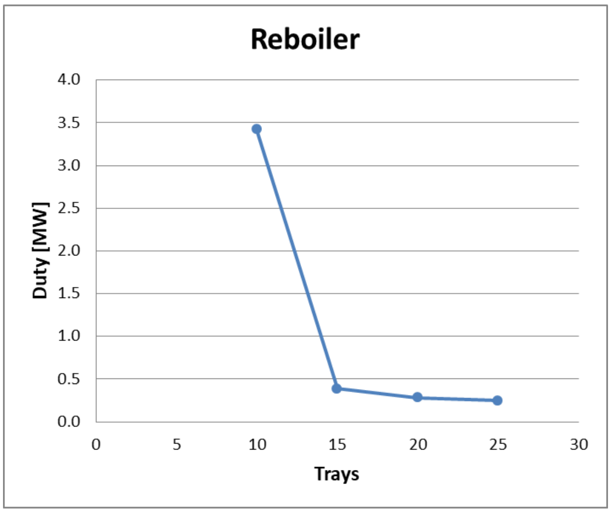


Figure 2.2.10 Optimization of feed trays for the column C-501. Reboiler duty as a function of the number of trays

The number of stages chosen for the operation of the C-501 column was equal to 25 (2.5 x 10).

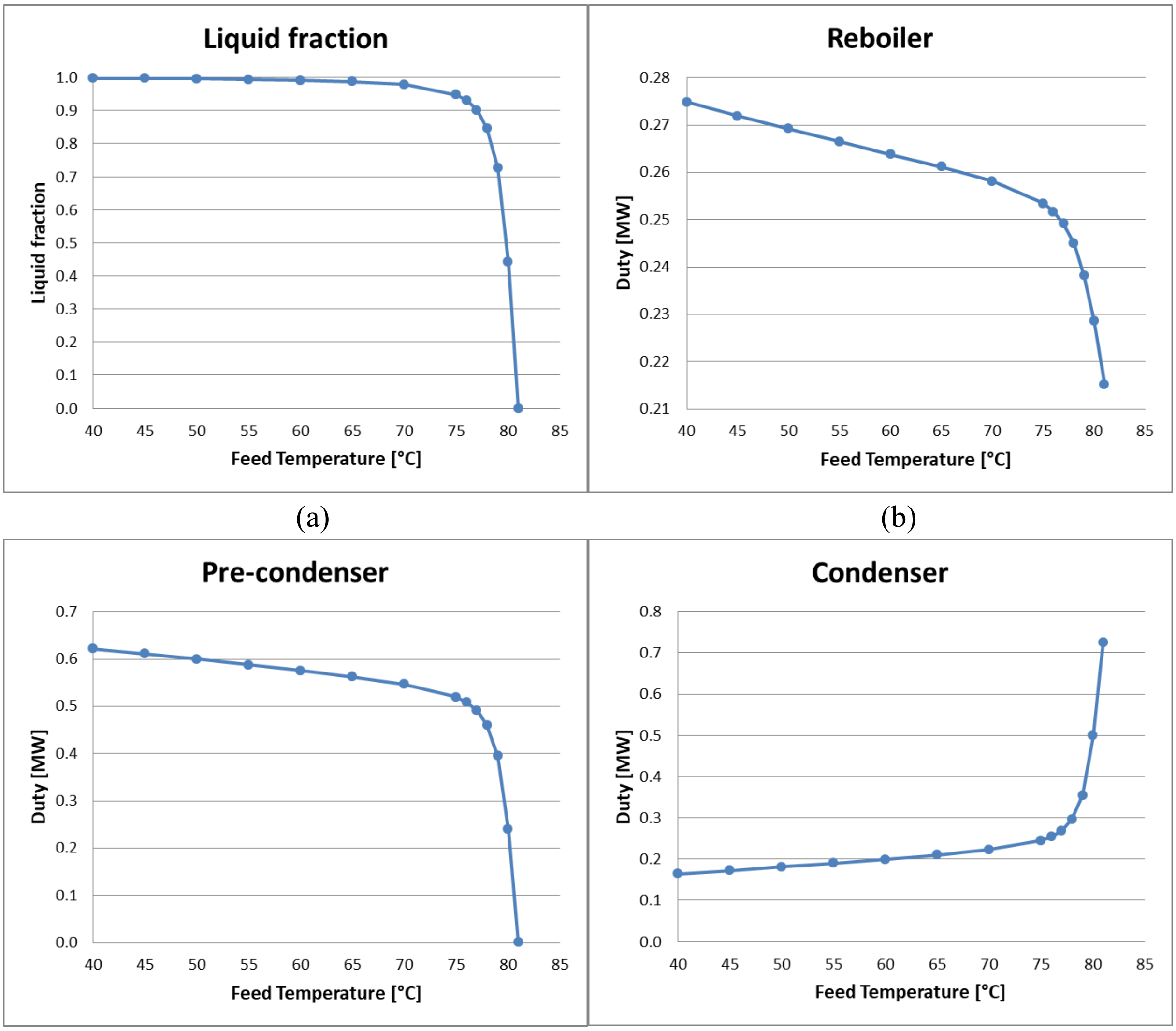
2.2.1.7 Scheme optimization: C-501 feed temperature

The next step was to find the influence of the feed temperature on the energy consumption of the column in terms of reboiler duty. A sensitivity analysis was carried out in this case, by varying the feed temperature from 40°C to 75°C with a step of 5°C and then from 75 to 81°C with a step of 1°C. The maximum temperature limit equal to 81°C was chosen as this is the temperature of the distillate in the form of the vapor exiting the C-401 column.

The results are presented in *Figure* ***2.2.11***.

From *Figure* ***2.2.11****(a)* it is possible to see how as the temperature increases, the feed phase changes from being completely liquid at 40°C to being completely vapor at 81°C. Consequently, feeding at 81°C instead of 40°C has the effect of decreasing the heat to be removed from the pre-condenser since, as already mentioned, the distillate leaves the C-401 column in the form of saturated steam.

As the temperature increases, the reboiler duty decreases. On the contrary, the heat to be removed from the column condenser increases. However, it can be observed that the decrease in the duty of the pre-condenser is slightly higher than the increase in the duty of the condenser. If we consider this last factor, together with the fact that by eliminating the pre-condenser the costs related to this exchanger are also eliminated, the choice falls on the elimination of the pre-condenser. Furthermore, in terms of utilities, a decrease in steam consumption has a greater impact on the separation cost than the increase in electricity required for the aero-condensers because of the higher cost of LPS.



(a) (b)

(c) (d)

Figure 2.2.11 Optimization of the feed temperature. Variation of feed liquid fraction, reboiler duty, pre-condenser duty, and condenser duty varying the feed temperature: (a) liquid fraction, (b) reboiler duty, (c) pre-condenser duty, (d) condenser duty

Therefore, the final choice was to eliminate the heat exchanger and let the feed enter the C-501 column at 81°C, equal to the outlet temperature of the distillate from the C-401 column.

2.2.2 Feed temperature influence (HOCO, HICO)

Also for the Mikitenko scheme, as well as for the basic scheme, two configurations for the E-301 exchanger were compared. The first configuration consists of the HOCO specification = 3°C and the second configuration consists of the HICO specification = 10°C.

Thanks to the specification HICO = 10°C the feed enters at 108.2°C. Also in this case, as in the basic case, the positive effect of the increase in the feed temperature on the energy consumption of the column has already been shown.

Table ***2.2.5*** and ***Table 2.2.6*** compare the two configurations in terms of consumption of utilities and separation costs. Furthermore, ***Table 2.2.6*** also shows the separation cost of the non-optimized starting reference scheme.

Table 2.2.5 Utility consumption for the two cases HOCO=3°C and HICO=10°C

		HOCO = 3°C	HICO = 10 °C
Electricity NWE	kWh/h	326.9	245.8
LPS NWE	t/h	36.8	31.7
CW NWE	t/h	191.1	137.1

Table 2.2.6 Separation cost as the sum of Capex and Opex for the two cases: HOCO=3°C and HICO=10°C

Normalized cost	Reference HOCO 3	HOCO = 3°C	HICO = 10 °C
Separation Cost	100.0	80.9	74.0
Capex	17.9	16.8	17.7
Opex (excl. Raw material)	82.1	64.1	56.3

As in the base case, the HICO = 10°C specification is more convenient in terms of both separation cost and utility consumption. We note a decrease in electricity consumption mainly due to the elimination of the aero-condenser to cool the bottom product of Column C-301. The duty of the column condenser increases, with an increase in electricity consumption. Nevertheless, the increase in electricity consumption of the column condenser is lower than the decrease in electricity consumption that occurs by eliminating the aero-condenser that cools the bottom product. Furthermore, by increasing the temperature of the feed we can see how this has a direct effect on the consumption of LPS which decreases. Finally, the amount of water required also decreases as the bottom product leaving E-304 is already at 44°C. The decrease in utilities is directly reflected in the Opex. Conversely, the Capex increases due to the presence of 9 BEU exchangers in series which are required to reach the specification.

In conclusion, compared to the reference case, the optimization of the scheme with the HOCO 3 specification allowed to reduce the separation cost by about 19.1%. Using the HICO 10 specification, however, the separation cost was reduced by approximately 26%.

2.2.2.1 Plates exchangers for HICO = 10 °C

As in the base case, it is possible to avoid placing 9 BEU exchangers in series using 2 plate exchangers in parallel to carry out the heat recovery.

As for the basic scheme, a more optimistic case is also presented in *Table* ***2.2.7***. Also in this case the global heat exchange coefficient of the plate exchanger is 2.5 times greater than that of a tubular exchanger. The results in terms of separation costs are shown below.

Table 2.2.7 Separation cost as the sum of Capex and Opex for the case HICO = 10 °C: the case with 9 BEU in series, the case with 2 plates exchangers in parallel, the case with 1 plate and exchange coefficient Ux2.5 (optimistic case)

Normalized cost	BEU x9	Plates x2	Plate x1, Ux2.5
Separation Cost	74.0	77.6	73.1
Capex	17.7	20.2	17.1
Opex (excl. Raw material)	56.3	57.4	56.0

The solution with 2 plate exchangers with heat exchange coefficient (U) equal to that of a tubular exchanger, is more expensive than the case with 9 BEU in series, although it is better from a practical point of view. The optimistic case, on the other hand, with a coefficient $U_2 = 2.5xU_1$ is the best from a practical and separation cost point of view. The separation cost for this case is about 26.9% lower than the reference case.

Also in this case, as for the basic scheme, for the optimistic case only the heat exchange coefficient U was changed, while the specification HICO = 10 °C and the installation factor for the calculation of the Erected cost of the exchanger remained unchanged.

The very optimistic case with HICO 3 was also simulated for the Mikitenko scheme but was not presented in this report for the same reasons described for the base case.

2.2.3 Scheme with compressor

Also for the Mikitenko, as for the base scheme, the scheme with the compression of the overhead vapors of the C-301 column was simulated. This operation is done to reduce the amount of energy required by the column as the compressed overhead vapors, condensing, provide all the necessary heat to the reboiler. The Mikitenko scheme with a compressor is shown in *Figure **2.2.12***. The compressor outlet pressure is 2.1 barg as in the basic case and the compressor outlet temperature is 168°C.

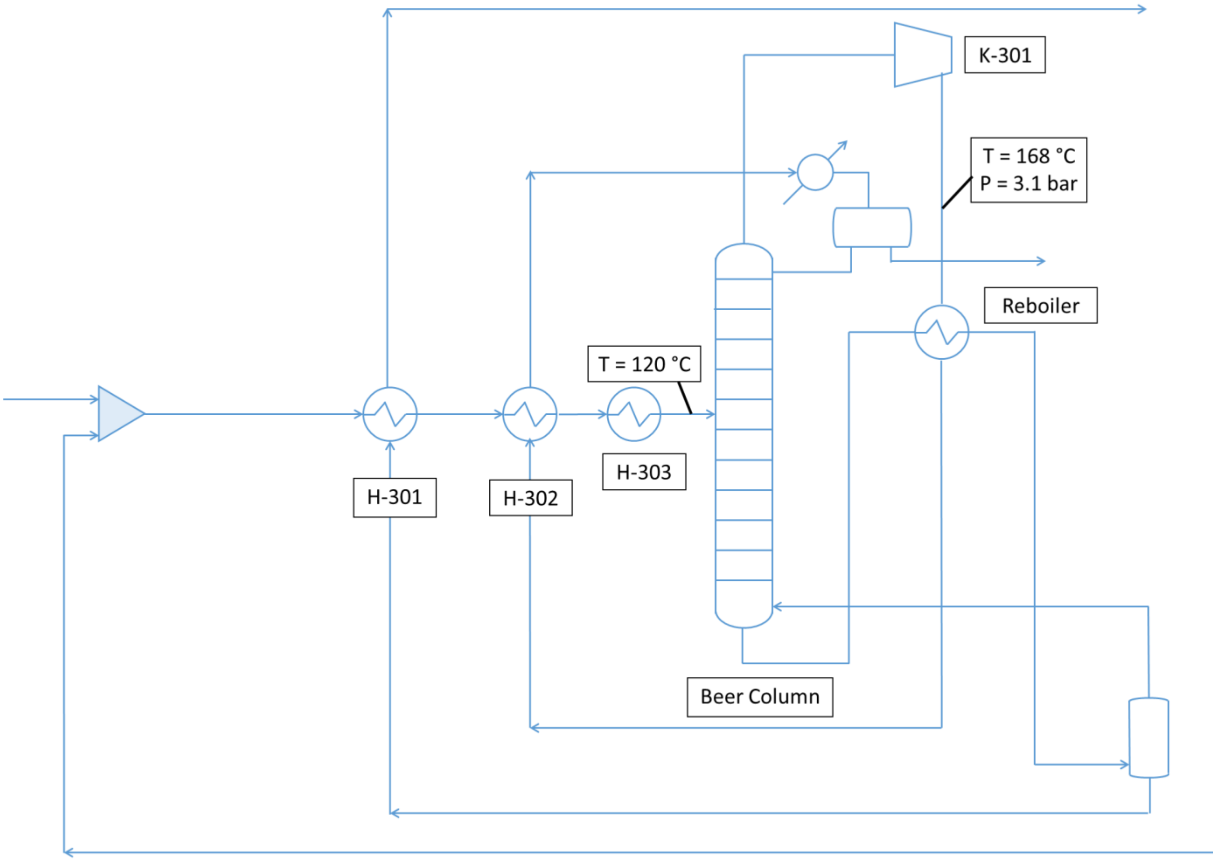


Figure 2.2.12 Mikitenko scheme: C-301 with compressor

As for the base case, it was necessary to add some heat exchangers. In particular, another exchanger was added to recover the heat of the overhead vapors after they supplied their heat to the reboiler. Then, a third exchanger was added to this line to bring the feed to 120°C. Also in this case, in fact, below this temperature and with the compressor at 2.1 barg, energy integration to the reboiler would not be possible. The results obtained with this configuration are reported in *Table **2.2.8*** and ***Table 2.2.9***.

Table 2.2.8 Utility consumption with and without the compressor

		Without K	With K
Electricity NWE	kWh/h	326.9	1703.5
LPS NWE	t/h	36.8	34.3
CW NWE	t/h	191.1	270.7

Table 2.2.9 Separation cost as the sum of Capex and Opex with and without the compressor

Normalized cost	Without K	With K
Separation Cost	80.9	100.4
Capex	16.8	29.6
Opex (excl. Raw material)	64.1	70.8

Also for the Mikitenko scheme, the addition of the compressor to recover the heat of the overhead vapors proves to be disadvantageous in terms of separation cost. Even in this case, we can see a significant increase in electricity consumption which is however compensated by a reduction in LPS consumption. Nevertheless, the consumption of LPS remains high as this must be supplied to the pre-heater to bring the feed to 120°C. Therefore, there is an increase in Opex. Furthermore, the addition of heat exchangers but above all the addition of the compressor almost double the Capex of the scheme. The increase in terms of Opex and Capex means that the separation cost of this scheme is higher than the basic Mikitenko scheme with specification HOCO = 3°C.

2.2.4 HOCO = 3 °C Optimized scheme

Figure 2.2.13 Mikitenko scheme: Optimized heat exchanger network – Confidential Data

Figure 2.2.14 Mikitenko scheme: Optimized scheme – Confidential Data

Table ***2.2.10*** and ***Table 2.2.11*** compare 5 cases: the optimized case (HOCO = 3°C), two optimized cases ($T_{out,w}$ = 45°C and $T_{out,w}$ = 40°C) and the optimized case with the HICO specification = 10°C.

As for the basic scheme it was decided to use 40 °C as the outlet temperature of the cooling water as this temperature was proposed by the energy optimization tool. Furthermore, by using a lower temperature than that of the reference case (45°C) it is possible to reduce the exchange surface required to carry out the cooling, therefore the number of shells required.

Table 2.2.10 Utilities consumption: comparison between the optimized case with HOCO = °C, the heat optimized case (Tout,w =45°C and Tout,w=40°C) and the optimized case with HICO=10°C: 2 plates and 9 BEU

		Case HOCO 3	Case HICO 10	Case FH Trim 40°C	Case FH Trim 45°C
Electricity NWE	kWh/h	326.9	245.8	55.5	55.5
LPS NWE	t/h	36.8	31.7	31.0	31.0
CW NWE	t/h	191.1	137.1	1196.9	797.9

Table 2.2.11 Separation cost as the sum of Capex and Opex: comparison between the optimized case with HOCO = 3°C, the heat optimized case (Tout,w = 45°C and Tout,w = 40°C) and the optimized cases with HICO = 10°C: 1 plate, Ux2.5, and 9 BEU

Normalized cost	HOCO = 3 °C	BEU x9	Platex1, Ux2.5	FH Trim 40	FH Trim 45
Separation Cost	80.9	74.0	73.1	66.1	65.7
Capex	16.8	17.7	17.1	11.1	11.7
Opex (excl. Raw material)	64.1	56.3	56.0	55.0	54.0

Comparing the heat optimized case with the 3 cases presented above, it is possible to note that the optimized case is the most advantageous both in terms of utilities and in terms of separation cost. The separation cost for the FH Trim 45 is the lowest and it is about 34.3% lower than the reference case.

2.2.5 IBEA feed concentration influence

By varying the concentration between 10 g/L and 75 g/L it was also possible to observe for the Mikitenko scheme the influence of the IBEA concentration in the feed on the energy consumption of the C-301 column. The heat optimized scheme was considered to perform the simulation. The effect of the concentration on the duty of the beer column reboiler is shown in *Figure **2.2.15***.

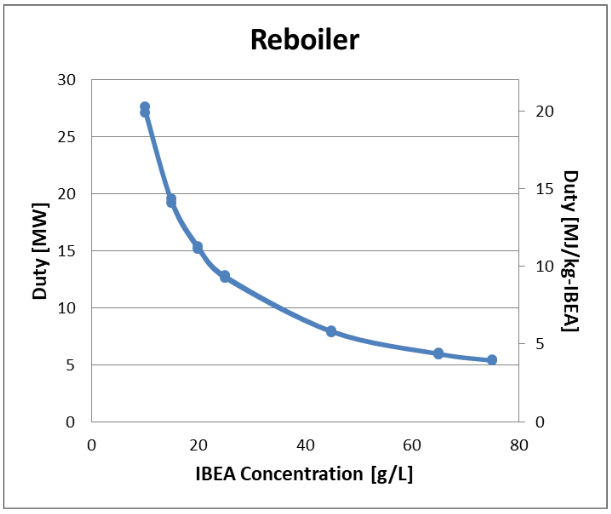


Figure 2.2.15 Influence of IBEA Concentration on C-301 energy consumption. C-301 Reboiler duty

As can be seen from the figure, as the IBEA concentration in the feed increases, the heat to be supplied to the reboiler decreases.

In particular, the reboiler consumption goes from approximately 27.6 MW to approximately 5.4 MW with a decrease of approximately 80%. This decrease is reflected in the consumption of LPS steam to be supplied to the beer column which is reduced from 51.9 t/h to 14.2 t/h and on the exchange surface of the reboiler which is reduced from 976 m² to 192 m². There is therefore a strong decrease in steam (one of the factors that most influence Opex because of its high cost) and in the exchange surface of the reboiler with a consequent decrease in Capex.

So, the increase in the concentration of IBEA entering the distillation scheme has a positive influence on the separation cost.

2.2.5.1 Separation cost vs. IBEA feed concentration

An economic evaluation was carried out to observe the influence of the IBEA concentration in the feed on the separation cost. *Figure* ***2.2.16*** shows the variation in the separation cost as the sum of Opex and Capex. As can be seen from *Figure* ***2.2.16***, the part that most affects the cost of separation is given by the Opex. In fact, for a concentration of IBEA of 10 g/L, Opex corresponds to 87% of the total cost, passing to 76% for a concentration of 75 g/L.

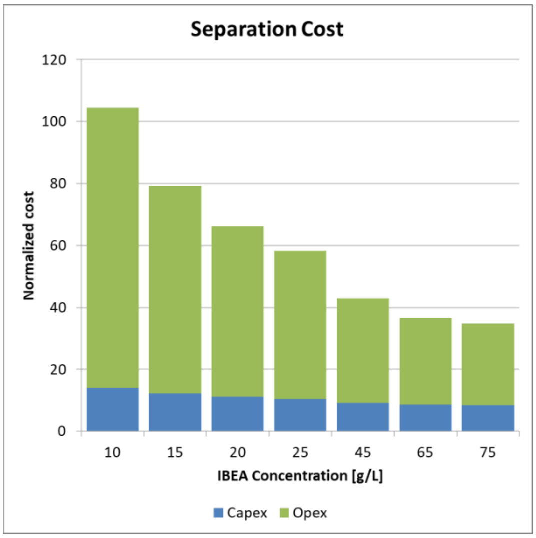


Figure 2.2.16 Influence of IBEA Concentration on the separation cost

It is possible to notice a decrease in both Opex and Capex as the concentration of IBEA in the feed increases. The decrease is greater for Opex and that is closely linked to the decrease in utility consumption. Furthermore, the decrease in separation cost is more important passing from 10 to 15 g/L. The influence of concentration becomes less and less important by moving to higher concentrations. Passing from 10 to 15 g/L there is a decrease in the separation cost of 24% while from 65 to 75 g/L the decrease in the separation cost is only 5%. *Figure* ***2.2.17*** shows a comparison between the optimized basic scheme and the optimized Mikitenko scheme of the variation of the separation cost varying the concentration of IBEA in the feeds.

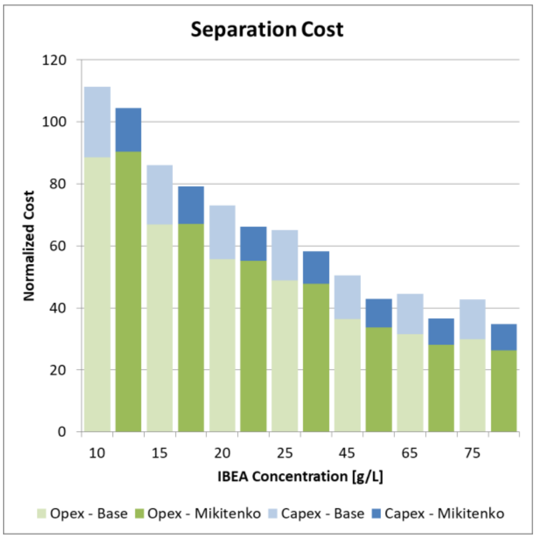


Figure 2.2.17 Influence of IBEA Concentration on the separation cost

In both cases, as previously discussed, the increase in the concentration of IBEA in the feed has a positive effect on the separation cost. Also, it appears that the Mikitenko scheme is cheaper than the base scheme at all concentrations. Finally, the percentage gain for the Mikitenko scheme in terms of separation cost increases as the concentration of IBEA in the feed increases. In fact, at 10 g/L the separation cost of the Mikitenko scheme is about 6.2% lower then the basic scheme. At 75 g/L, on the other hand, the separation cost of the Mikitenko scheme is about 18.6% lower then the basic scheme.

2.2.6 Acid path

Considering the scheme with HOCO = 3 °C, the following tables show how the organic acids are distributed between the various columns and therefore between the various products of the Mikitenko scheme. In particular, *Table **2.2.12*** to ***Table 2.2.13*** will show how acids are distributed among the various flows of the beer column and the butanol column. The intermediate flows between the two columns are shown in red.

Table 2.2.12 Acid distribution: beer column

		FEED_C1	BOTTOM_C1	OVHD_GAS	PROD_C1
Acetic	kg/h	452.9	450.2	1.3 E-03	3.5
Butyric	kg/h	453.3	429.8	1.5 E-03	24.3

Table 2.2.13 Acid distribution: butanol column

		PROD_C1	DRAW_C2	BOTTOM_C2	PROD_C2
Acetic	kg/h	3.5	0.8	2.7	5.6 E-11
Butyric	kg/h	24.3	0.8	23.5	1.4 E-14

*Table **2.2.12*** shows that most of the acid contained in the feed (FEED_C1) comes out in the stream BOTTOM_C1, the bottom product of the beer column. Only a small amount of the two organic acids end up in the distillate (PROD_C1) and pass to the butanol column. Then, a small amount of the two acids end up in DRAW_C2 that is recycled to the beer column and the remaining amount of the two acids go out in the bottom of the butanol column (BOTTOM_C2). *Table **2.2.14*** summarizes the acid path showing the acid distribution in the overall separation scheme.

Table 2.2.14 Acid distribution: separation scheme

		FEED_C1	BOTTOM_C1	BOTTOM_C2
Acetic	kg/h	452.9	99.4 %	0.6 %
Butyric	kg/h	453.3	94.8 %	5.2 %

2.2.7 Effect of the quality of the vinasses on the separation cost

Another factor that can have an impact on the separation cost is the quality of the vinasses, i.e. the quantity of IBEA present in the vinasses. Not knowing the maximum amount of alcohol accepted for wastewater treatment (also influenced by other factors) a study was done highlighting how the amount of IBEA accepted in wastewater impacts the separation cost. Three concentrations of IBEA in the vinasses were considered for the study: 100, 200, and 300 ppm. To see the impact of the IBEA concentration the optimized Mikitenko scheme was considered.

Table ***2.2.15*** shows how the IBEA flow in kg/h varies in the vinasses and the quantity of IBEA produced, as well as the quantity of IBEA in the vinasses. It was decided not to go beyond 300 ppm to avoid significant losses of IBEA, already equal to 1.53% for a concentration of 300 ppm.

Table 2.2.15 Variation of the quantity of IBEA in the vinasses and of IBEA produced as the quality of the vinasses varies

Vinasses quality	ppm wt	100	200	300
Feed	[kg/h]	5000	5000	5000
Vinasses	[kg/h]	25.5	50.9	76.4
IBEA product	[kg/h]	4974.5	4949.1	4923.6
IBEA lost	[%]	0.51	1.02	1.53

The results in terms of utility consumption and separation cost as the sum of Capex and Opex are shown in *Table* ***2.2.16*** and ***Table 2.2.17***. It can be noted that in terms of utilities there is a decrease in the consumption of LPS and cooling water. The decrease in LPS has positive effects on Opex which decreases by about 5% from 100 to 200 ppm and by another 3% from 200 to 300 ppm. As for Capex, there are no major variations. The small changes in Capex are essentially due to the reduction in the size of some heat exchangers, given the lower consumption of utilities. In general, however, there is a reduction in the separation cost which decreases by about 7%, going from 100 ppm in vinasses to 300 ppm.

Table 2.2.16 Utility consumption varying the quality of the vinasses

Vinasses quality	ppm wt	100	200	300
Electricity NWE	kWh	54.5	55.5	55.5
LPS NWE	t	31	29.1	28
CW NWE	t	1200	1101.3	1050.3

Table 2.2.17 Separation cost as the sum of Capex and Opex varying the quality of the vinasses

Vinasses quality	ppm wt	100	200	300
Separation Cost	Normalized cost	66.4	63.3	61.7
Capex		11.1	11.0	11.0
Opex (excl. Raw material)		55.3	52.3	50.7

It should be noted that the values of the separation cost are related to the production of IBEA as reported in *Table* ***2.2.15***. It is possible to notice a small difference between the value reported at 100 ppm in ***Table 2.2.17*** and the value in ***Table 2.2.11***. The main causes of this difference are two: first of all in ***Table 2.2.11*** the separation cost refers to 5000 kg/h while in ***Table 2.2.17*** the quantity of IBEA lost in the vinasses was considered (5000 - 25.5 kg/h). Furthermore, the column specification considered in the calculation of ***Table 2.2.11*** was a loss of IBEA in the vinasses of 26 kg/h, or about 104 ppm, a little more than 100 ppm considered in ***Table 2.2.17***.

Besides, the possibility of recycling the vinasses could be taken into consideration. Recycling the vinasses could have a positive effect on the wastewater treatment and the IBEA loss, as part of the lost IBEA is recycled back into the fermenter. On the other hand, the species in the vinasses mustn't exceed the toxicity limits of the microorganisms in the fermenter.

2.3 ELL

To reduce the energy consumption of the separation of IBEA from the fermentation broth, it is possible to use a hybrid extraction-distillation system. Unlike extraction systems inside the fermenter, with the external extraction system, it is possible to work with solvents that are toxic to microorganisms and at temperatures higher than those acceptable to microorganisms.

The performance of the extraction–distillation process greatly depends on the choice of the solvent. Different authors have therefore conducted solvent screenings, where the possible solvents were chosen based on different criteria such as high capacity, high selectivity, low viscosity, different density than water, commercially available at low cost. [9][10][11][12]

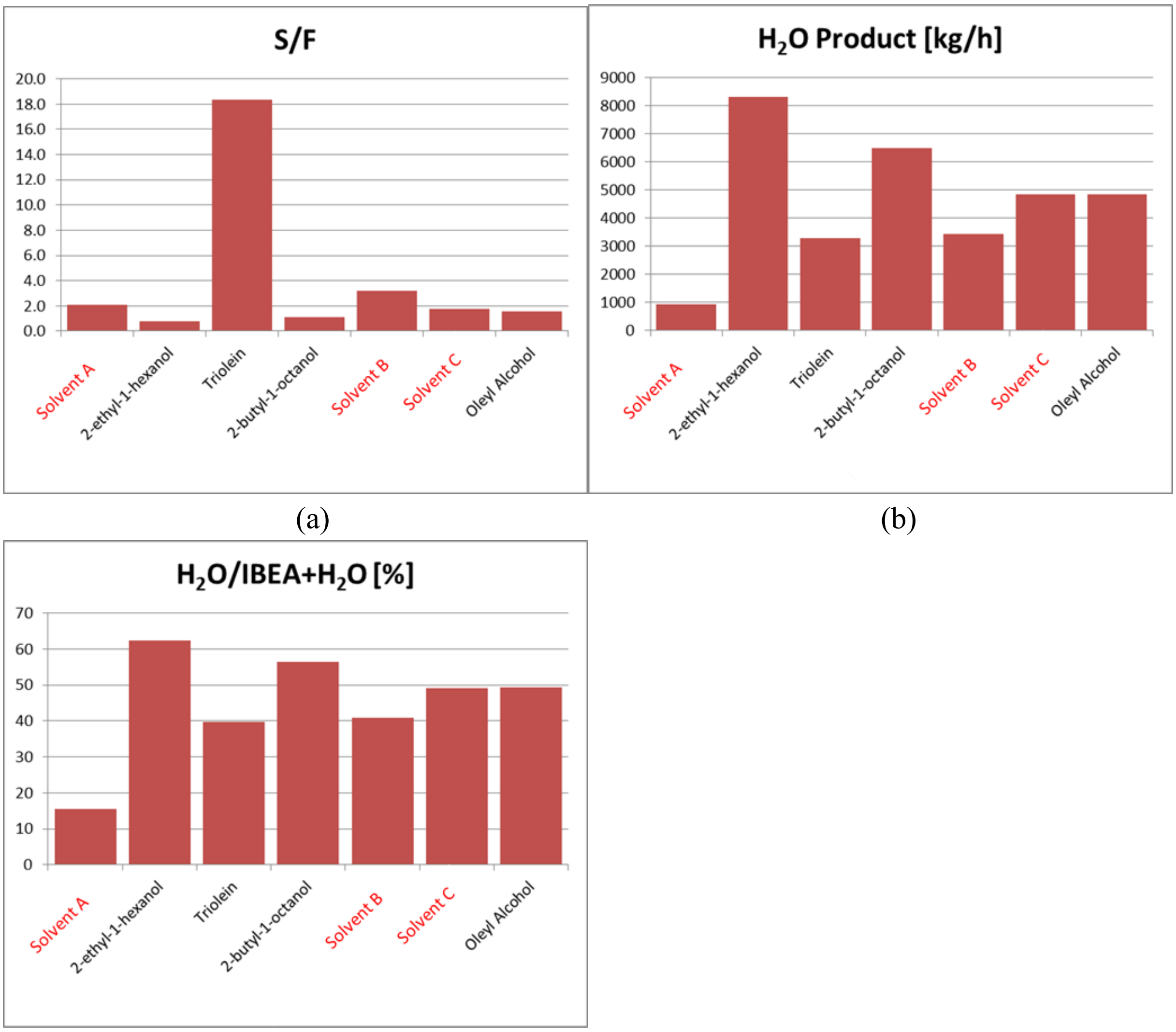
Among the various solvents in the literature, the following have been chosen to simulate a liquid-liquid extraction column in which the stream leaving the fermenter is introduced from the top of the column and the chosen solvent from the bottom:

- Solvent A (confidential)
- 2-ethyl-1-hexanol
- Triolein
- 2-butyl-1-octanol
- Solvent B (confidential)
- Solvent C (confidential)
- Oleyl Alcohol

To simulate and compare the various solvents, based on the data found in literature, it was decided to insert the two streams at 80 °C. It should be remembered that the production of IBEA considered is 5000 kg/h. The results are shown in *Figure* ***2.3.1***

Figure ***2.3.1*** *(a)* shows the ratio between the amount of solvent needed to carry out the liquid-liquid extraction and the stream leaving the fermenter. The amount of solvent was evaluated to have a concentration of IBEA in the aqueous phase (vinasses) of 100 ppm. Observing the figure, due to the high flow rate required, it was, therefore, decided not to use Triolein to perform the extraction.

Figure ***2.3.1*** *(b)* shows the influence of the solvent on the amount of water in the organic phase leaving the extractor. The organic phase is subsequently sent to a distillation column for the recovery of the solvent. The amount of water in the organic phase therefore corresponds to the amount of water present together with IBEA in the product of the distillation column. The percentage of water present in the distillation product was then calculated (as the ratio between H_2O and the sum between H_2O and IBEA). *Figure* ***2.3.1*** *(c)* shows the influence of the solvent on this ratio. The reason this ratio was calculated was to be able to compare the liquid-liquid extraction scheme with the basic scheme. The percentage of water in the product of the beer column of the basic scheme is about 40%.



(a) (b)

(c)

Figure 2.3.1 Influence of the chosen solvent on the liquid-liquid extraction process: (a) ratio between needed solvent and feed from fermenter; (b) water in the extracted phase; (c) percentage of water in the extracted phase

Implementing a hybrid extraction-distillation system has the purpose of decreasing the separation of energy demand as long as a product with the same characteristics or with better characteristics in terms of the percentage of water is obtained. The only two solvents that make it possible to obtain a product with less than 40% of water are *Solvent A* and Triolein (which we have previously excluded). Solvent B, which gives a result close to 40 %, could be studied later if needed. Nonetheless, 3 of the 7 solvents presented were examined. These 3 solvents are *Solvent A*, 2-ethyl-1-hexanol, and Oleyl Alcohol and they have been chosen as the most used and studied in the bibliography.

The same previous considerations were made on these 3 solvents (amount of solvent and percentage of water in the product) for 3 different specifications of the vinasses leaving the extractor, in particular 100, 200, and 300 ppm of IBEA. The results are reported in *Table **2.3.1***.

From the results presented in *Table **2.3.1***, it was decided to use *Solvent A* as a solvent for liquid extraction. This solvent, although it has a slightly higher S/F ratio among the three, allows obtaining a product with a quantity of water much lower than that of the product obtained with the base scheme.

Table 2.3.1 Solvent influence on S/F ratio and percentage of water in the product for three different qualities of vinasses

Solvent	IBEA loss	S/F	$H_2O/(IBEA+H_2O)$
	ppm wt	[-]	[%]
Solvent A	100	2.06	15.6
	200	1.29	11.0
	300	1.21	10.5
2-ethyl-1-hexanol	100	0.75	62.4
	200	0.62	58.5
	300	0.53	54.6
Oleyl Alcohol	100	1.55	49.2
	200	1.27	44.6
	300	1.13	41.9

The hybrid extraction-distillation scheme simulated using *Solvent A* as the solvent is shown in *Figure* **2.3.2**.

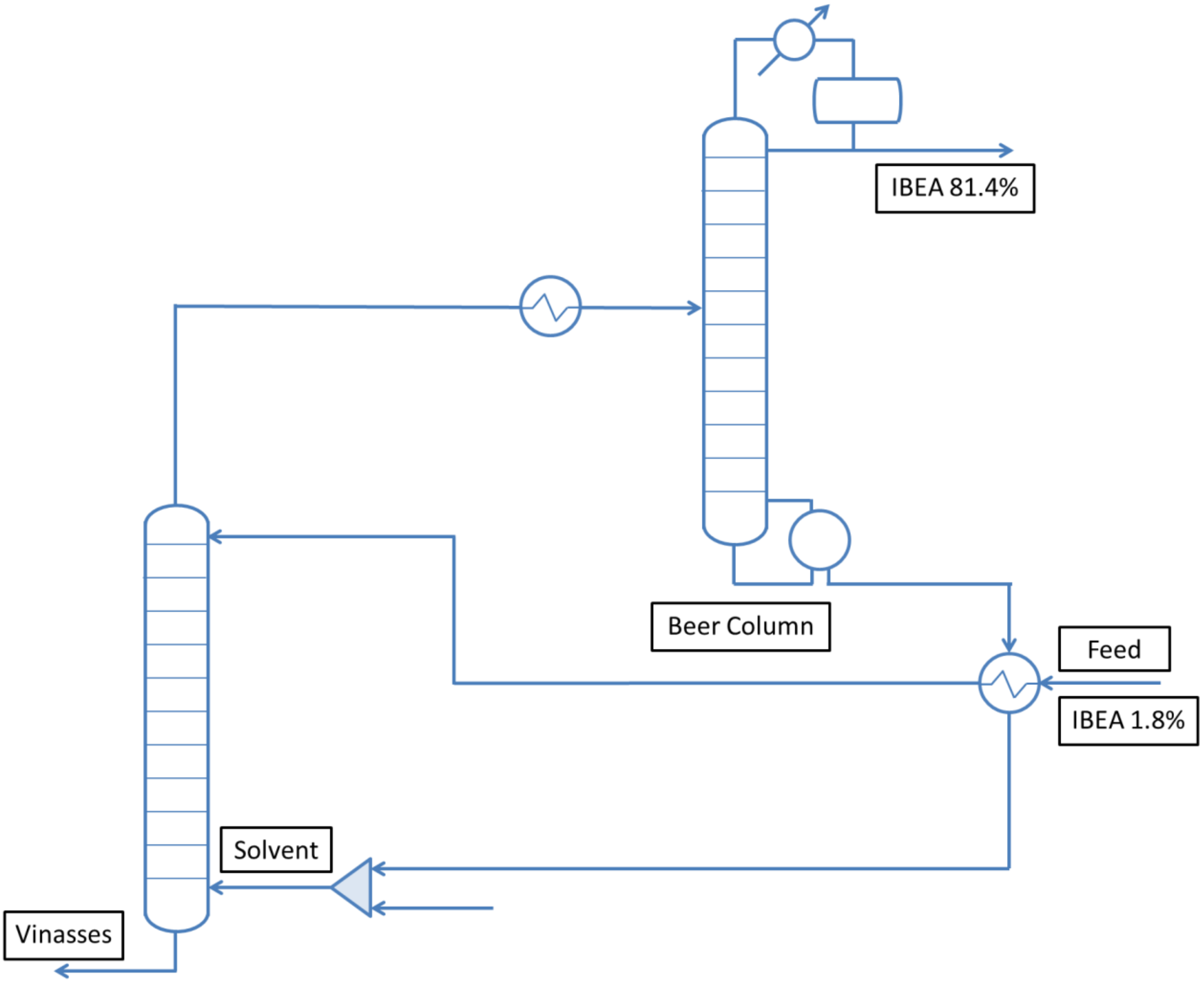


Figure 2.3.2 Extraction-Distillation hybrid process

In *Figure* **2.3.2** we can see how the feed enters from the head of the column in countercurrent to the solvent inserted from the bottom of the column. The aqueous phase (vinasses) is eliminated from the bottom of the column while the organic phase exiting the head of the column is sent to a distillation column which produces IBEA at the top and recovers the solvent at the bottom of the column. The solvent leaves the column at about 138°C and is used to pre-heat the feed (leaving the fermenter at 36°C) before re-entering the extraction column. The heat exchanger to pre-heat the feed was simulated with a specification HOCO = 3°C. The simulation results are reported in *Table **2.3.2*** which compares the quantity of solvent used and the energy consumption of the distillation column as the quality of the vinasses varies.

Table 2.3.2 Influence of the quality of the vinasses on S/F and the energy consumption of the distillation column

Extraction L-L	IBEA loss	ppm wt	100	200	300
	S/F	[-]	1.97	1.32	1.25
	Solvent T	[°C]	88.4	78.2	76.9
	Feed T	[°C]	85.4	75.2	73.9
	$H_2O/(IBEA+H_2O)$	[%]	18.6	10.4	9.6
	Solvent loss	[kg/h]	41.3	30.3	29.2
Distillation	Duty Reboiler	MJ/kg IBEA	13.2	10.5	10.2
	Duty Condenser	MJ/kg IBEA	2.6	2.0	2.0

The percentage of water present in the final IBEA product goes from 9.6% (for a vinasses quality of 300 ppm by IBEA) to 18.6% (100 ppm). The ELL scheme can therefore be considered as an IBEA concentration scheme.

The amount of solvent lost and the amount of water that is transported with the solvent depending on the solubility of the water in the solvent and of the solvent in water. The values obtained with the thermodynamic method used for the simulation were compared with those present in the literature.[10] By simulating a stream of water and solvent it was possible to compare the data of the in-house model with those in the literature. In the literature, the values of the UNIFAC model at 25°C and the experimental values at 25 and 80°C are reported. The results of the model used for the simulation and those in the literature have the same order of magnitude. Nevertheless, the deviation of the two values increases as the temperature increases, passing from 25 to 80°C. The values found in the literature are reported in *Table **2.3.3***.

The simulated absorption column works at approx. 80°C.

- Looking at *Table **2.3.3***, the model predicted water content of solvent exiting the absorption column is probably higher than the one which could be calculated from the measured data, by approx. 30%. This data should be studied later. Indeed, if more accurate data are available, the even lower water content in the concentrated IBEA stream could be achieved.
- The solvent in water content is also important data. Indeed, the vinasses could be recycled to the fermenter, under the toxic limits. The toxicity of *Solvent A* at the levels shown in *Table **2.3.3*** should be studied later. Moreover, before recycling, the vinasses undergo cooling: the solubility of *Solvent A* will be lowered to near their 25°C levels by this mean (an order of magnitude lower than at 80°C).

Table 2.3.3 Solubility of solvent in water and water in the solvent at 25 and 80 °C

	UNIFAC 25 °C	Measure 25 °C	Model 25 °C	Measure 80 °C	Model 80 °C
Water in solvent (mol frac)	0.0011	0.0031	0.0024	0.0074	0.0104
Solvent in water (mol frac)	4e-6	7.8e-6	7.1e-6	-	1.9e-5

2.3.1 IBEA quality by varying the quality of the vinasses

Considering the ELL scheme as an IBEA concentration scheme, an important aspect of the scheme therefore becomes the amount of water present in the product overhead of the distillation column. From *Table **2.3.2*** it was possible to note that the amount of water present in this stream depends on the quality of the vinasses. In fact, as the concentration of IBEA in the vinasses increases, the percentage of water in the overhead product of the column decreases.

In *Table **2.3.4*** a comparison is made between the overhead product of the distillation column of the basic scheme and the overhead product of the column of the ELL scheme with 100 ppm of IBEA in the vinasses. To compare the two cases, scheme 46 with 40°C trim (100 ppm of IBEA in vinasses) was taken as a reference as a basic scheme.

In *Table **2.3.4*** it can be seen that, unlike all the other species present in the stream, the variation in the percentage of water in the stream is higher. The mass concentration of water in the stream becomes less than half by passing from the basic scheme to the ELL scheme.

Moreover, since the quantity of ethanol present both in the feed and in the overhead product is negligible compared to that of water, isopropanol and butanol, it is possible to represent on a water-isopropanol-butanol ternary diagram how the quality of the product varies, in terms of water concentration, by varying the quality of the vinasses.

Table 2.3.4 Mass composition of the overhead product: base scheme (case 46, trim 40°C) and ELL

	Case 46, Trim 40 °C	ELL
H2O	0.4051	0.1861
IPROPNOL	0.2369	0.3296
BUTANOL	0.3269	0.4526
ETHANOL	4.90E-03	3.78E-03
ACETONE	0.0185	0.0262
ACETIC	5.38E-04	1.64E-03
BUTYRIC	0.0049	
Solvent A		9.02E-05

The results are shown in *Figure **2.3.3***.

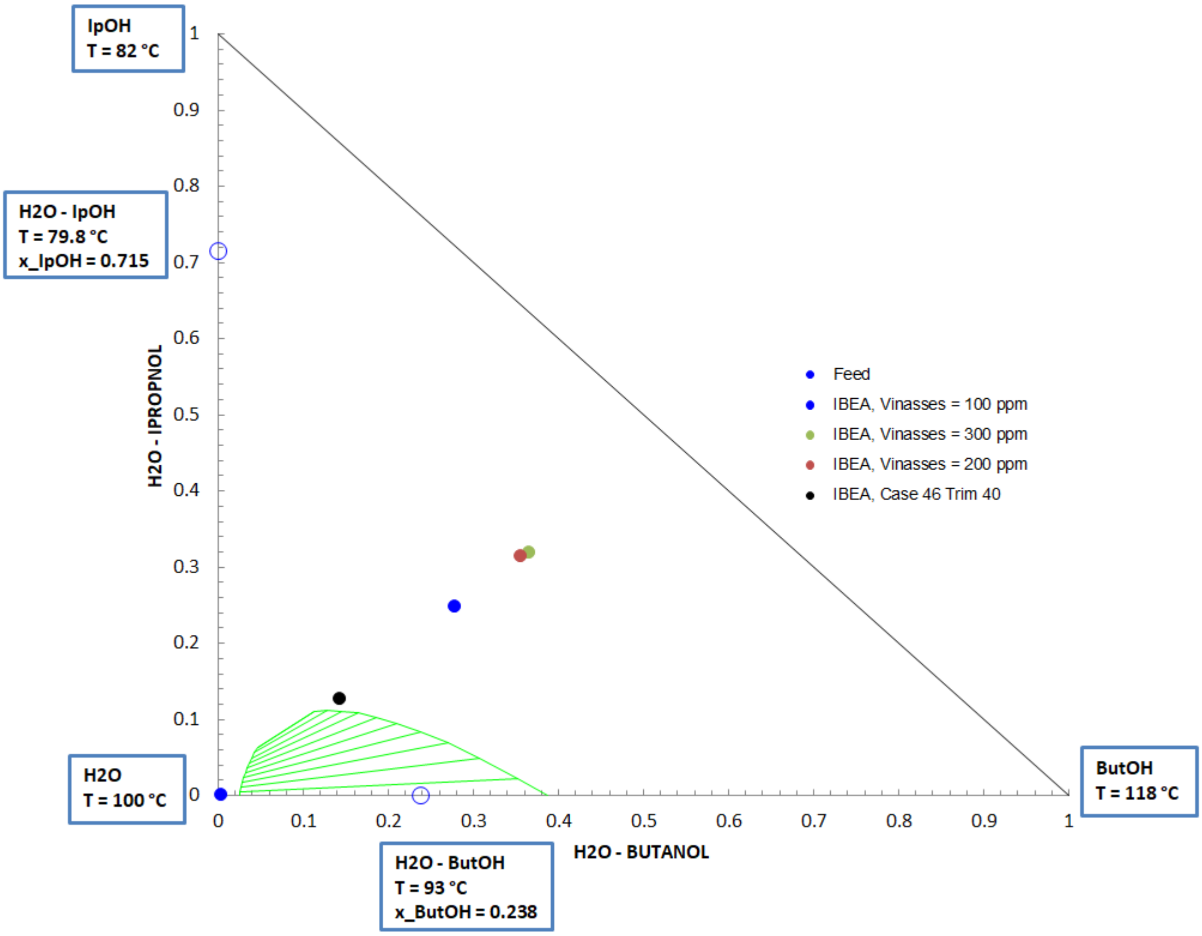


Figure 2.3.3 Water-Isopropanol-Butanol ternary diagram: influence of the quality of the vinasses IBEA water concentration. Molar compositions.

2.3.2 Feasibility of liquid-liquid extraction and column sizing

Finally, an economic evaluation of the simulated scheme was carried out.

The first step for sizing the liquid-liquid extraction column was to verify the feasibility of the extraction in terms of the properties of the two fluids. In particular, it was verified that:

- difference between densities > 50 kg/m^3
- difference between viscosities < 500 cP
- difference between interfacial tensions > 2 mN/m

The properties of the fluids meet these specifications. The properties of the fluids are shown in *Table* ***2.3.5***.

Table 2.3.5 Properties of the fluids for sizing the liquid-liquid extraction column

	Density	Viscosity	Interfacial tension
	Kg/m^3	cP	mN/m
Feed	938.6	0.357	61.83
Solvent	818.9	0.372	22.67

The results of the economic evaluation of the ELL scheme are presented in *Table* ***2.3.6*** and ***Table 2.3.7***. For the total evaluation of the separation cost of IBEA and to be able to make a comparison with the previous schemes, it is necessary to add the columns for the elimination of acetone and the separation of butanol from isopropanol and ethanol. The evaluation of the total separation cost will not be done in this Thesis. The comparison will be done between the ELL schema and the beer column of the base scheme since for both of them the purpose is to concentrate on IBEA. It should be remembered at this point that the beer column of the base scheme (case 46, Trim 40) concentrates the feed to about 40 wt% of water, while ELL to about 9.6 to 18.6 % wt (*Table* ***2.3.2*** and *Table* ***2.3.4***).

Table 2.3.6 Utility consumption varying the quality of the Vinasses

Vinasses quality	ppm wt	100	200	300	Basic scheme 100 ppm
Electricity NWE	kWh/h	97.8	66.6	63.6	233.9
LPS NWE	t/h	31.2	24.8	24.0	23.8
CW NWE	t/h	-	-	-	273.6

Table 2.3.7 Separation cost as the sum of Capex and Opex varying the quality of the vinasses

Vinasses quality	ppm wt	100	200	300	Basic scheme 100 ppm
Separation Cost	Normalized cost	92.9	80.0	78.6	51.8
Capex		31.9	29.7	29.5	10.1
Opex (excl. Raw material)		61.0	50.3	49.1	41.6

From ***Table 2.3.7*** it can be seen how the effect of the quality of the vinasses on the separation cost is important going from 100 to 200 ppm. In this case, there is, in fact, a reduction of the separation cost of about 14%. Instead, with 300 ppm of IBEA in the vinasses, there is only a 2% reduction compared to the case with 200 ppm. Finally, comparing these results with the basic scheme it is possible to note that, if we consider the ELL scheme as a method of IBEA concentration, the quantity of water leaving the distillation column is lower, but the separation cost of this scheme is about two times that of the beer column. Therefore, to verify that the ELL schema is more advantageous than the single beer column it is necessary to evaluate the complete schema.

2.4 Diaz

As with the ELL scheme, another possible scheme for concentrating IBEA is a combination of extractive and azeotropic distillation. In this case, the butanol present in the feed is used as an entrainer in a complex reflux system. [2]

The distillation scheme (from now called Diaz scheme from the name of the author of the bibliographic article) involves two distillation columns. The scheme is presented in *Figure* ***2.4.1***.

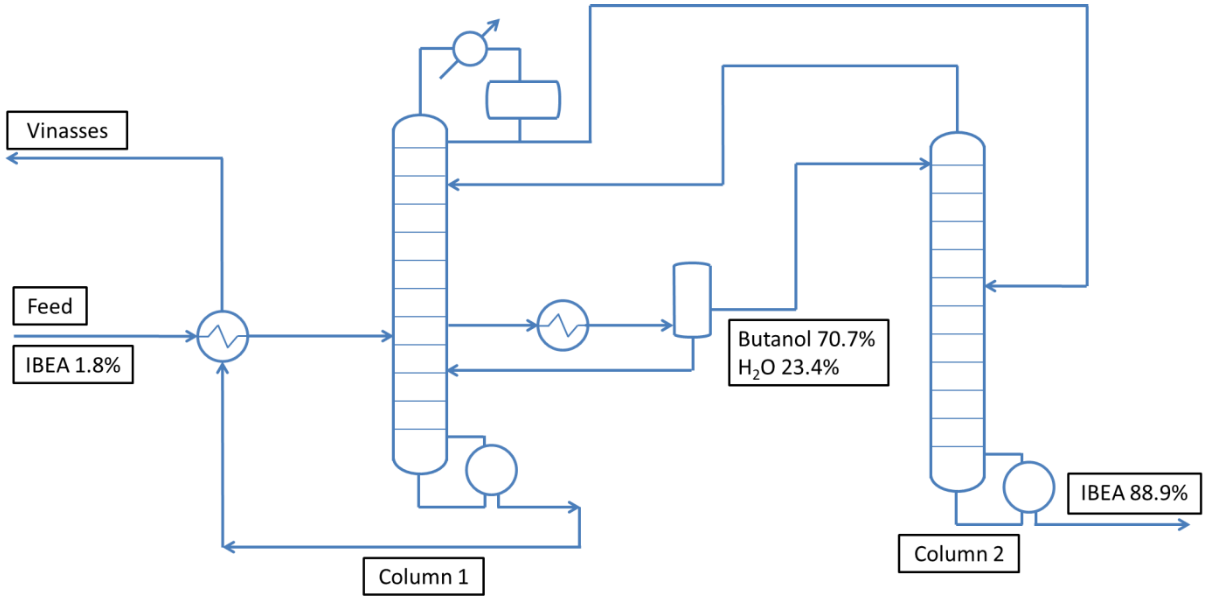


Figure 2.4.1 Diaz scheme: IBEA production and dehydration using butanol as entrainer

The feed leaving the fermenter is introduced into the first column after being pre-heated by the vinasses coming out from the bottom of the column.

Due to the immiscibility field between water and butanol, two liquid phases are present on some plates of the column, one rich in water and one rich in butanol. The phase rich in butanol is then extracted and sent to the top of the second column. It should be remembered that there is an azeotrope between water and butanol. Since this azeotrope is within the immiscibility field, it is possible to break this azeotrope by simple decantation. From the head of the first column, a stream composed mainly of water and isopropanol (and ethanol) with azeotropic composition is produced. This stream becomes the feed of the second column. In the second column, using the butanol extracted from the first column as an entrainer, a stream consisting mainly of water is obtained at the top and a stream consisting of dehydrated IBEA at the bottom. This is possible because, as shown in *Figure **2.4.2***, as the butanol/alcohol ratio increases (with alcohol we mean isopropanol and ethanol), the relative volatility of isopropanol and ethanol changes, thus becoming heavier components than water at high concentrations of butanol.

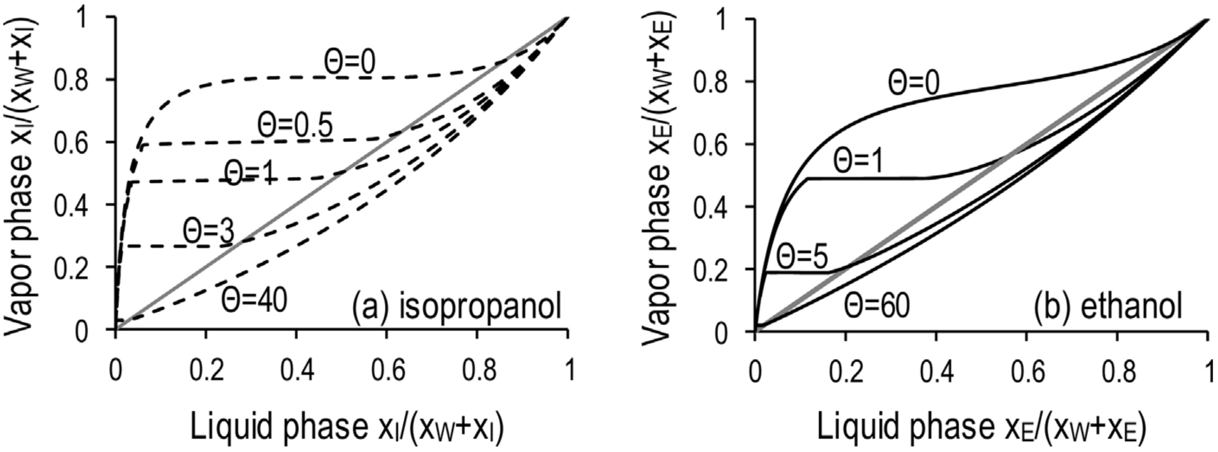


Figure 2.4.2 Water-isopropanol and ethanol-water equilibriums at different butanol/alcohol ratio on the mass basis [2]

The simulation results are shown in *Table **2.4.1*** which compares the energy consumption of the two distillation columns as the quality of the vinasses varies. Moreover, the table shows the percentage of water in the IBEA product. This percentage varies from 6.33% (300 ppm of IBEA in the vinasses) to 7.29% (100 ppm). Therefore, the Diaz scheme, as the ELL scheme, can be considered as an IBEA concentration scheme.

It should be mentioned that authors [2] claim to achieve complete dehydration of IBEA. Nevertheless, the quality of vinasses is not mentioned in their work. Moreover, their work was done with higher feed concentrations of IBEA, especially as far as butanol is concerned (14.6 g/L of butanol). *Table **2.4.1*** reports the best results we could achieve in terms of IBEA dehydration with our given feed concentrations.

Table 2.4.1 Influence of the quality of the vinasses on the water % in the product and the energy consumption

IBEA loss	ppm wt	100	200	300
H_2O	% wt	7.29	6.68	6.33
Duty Reboilers	MJ/kg IBEA	9.94	9.79	9.76
Duty Condenser	MJ/kg IBEA	7.83	7.68	7.64

2.4.1 IBEA quality by varying the quality of the vinasses

Considering the Diaz scheme as an IBEA concentration scheme, an important aspect of the scheme therefore becomes the amount of water present in the final product. *Table **2.4.1*** shows that the amount of water decreases as the IBEA in the vinasses increases.

*Table **2.4.2*** compares the top product of the distillation column of the basic scheme (case HICO 10) and the product of the Diaz scheme with 100 ppm of IBEA in the vinasses. The Diaz feed/effluent exchanger's specification has been set as HICO 10 because this specification is indicated in the literature. Furthermore, the Diaz scheme does not converge below 72°C. A possible but not simulated option could be a HOCO 3 exchanger and a pre-heater. *Table **2.4.2*** shows that with the Diaz scheme there is a reduction of 82% in the mass fraction of water in the product and an increase in the mass fraction of isopropanol, ethanol, and butanol.

Nevertheless, there is also an increase in unwanted products, i.e. acetic acid, butyric acid, and acetone, which must be then removed.

Table 2.4.2 Mass composition of the basic scheme (HICO 10) product and the Diaz scheme product

	Base, HICO 10	Diaz	
H2O	0.4043	0.0729	- 82.0 %
IPROPNOL	0.2369	0.3709	+ 56.6 %
ETHANOL	4.88E-03	7.27E-03	+ 49.0 %
BUTANOL	0.3271	0.5104	+ 56.0 %
ACETIC	4.86E-04	7.51E-04	+ 54.6 %
BUTYRIC	5.60E-03	8.15E-03	+ 45.6 %
ACETONE	0.0185	0.0296	+ 60.0 %

As for the ELL scheme, taking into consideration the three species most present in the product, the ternary diagram of water – isopropanol - butanol was traced. *Figure **2.4.3*** shows the variation of the product obtained by varying the quality of the vinasses. Also in *Figure **2.4.3***, a comparison is made between the ELL scheme and the Diaz scheme.

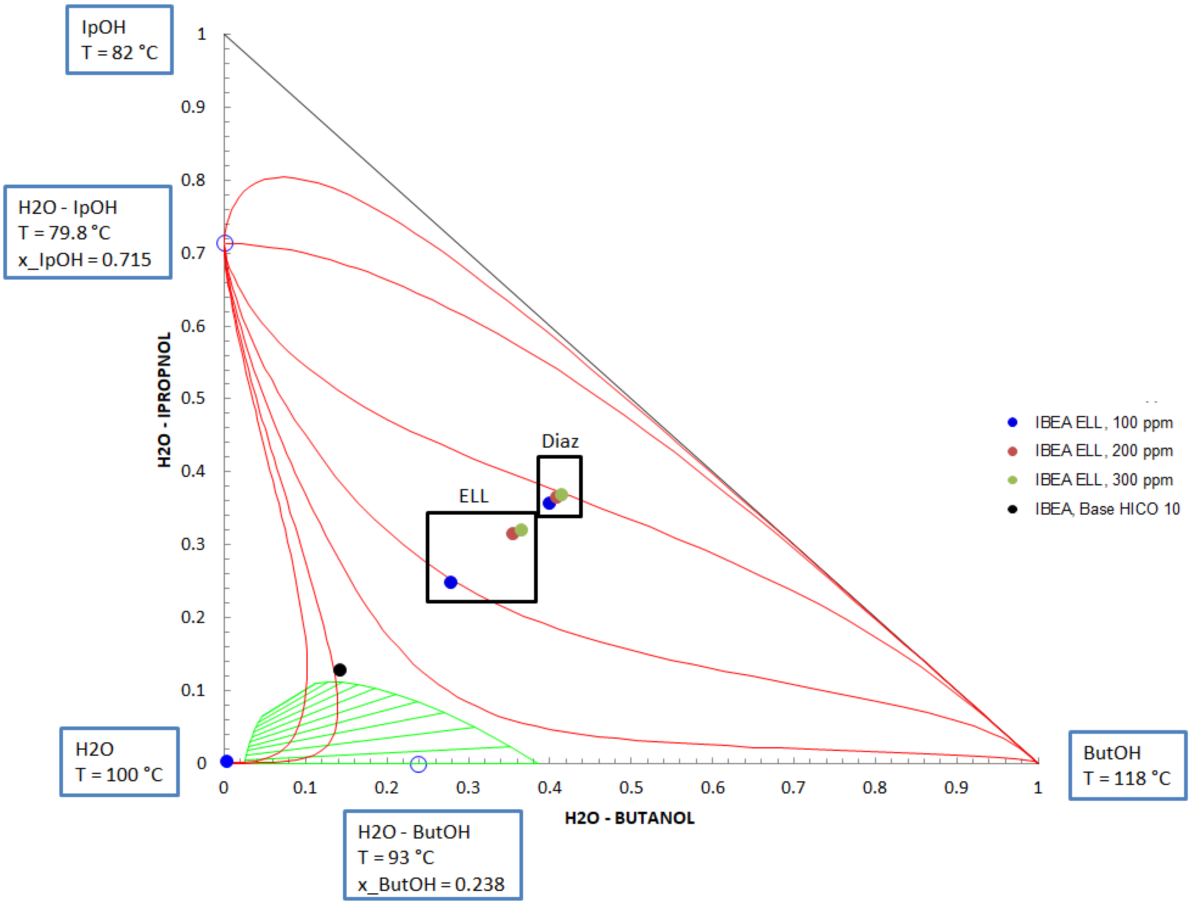


Figure 2.4.3 Water-Isopropanol-Butanol ternary diagram: influence of the quality of the vinasses IBEA water concentration

The diagram highlights how the Diaz scheme allows us to obtain a more concentrated product in IBEA. It is also possible to note that the effect of the quality of the vinasses on the concentration of the final product is less important for the Diaz scheme than for the ELL scheme.

2.4.2 Diaz scheme separation cost

Finally, an economic evaluation of the simulated scheme was carried out.

The results of the economic evaluation of the Diaz scheme are presented in *Table **2.4.3*** and ***Table 2.4.4***. As for the ELL scheme, for the total separation cost evaluation of IBEA and to be able to make a comparison with the complete basic scheme and the Mikitenko scheme it is necessary to add the columns for the elimination of acetone and the separation of butanol from isopropanol and ethanol. The complete scheme separation cost evaluation will not be done in this report. The comparison will be made between the Diaz scheme and the beer column of the base scheme as both have the purpose of concentrating IBEA.

Table 2.4.3 Utility consumption varying the quality of the vinasses

Vinasses quality	ppm wt	100	200	300	Base Ux2.5
Electricity NWE	kWh/h	1.0	1.0	1.0	194.3
LPS NWE	t/h	23.4	23.1	23.0	22.0
CW NWE	t/h	891.0	865.8	865.8	94.3

Table 2.4.4 Separation cost as the sum of Capex and Opex varying the quality of the vinasses

Vinasses quality	ppm wt	100	200	300	Base Ux2.5
Separation Cost	Normalized cost	48.1	47.5	47.4	46.8
Capex		7.2	7.2	7.2	9.1
Opex (excl. Raw material)		40.8	40.3	40.1	37.8

Table 2.4.4 shows that for the Diaz scheme the effect of the quality of the vinasses on the separation cost is negligible. There is a decrease of about 1% going from 100 to 300 ppm of IBEA in the vinasses. Furthermore, with the same IBEA in the vinasses (100 ppm) the separation cost of the Diaz scheme is 2.8% higher than that of the base scheme.

Nevertheless, as seen previously, the Diaz scheme allows us to obtain a product with a mass fraction of water lower than 82% compared to the base case. Therefore, to see if the Diaz scheme is more advantageous than the single beer column it is necessary to evaluate the complete scheme.

3 Isopropanol dehydration

The basic scheme and the Mikitenko scheme allow us to separate the feed coming from the fermenter obtaining a stream of vinasses containing mainly water, a stream containing mainly acetone, one of butanol, and one of isopropanol and ethanol.

This last stream, due to the water-ethanol and water-isopropanol azeotropes, contains a certain amount of water that is not negligible. For this reason, a dehydration step is foreseen for this current.

Five methods found in the literature have been considered to carry out the dehydration of this current.[13][14] These methods are:

- Pressure Swing Distillation
- Same Pressure Distillation
- Azeotropic distillation with Cycle Hexane/Benzene
- Pervaporation
- Adsorption

3.1 Pressure Swing Distillation / Same Pressure Distillation

Taking a generic ternary mixture C1-C2-C3 with a binary azeotrope C2-C3, the separation using the Pressure Swing Distillation (PSD) scheme involves the use of three distillation columns that work at different pressures. Separation is possible since the composition of the azeotrope at pressure p1 is different from that at pressure p2. By drawing the ternary diagram C1-C2-C3 it is possible to observe the feasibility of distillation.[13][15][16] On the diagram (*Figure **3.1.1***) the distillation boundaries can be observed: only by working at two different pressures is it possible to overcome the distillation boundary at pressure p1 to obtain a stream of pure C3.

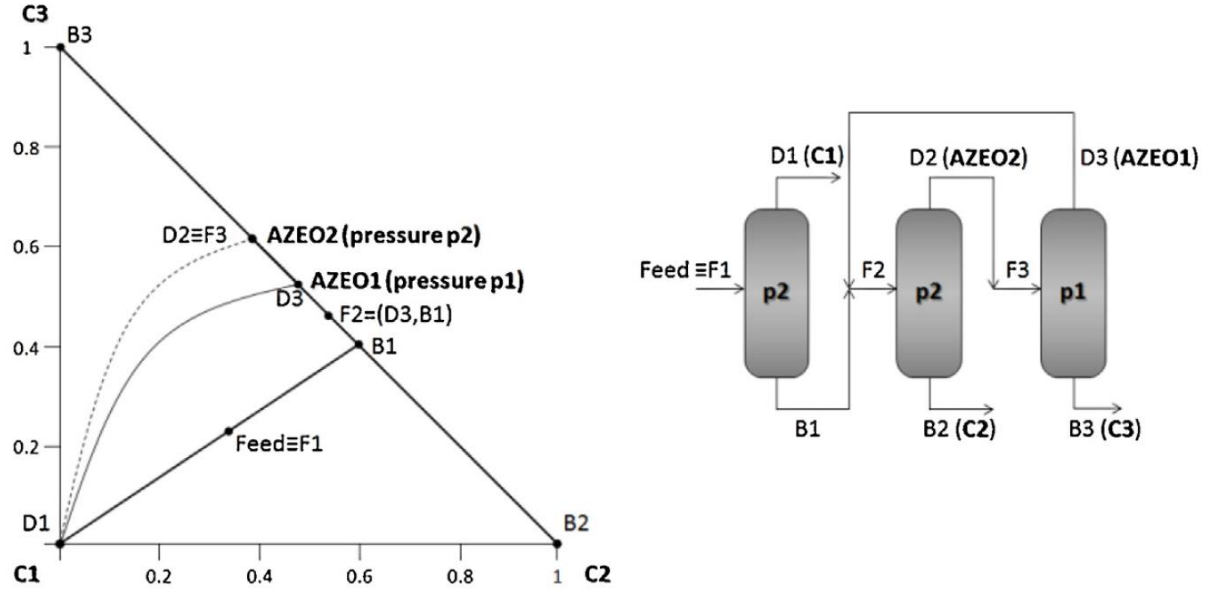


Figure 3.1.1 Illustrative example: feasibility of Pressure Swing Distillation

In the case of our stream C1, C2 and C3 are respectively ethanol, water, and isopropanol. In this way, entering with a feed with composition F1 it is possible to obtain from the head of the first column a stream containing mainly ethanol (with azeotropic composition: the case illustrated in the figure is an example in which there is no azeotrope between C1 and C2, present instead of in our case between ethanol and water). The bottom product of the first column (B1) is mixed with the top product of the third column (D3) thus obtaining the feed of the second column (F2). This feed is composed of water and isopropanol, with a quantity of water higher than that of the azeotrope at pressure p1. In this way, it is possible to obtain at the bottom of the second column a stream composed mainly of water (B2) and at the top a stream of azeotropic composition at pressure p2 (D2: AZEO2).

The top product of the second column becomes the feed of the third column (F3). The third column operates at a pressure p1 ≠ p2. At pressure p1 the azeotrope between water and isopropanol is richer in water than the azeotrope at pressure p2. This makes it possible to distill the F2 feed obtaining at the bottom of the column a stream composed mainly of isopropanol and at the top of the column a stream with the azeotrope composition at pressure p1.

The same pressure distillation instead operates with three columns at the same pressure. In this case, the separation of the C2-C3 azeotrope is only possible by recycling part of the C3 product. Only in this way is it possible to overcome the distillation boundary and make it possible to produce a stream containing mainly C3.

Figure ***3.1.2*** shows the ternary diagram associated with the separation scheme for the same pressure distillation.

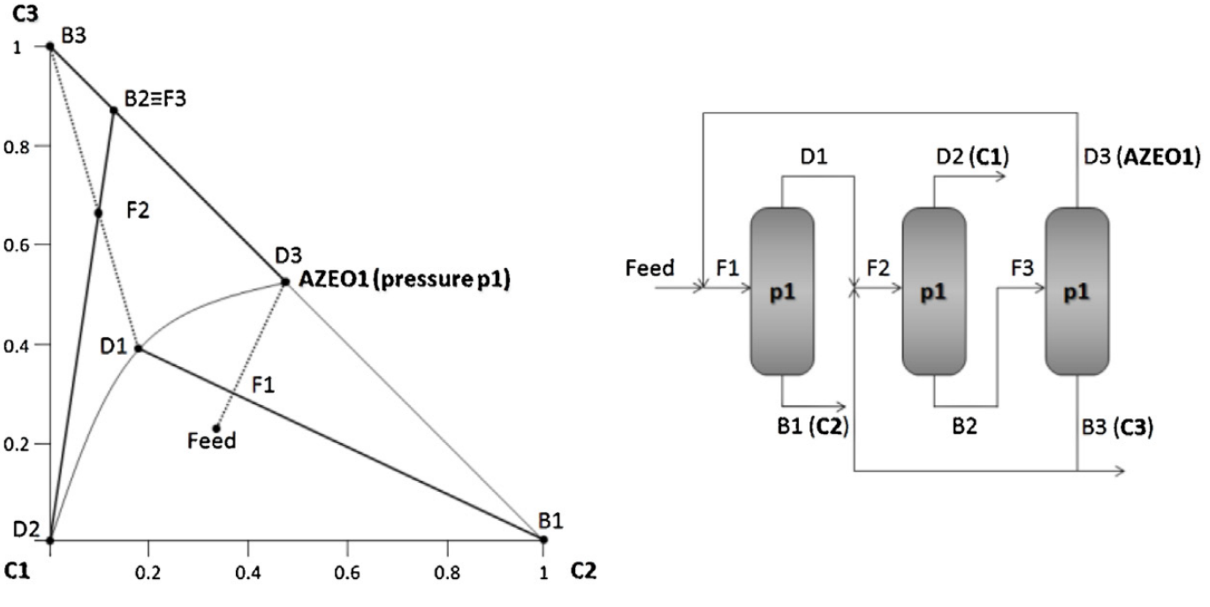


Figure 3.1.2 Illustrative example: feasibility of Same Pressure Distillation

In this case, the three columns all operate at the same pressure, p1. First, the feed is mixed with the top product of the last distillation column with a water-isopropanol azeotrope composition at pressure p1 (D3). The two mixed streams (F1) are sent to the first column from which a stream of pure water is obtained at the bottom (B1) and a stream D1 is produced at the top of the column. This stream is mixed with part of the pure isopropanol produced by the third column.

The mixture of the two streams is necessary to make the feed of the second column (F2) overcome the distillation boundary, thus obtaining an ethanol stream as the top product of the second column (D2) and a bottom product of the second column (B2), free of ethanol, and with a quantity of isopropanol higher than that of the azeotrope. This stream becomes the feed of the third column (F3) where a stream (D3) with azeotropic composition at pressure p1 is produced at the top of the column and a stream (B3) of pure isopropanol at the bottom.

3.1.1 PSD simulation with the hydrate IPA from the basic scheme

The last step of the basic scheme involves the elimination of acetone from the stream containing isopropanol and ethanol. From this distillation column, pure acetone is obtained at the top of the column and a stream of hydrated alcohol at the bottom of the column. The amount of water present in this stream is not negligible. A dehydration unit is, therefore, necessary for the elimination of a large part of the water. Although both methods presented above are suitable for dehydration of isopropanol and ethanol, only PSD has been considered to simulate the dehydration of the two alcohols.[13] The same Pressure Distillation could be studied later if needed. The mass and molar composition of the feed is reported in *Table **3.1.1***. Due to convergence and stability problems of the simulated scheme, the acetone (0.10% of the feed) was removed from the feed.

Table 3.1.1 Dehydration scheme: Mass and molar feed composition

	Mass Composition	**Molar Composition**
H2O	0.1206	0.3127
BUTANOL	0.0012	0.0007
IPROPNOL	0.8595	0.6678
ETHANOL	0.0177	0.0180
ACETONE	0.0010	0.0008

To verify the feasibility of dehydration of our stream, the ternary diagram (molar composition) Ethanol-Water-Isopropanol was drawn as shown in *Figure **3.1.4***.

On the diagram, it is possible to note the azeotropes at the different pressures (0.05 bar, 1 bar, and 10 bar). The diagram also shows the residual curves at 1 bar which clearly show the division of the diagram into two distinct distillation zones divided by a distillation boundary that connects the water-ethanol azeotrope with the water-isopropanol azeotrope. Zone I is defined as the one to the right of this border and Zone II the one on the left. However, it is necessary to specify that it is not possible to accurately predict the PSD dehydration scheme with the model used. First of all, it is not possible to accurately predict the azeotrope at 1 bar as the experimental data at 1 bar are very dispersed. Furthermore, there are no experimental data at 10 bar. The only information available is an azeotrope at 9.101 bar. *Figure **3.1.3*** shows the experimental data cloud at 1 bar.

Figure 3.1.3 Experimental data for isopropanol-water azeotrope at 1 bar – Confidential data

As in the case of the examples shown in *Figure 3.1.1* and *Figure 3.1.2* our feed is located in Zone I but unlike the examples our feed contains only a small percentage of ethanol, bringing point F1 very close to the isopropanol-ethanol diagonal.

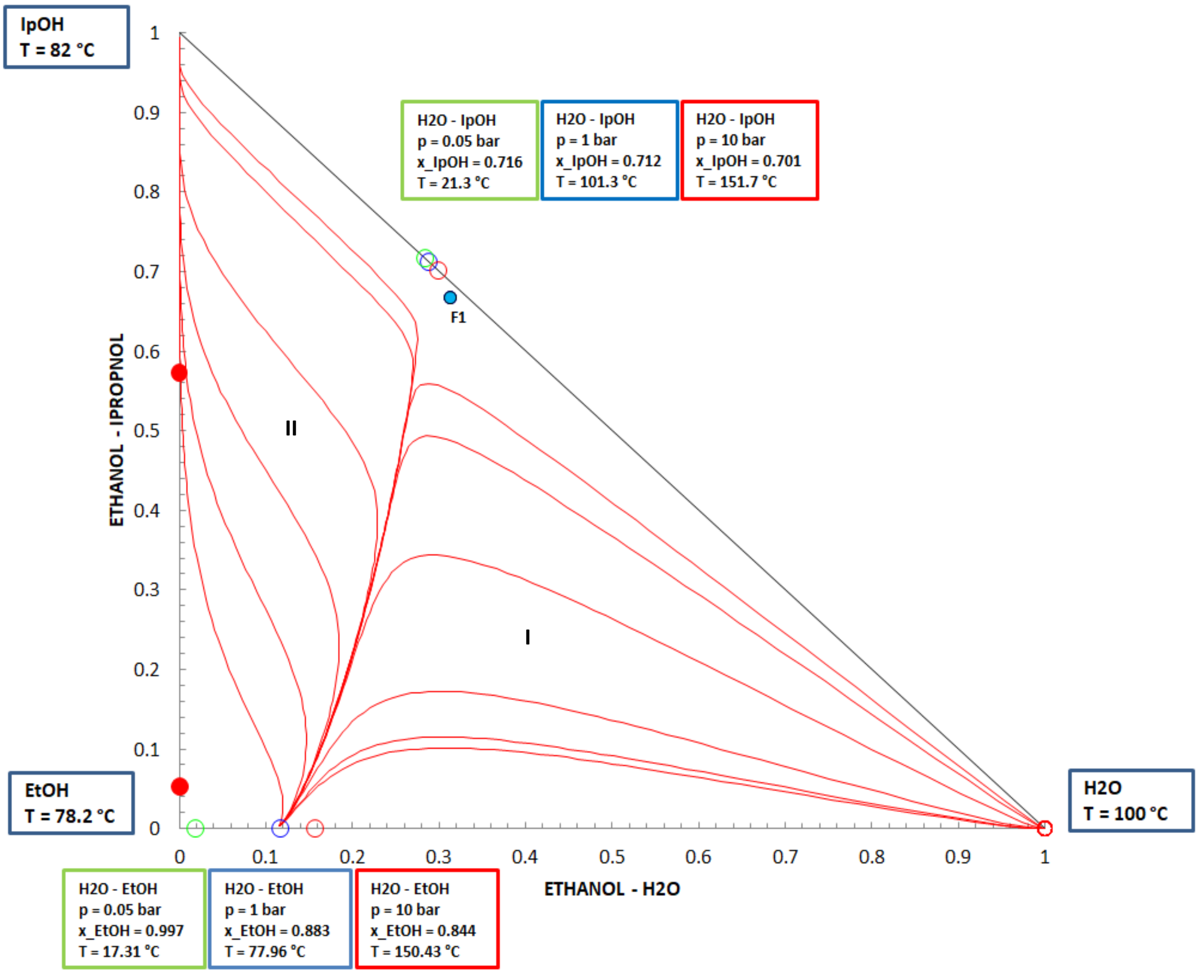


Figure 3.1.4 Simulated ternary diagram (molar composition)

The simulated pressure swing distillation scheme is shown in *Figure 3.1.5*.

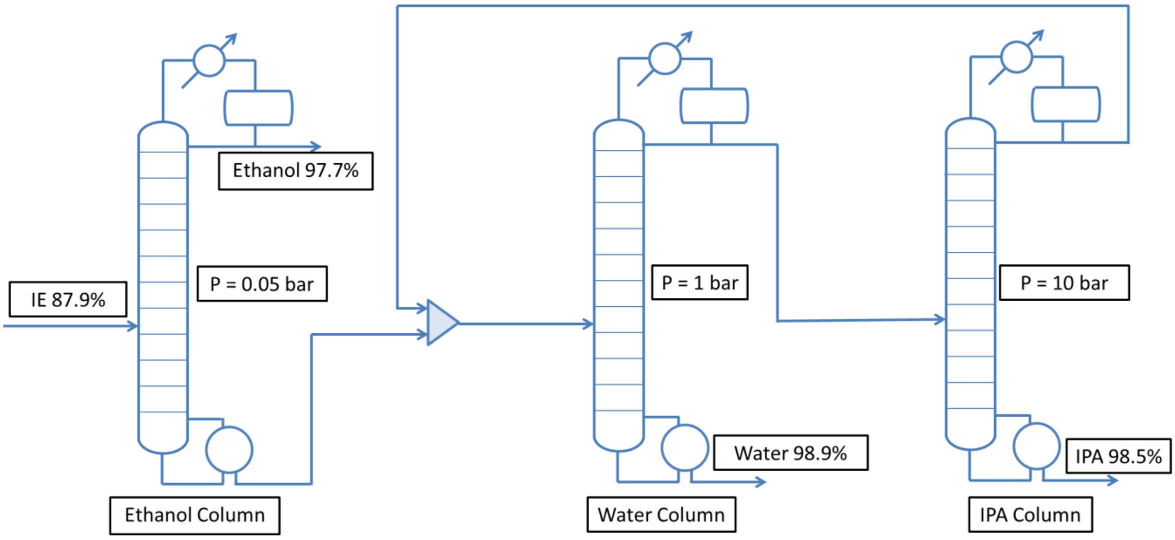


Figure 3.1.5 Simulated Pressure Swing Distillation scheme

The results in terms of the molar composition of the simulation are shown in *Figure* ***3.1.6***.

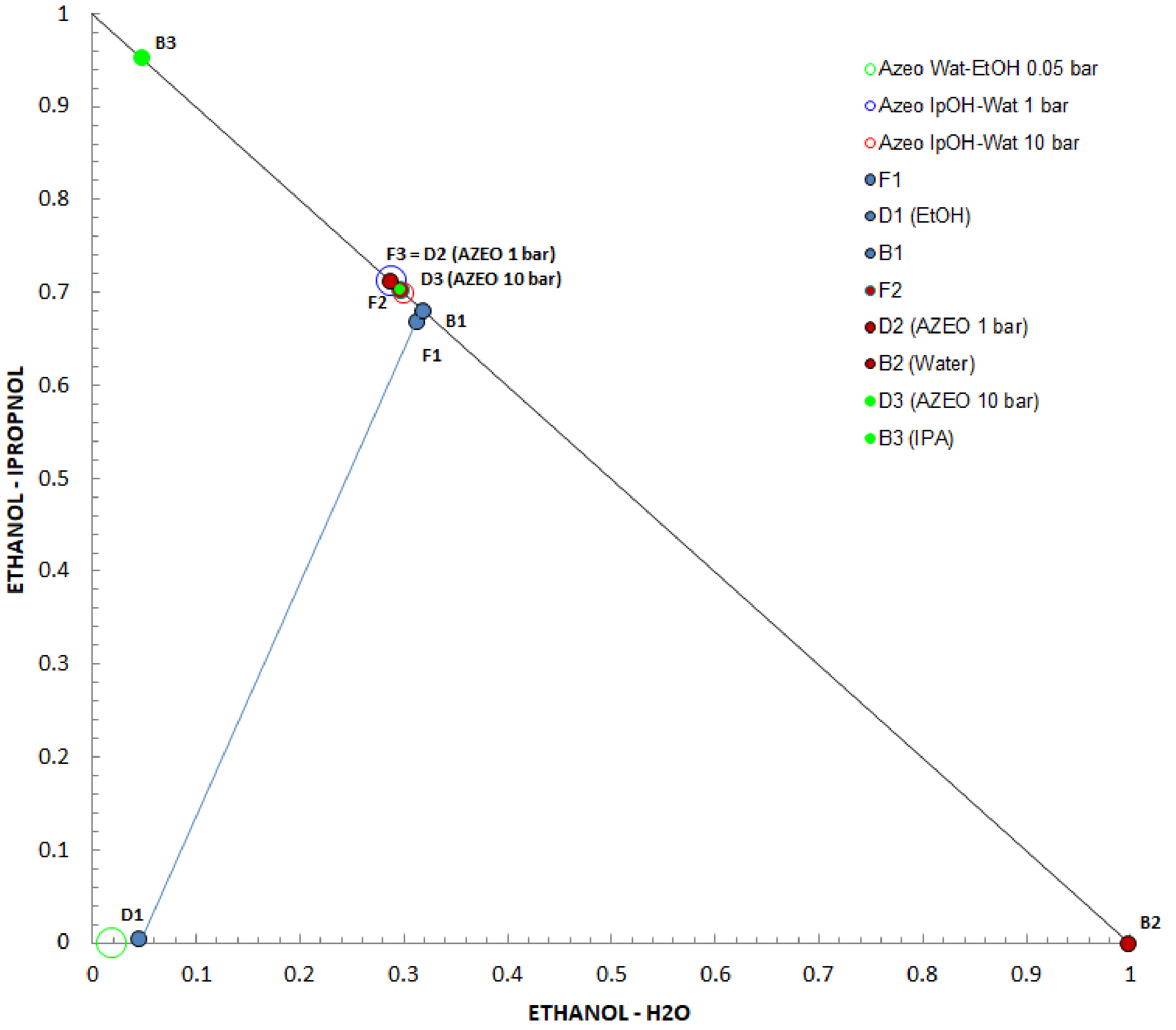


Figure 3.1.6 Simulated ternary diagram (molar composition): feed and products compositions

The first step for dehydration of isopropanol and ethanol is the elimination of ethanol from the stream. The column to eliminate ethanol (C-701) works at a pressure of 0.05 bar. It exploits the fact that at this pressure the water-ethanol azeotrope contains a molar fraction of ethanol of 0.997 as shown in *Figure* ***3.1.4***.

The specifications of the C-701 column are:

- Recovery of 99 % of ethanol at the top of the column
- Recovery of 99.99 % of isopropanol at the bottom of the column

The goal in terms of performance of the C-901 column is to reach a composition of 98.5% wt of isopropanol at the bottom of the column. Given the proximity of the two azeotropes at 1 and 10 bar, at first, we tried to reach the convergence of the scheme.

To do this, the following have been chosen as specifications:

- C-801: recovery of all butanol at the bottom and recovery of isopropanol at the bottom of the column equal to 0.0001;
- C-901: recovery of isopropanol at the bottom equal to 0.9998.

After reaching convergence, the goal was 98.5% wt at the bottom of the second column. To do this it was necessary to set a material balance of isopropanol and water as specifications of the two columns. The specification is:

- C-801: Water flowrate at the bottom = 231.4502 kg/h;
- C-901: Water flowrate at the bottom = 27.75 kg/h and isopropanol flowrate at the bottom = 1851.4148 kg/h.

3.1.1.1 Scheme optimization: C-301 feed tray and number of trays

An optimization study was carried out on this column in terms of the influence of the number of trays and the feed tray on the energy consumption of the column. The results are shown in *Figure **3.1.7***.

To carry out this separation, the column needs a minimum number of trays equal to 60 trays. For this reason, following the same reasoning of the previous chapters for the optimization of the base scheme and the Mikitenko scheme, it was chosen to operate with a column with 120 trays. The duty is thus reduced from about 44 MW to about 3.5 MW.

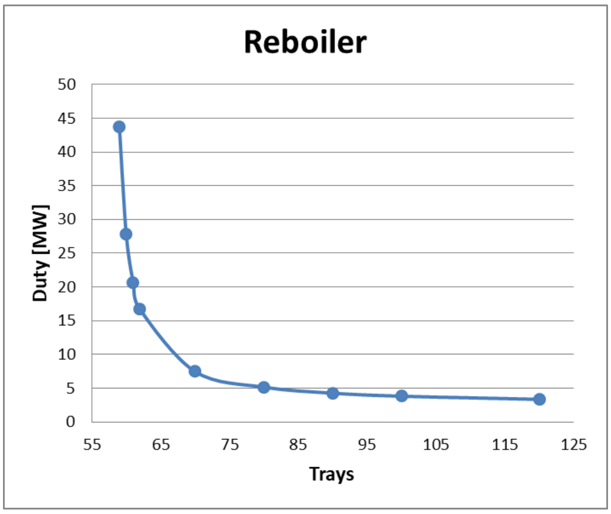


Figure 3.1.7 Optimization of feed trays for the column C-701. Reboiler duty as a function of the number of trays

As can be seen in *Figure **3.1.4***, at 0.05 bar, and with the composition of the azeotrope, the temperature of the distillate is 17.31°C. In the simulated case, the temperature of the distillate obtained is 17.35°C. To condense the vapors in the condenser it was decided to use glycolated water (chilled water in the following tables) at 4°C. At the reboiler, the temperature is around 21.3°C. To provide heat to the reboiler (3.35 MW) it was decided to recover part of the heat from the condenser of the C-801 column whose vapors are at a temperature of 79.5°C. An aero condenser is used to subtract the remaining heat from the C-801's condenser (20.16 MW).

The number of trays of the C-801 (water column) and the C-901 (isopropanol column), as well as the position of the feed tray, have not been optimized. The number of trays for both columns is equal to 50 as found in the literature.[13] However, it can be noted that energy integration has been made between the C-801 column and the C-901. The temperature and duty at the C-801 reboiler are respectively 98°C and 20.3 MW while the temperature and duty at the condenser of the C-901 are 151.7°C and 19.3 MW respectively. An energy integration is therefore possible. In this way, all the heat from the condensation of the overhead vapors is transferred to the liquid in the C-801 reboiler. The remainder of the heat to be supplied to the reboiler is provided by LPS. For the C-901 reboiler, MPS at 180°C was used.

3.1.1.2 PSD: Economic evaluation

*Table **3.1.2*** shows the in-house basis prices that have been considered for economical evaluation. ***Table 3.1.3*** and ***Table 3.1.4*** show the results of the PDS economic evaluation. The results in the table are related to the total production of IBEA (5 t/h) and the production of isopropanol (1.85 t/h).

Table 3.1.2 IFPEN in-house price data for the utility price

	Price	
Electricity NWE	*Confidential Data*	€/kWh
LPS NWE		€/t
MPS NWE		€/t
Chilled Water		€/t

Table 3.1.3 PSD utility consumption

		PSD
Electricity NEW	kWh/h	358.2
LPS NEW	t/h	1.6
MPS NEW	t/h	40.7
Chilled Water	kWh/h	3476.1

Table 3.1.4 PSD separation cost as the sum of Capex and Opex: results related to the total production and the isopropanol production

Normalized cost	PSD/IBEA	PSD/IPA
Separation Cost	109.4	288.0
Capex	25.2	66.4
Opex (excl. Raw material)	84.2	221.6

The results in the table show how this dehydration process is an onerous process both in terms of Opex and in terms of Capex. The consumption of utilities is high and this falls directly on the Opex. Furthermore, 3 distillation columns are needed, one of which has 120 trays working at 0.05 bar, one with 50 trays at 1 bar, and one with 50 trays at 10 bar. Moreover, the cost of the first column vacuum pump must be added to the cost of total separation. For a first estimate of the separation cost, the cost of the vacuum pump was neglected because there is not enough data to estimate the cost of the pump and because, given the high cost of the PSD scheme, it was deemed unnecessary to go into more detail. Comparing the result related to the production of IBEA, the dehydration process using PSD is more onerous than the alcohol separation process itself.

3.2 Azeotropic Distillation with Cyclohexane/Benzene

The second method to dehydrate isopropanol (and ethanol present in small quantities) is the azeotropic distillation with the use of a third body that allows the separation of the azeotrope, otherwise impossible by simple distillation. The third body added to the water-isopropanol mixture with azeotropic composition is benzene.

The water-isopropanol-benzene system presents under atmospheric pressure 3 binary azeotropes including the water-benzene hetero azeotrope and a ternary hetero azeotrope. *Table **3.2.1*** shows the boiling temperatures of the three pure components (water, isopropanol, and benzene) and those of the 4 azeotropes with the related molar composition.

Table 3.2.1 Pure components and azeotropes boiling temperature and composition

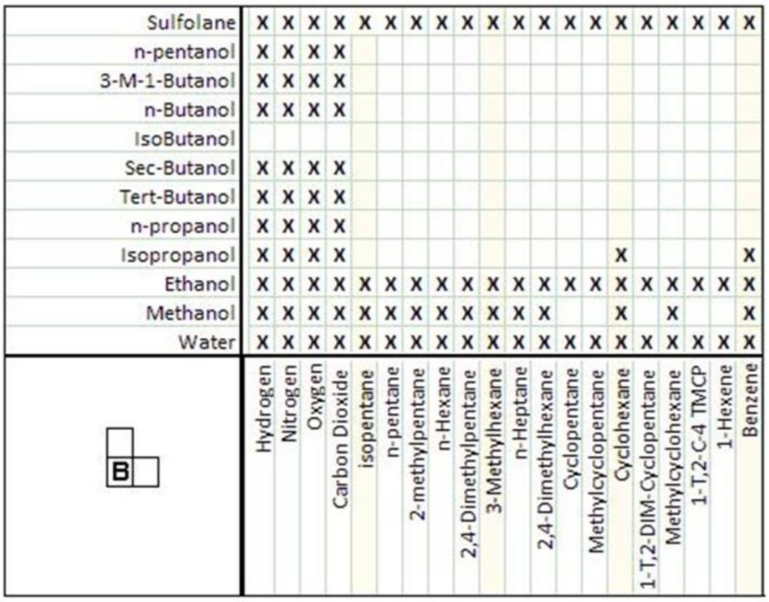
T_{eb}	Molar Composition		
[°C]	Water	Isopropanol	Benzene
100.0	1		
82.2		1	
80.1			1
80.2	0.323	0.677	
69.3	0.299		0.701
71.5		0.421	0.579
65.7	0.237	0.244	0.518

Water-isopropanol and isopropanol-benzene are completely miscible in the liquid phase. The water-benzene mixture is completely immiscible. The total immiscibility of the water-benzene mixture generates for water-isopropanol-benzene mixtures a relatively large area of partial immiscibility within the diagram and the ternary hetero azeotrope has a composition that is located in this zone of partial immiscibility. The ternary diagram (*Figure **3.2.2***) under atmospheric pressure therefore comprises 7 singular points:

- pure substances: isopropanol 82.2°C, benzene 80.1°C, water 100°C;
- binary azeotropes: isopropanol-benzene (homo azeotrope) 71.5°C, water-benzene (hetero azeotrope) 69.3°C, water-isopropanol (homo azeotrope) 80.2°C;
- ternary hetero azeotrope: water-isopropanol-benzene: 65.7°C.

The total reflux distillation curves, therefore, start from the various "pure" points and converge towards the ternary hetero azeotrope. The distillation system, therefore, has 3 zones I, II, III.

The thermodynamic model used to simulate the azeotropic distillation and the ternary diagram is the model ALCOHOL from PROII V 10.2 software, a model recommended for all alcohol dehydration systems by SIMSCI. The alcohol model uses the NRTL liquid activity method to calculate phase equilibrium. This model uses a special databank of NRTL parameters containing interaction parameters expressly regressed under temperature and pressure conditions commonly found in dehydration systems. The use of this thermodynamic model is possible only for bodies for which binary parameters have been set. *Figure **3.2.1*** shows all the pairs for which the parameters have been set. For all the pure bodies present in the dehydration scheme (Benzene, Cyclohexane, Isopropanol, Ethanol, and water) the binary parameters have been set.



	Hydrogen	Nitrogen	Oxygen	Carbon Dioxide	isopentane	n-pentane	2-methylpentane	n-Hexane	2,4-Dimethylpentane	3-Methylhexane	n-Heptane	2,4-Dimethylhexane	Cyclopentane	Methylcyclopentane	Cyclohexane	1-T,2-DIM-Cyclopentane	Methylcyclohexane	1-T,2-C-4 TMCP	1-Hexene	Benzene
Sulfolane	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
n-pentanol	X	X	X	X																
3-M-1-Butanol	X	X	X	X																
n-Butanol	X	X	X	X																
IsoButanol																				
Sec-Butanol	X	X	X	X																
Tert-Butanol	X	X	X	X																
n-propanol	X	X	X	X																
Isopropanol	X	X	X	X											X					X
Ethanol	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Methanol	X	X	X	X	X	X	X	X	X	X	X	X			X		X			X
Water	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

Figure 3.2.1 Binary interaction set for the ALCOHOL model

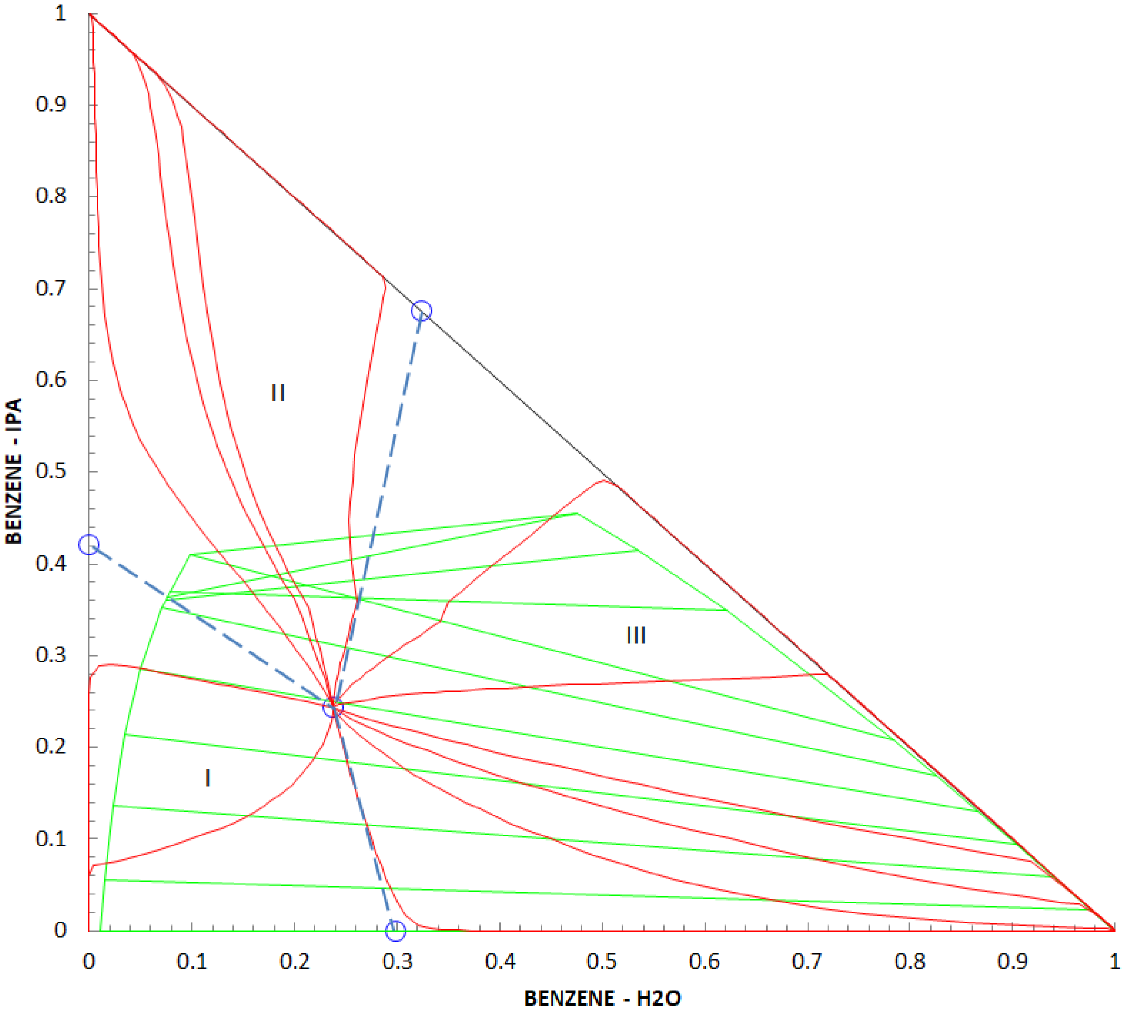


Figure 3.2.2 Water-Isopropanol-Benzene ternary diagram

3.2.1 Simulation of Azeotropic distillation

The feed which leaves the distillation column for the removal of acetone (base case) with the water-isopropanol azeotropic composition is sent to this azeotropic distillation unit.

If benzene is added to this water-isopropanol mixture, a feed composition is obtained located in zone II and, taking into account the distillation curves at total reflux, it is possible to obtain from the bottom of the first column of pure isopropanol and the ternary hetero azeotrope from the head of the column. After condensation, the hetero azeotrope separates into two liquid phases: a phase rich in water and a phase rich in benzene. In these two liquid phases, due to the composition of the ternary hetero azeotrope, isopropanol is also present.

The phase rich in benzene is returned to reflux from column C1. The water-rich phase, distillable in field I, is sent to a C2 column which produces water at the bottom of the column and a distillate similar to the ternary hetero azeotrope at the top of the column which is returned to the first column. The simulated azeotropic distillation scheme is shown in *Figure **3.2.3***.

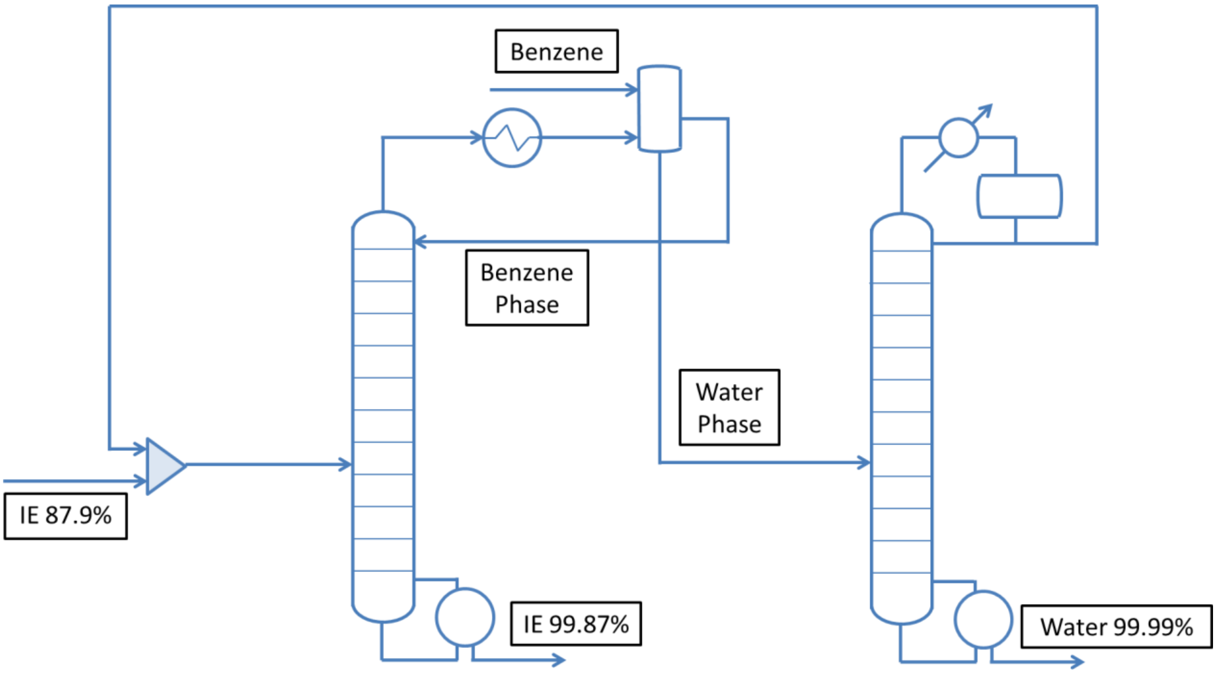


Figure 3.2.3 Simulated azeotropic distillation scheme with benzene as a third body to break the water-isopropanol azeotrope

Therefore, benzene has the function of making a ternary hetero azeotrope appear at a low boiling temperature. Furthermore, the addition of benzene causes a large demixing zone to appear in the liquid phase. Both of these changes allow the isopropanol-water azeotrope to be bypassed.

Due to the toxicity problems of benzene, the same type of operation has been performed with cyclohexane. *Table **3.2.2*** shows the boiling temperatures of the three pure corps and those of the 4 azeotropes with the related molar composition when cyclohexane is used as a third body to break the isopropanol-water azeotrope.

Table 3.2.2 Pure corps and azeotropes boiling temperature and composition

T_{eb}	Molar Composition		
[°C]	Water	Isopropanol	Cyclohexane
100.0	1		
82.2		1	
80.7			1
80.2	0.323	0.677	
69.4	0.300		0.700
69.3		0.393	0.607
63.7	0.210	0.254	0.535

The ternary diagram (*Figure **3.2.4***) under atmospheric pressure therefore comprises 7 singular points:

- pure substances: isopropanol 82.2°C, cyclohexane 80.7°C, water 100°C;
- binary azeotropes: isopropanol-cyclohexane (homo azeotrope) 96.3°C, water-cyclohexane (hetero azeotrope) 69.4° C, water-isopropanol (homo azeotrope) 80.2°C;
- ternary hetero azeotrope: water-isopropanol-cyclohexane 63.7°C.

As for the benzene, the total reflux distillation curves start from the various pure points and converge towards the ternary hetero azeotrope. The distillation system, therefore, has 3 zones I, II, III.

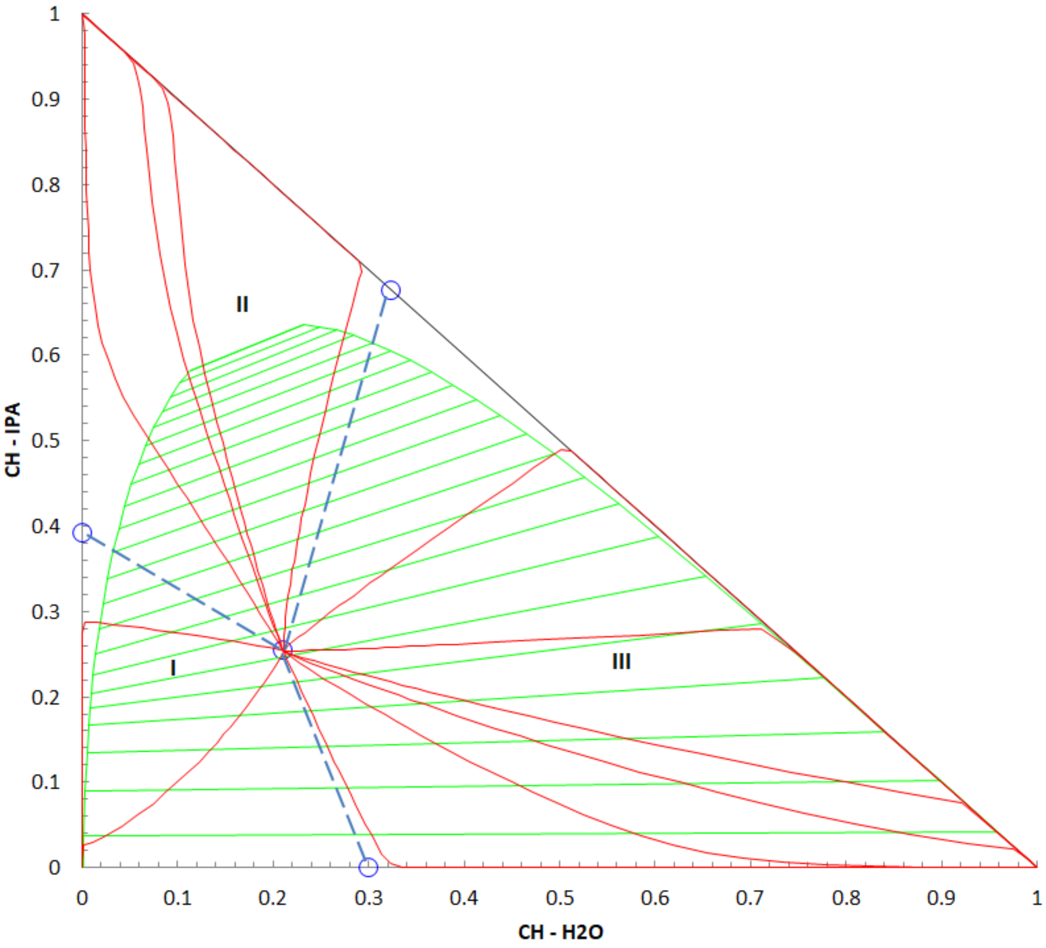


Figure 3.2.4 Water-Isopropanol-Cyclohexane ternary diagram

3.2.1.1 Azeotropic distillation economic evaluation

Table ***3.2.3*** shows the in-house basis prices that have been considered for the azeotropic distillation economic evaluation. ***Table 3.2.4*** and ***Table 3.2.5*** show the results of the economic evaluation for both azeotropic distillations with benzene and cycle hexane. The results in the table are related to the total production of IBEA (5 t/h) and the production of isopropanol (1.85 t/h).

Table 3.2.3 IFPEN in-house price data for the utility price

	Price	
Electricity NWE	*Confidential Data*	€/kWh
LPS NWE		€/t
Cyclohexane		€/t
Benzene		€/t

Table 3.2.4 Azeotropic distillation utility consumption: the case with benzene and case with cycle hexane

		Benzene	CH
Electricity NWE	kWh/h	38.4	26.3
LPS NWE	t/h	3.7	2.5
Cyclohexane	kg/h		0.0189
Benzene	kg/h	0.0189	

Table 3.2.5 Azeotropic distillation separation cost as the sum of Capex and Opex: the case with benzene and case with cycle hexane

Normalized cost	Benzene/IBEA	Benzene/IPA	CH/IBEA	CH/IPA
Separation Cost	11.1	30.0	8.9	24.0
Capex	3.8	10.3	3.5	9.5
Opex (excl. Raw material)	7.3	19.8	5.4	14.5

The results obtained in terms of energy consumption were compared with those of the engineering technique (*Table* ***3.2.6*** and ***Table 3.2.****7*).[14]

Table 3.2.6 Azeotropic distillation utility consumption in kWh to dehydrate 100 kg of isopropanol

		Reference	Benzene	CH
Electricity NWE	kWh	19	2	2
LPS NWE	kWh	17	118	79
Total	kWh	36	120	81

Table 3.2.7 Azeotropic distillation utility consumption in MJ/kg IPA and MJ/kg IBEA

	Reference		Benzene		CH	
	MJ/kg IPA	MJ/kg IBEA	MJ/kg IPA	MJ/kg IBEA	MJ/kg IPA	MJ/kg IBEA
Electricity NWE	0.684	0.253	0.075	0.028	0.051	0.019
LPS NWE	0.612	0.226	4.227	1.564	2.856	1.057
Total	1.296	0.480	4.302	1.592	2.907	1.076

Unlike the reference results, there is significantly lower consumption of electricity used to condense the vapors and for the pumps. However, there is greater use of steam to be supplied to the two columns. These differences may have been caused by the thermodynamic method used for the simulation. Furthermore, in the technical note, it is specified that to obtain the values in the table various simplifications have been made and a simulation of the scheme has not been made.[17] The orders of magnitude of the results obtained by the simulations seem more realistic than those of the reference.

The solvent supply was roughly calculated by evaluating the volume of the two columns, adding the two volumes, and multiplying the total volume x3 to also take the pipes into account. Then, knowing the density of benzene and cyclohexane, as well as their price, it was possible to calculate the contribution of the solvent on the Direct Owner's Cost. The calculations are shown in *Table **3.2.8***.

Table 3.2.8 Calculation of the contribution of the solvent on the Direct Owner's Cost

Solvent	Item	Description	Height	Diameter	Volume	Volumex3	Density	Mass	Price	Cost
			m	m	m3	m3	kg/m3	t	€/t	M€
BENZENE	C-701	Azeo. Column	18.8	1.2	19.538					
	C-801	Drier Column	17.5	0.4	2.204					
					21.742	65.226	876	57.138	955.844	0.055
CH	C-701	Azeo Column	18.97	0.95	13.446					
	C-801	Drier Column	17.38	0.6	4.914					
					18.36	55.081	779	42.908	1 130.99	0.049

It is easy to see that, unlike the PSD dehydration scheme, azeotropic distillation is more convenient. Taking into consideration the separation cost referred to the production of IBEA, the azeotropic distillation cost is 1/10 then the PSD.

This gain in terms of separation costs is even more significant if cyclohexane is used as a third body to break up the isopropanol-water azeotrope. Furthermore, the use of cyclohexane also has the advantage of being less toxic than benzene.

3.3 Pervaporation

Membrane technologies have recently emerged as an additional category of separation processes over established mass transfer processes. These separation technologies offer numerous advantages over existing mass transfer processes, such as high selectivity, low power consumption, moderate cost/performance ratio and, compact and modular design. In recent years, pervaporation has established itself as one of the most promising membrane technologies for a wide range of applications: from dehydration of organic compounds to recovery of organic compounds from water and separation of organic mixtures. As a not yet well-established technology, pervaporation as a single process often has to compete with conventional processes such as distillation, liquid-liquid extraction, adsorption, and stripping, which are reliable and the cost of which can be easily calculated by industry.

3.3.1 Separation Principle

The evaporation of a liquid mixture through a dense membrane leads to the formation of vapor in the downstream compartment which has a composition generally different from that of the feed from which it comes. The mass transfer is maintained by keeping the downstream compartment at low pressure by pumping and condensing the vapors onto a cold wall. This selective transfer, first observed in 1906 with mixtures of hydrocarbons and alcohol, received the definitive name of pervaporation in an article published in 1917.[18]

Pervaporation is a process in which the transferred species pass into the vapor phase but, unlike the simple evaporation that occurs in simple distillation, the membrane acts as a third solid body. Due to the membrane, there is an irregular dissolution of the species on the upstream face in contact with the liquid. This causes a change in the composition of the mixture that crosses the upstream membrane interface. Following this thermodynamic factor, a second factor intervenes in the kinetic order, to modify the composition of the transferred mixture: the unequal mobility of the species in the material (diffusivity). This second process is the main limiting factor in the transfer of the material and explains why the thickness of the active layer of the membranes is always very low. The mass transfer in pervaporation is therefore based on a mechanism, in three phases :[19]

1. The dense membrane behaves like a solvent layer which selectively dissolves the adjacent liquid mixture. This solvation selectivity constitutes the first stage of the transfer and is strongly conditioned by the respective affinities between the membrane material and the species present in the feed.
2. The species absorbed in the dense film diffuse under the influence of the local activity gradient that exists for each species and at each point of the membrane.
3. The last phase of the transfer consists of desorption, at reduced pressure, of the molecules that have reached the downstream face. Under normal operating conditions, the latter process is much faster than the previous ones and it is recognized that it does not play a role in transfer selectivity or transfer flow control. Under a sufficient reduced pressure (less than 10 mm Hg), the vapors are discharged practically continuously into the condenser without solvation of the downstream face of the membrane. This is equivalent to admitting that concentrations are practically zero near the interface downstream of the membrane.

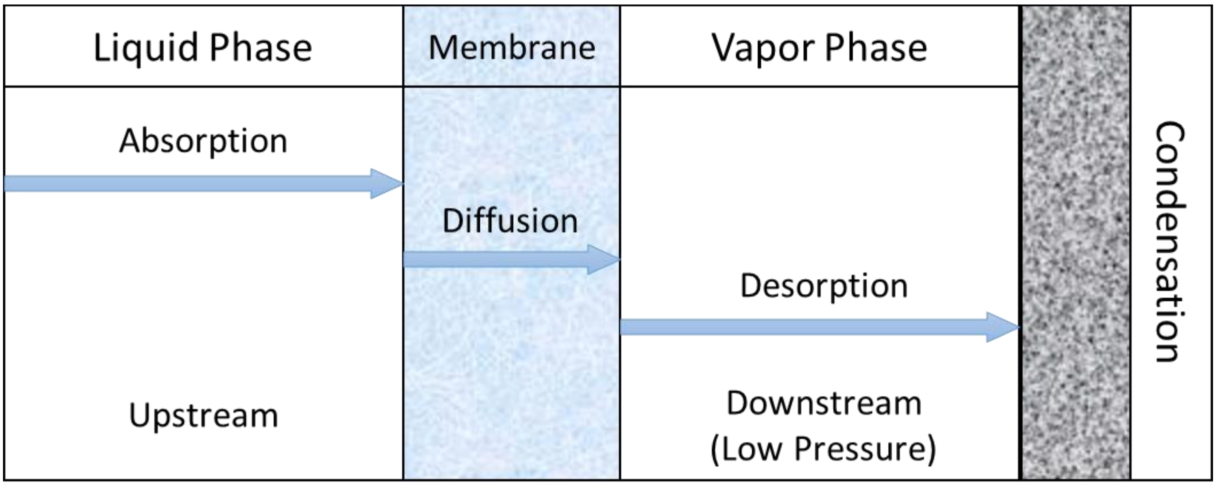


Figure 3.3.1 Pervaporation mass transfer diagram

The mass transfer is followed by the following two induced phenomena:[14]

- The upstream layer which is in contact with the liquid charge is more or less strongly solvated by this liquid while the layer in contact with the vapor is practically dry. A concentration gradient is therefore established between the upstream and downstream faces, the greater the more the material can swell in the treated mixture. This asymmetry generates mechanical stresses that must be managed either by limiting the swelling of the membrane through physical or chemical modifications of the same or by operating in a limited composition range.
- The vaporization of the pervaporate downstream of the membrane is followed by the absorption of the enthalpy of vaporization. The vaporization heat is essentially provided by the upstream liquid, whose temperature drops in contact with the membrane. This phenomenon, therefore, requires having heat exchangers in the upstream circuit to heat the feed and thus maintain the amplitude of the transfer at an acceptable level. Therefore, it is much more interesting to carry out the extraction of the minority compound, which limits the necessary membrane surface and above all the vaporization energy, since - unlike distillation - only the transferred fraction consumes energy. Furthermore, the vaporization heat can be provided at moderate temperature levels. This possibility can be exploited through two practical aspects: first, a pervaporation plant can recover the energy of various industrial fluids (from 50 to 120°C). Then, the possibility of operating at mild temperatures (from 30 to 80°C) also allows the pervaporation of thermosensitive products (aromas and compounds deriving from biotechnologies).

One of the advantages of the pervaporation process is the transfer selectivity and the energy required. Pervaporation membranes are developed for very specific applications and their selectivity is generally very high. When pervaporation is performed as a purification process, the high selectivity of the membranes results in the vaporization of a very limited fraction of the feed, which implies a considerable cost saving when compared to the energy required by the distillation. Furthermore, pervaporation can be very selective in composition areas where a conventional separation process is no longer selective (case of azeotropic or pseudo-azeotropic compositions). This technique is therefore presented as an alternative and complementary separation method to distillation. In fact, among the possible associations, distillation is the unitary operation most often coupled with pervaporation. For example, in azeotropic distillation, a hybrid distillation-pervaporation process allows separation to be carried out avoiding the need for a third body that contaminates the final product and the additional cost of using three coupled columns. The industrial devices used are most often of the filter press type. The basic elements are stacked to form modules of a few square meters of the membrane. All these modules are arranged in series in a compartment where the partial pressure is maintained at the chosen level by controlling the temperature of the condenser. A heat exchanger is interposed between each module to keep the pervaporate flow at its maximum level. The sizing of the system is carried out in such a way that the temperature variation range remains within a range such that the transfer flows remain constant. In some cases, if the feed is directly available in the form of steam, the implementation of the pervaporation process can be simplified by placing the modules directly in contact with the steam such as, for example, in the upper part of a distillation column, this which leads to the economy of a heat exchanger. This mode of operation is usually called "vapor permeation". Another advantage of the pervaporation process is that it is fully controlled by the two limit temperatures (liquid feed and cold wall) when the feed rate and feed composition are set.

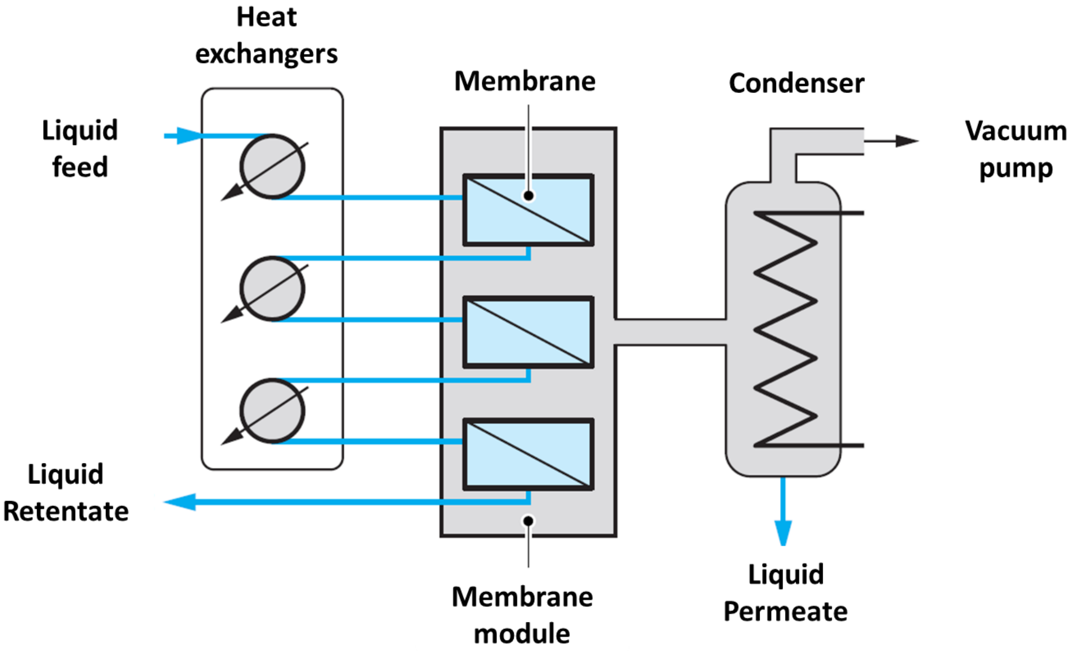


Figure 3.3.2 Schematic diagram of the three-module membrane pervaporation system

3.3.2 IPA dehydration process

Several hybrid distillation-pervaporation processes are present in the literature.[20] The next list presents some of these processes.

3.3.2.1 Schema 1

The overhead product of an IPA distillation column, a ternary mixture of isopropanol, ethanol, and water, was dehydrated by a pervaporation unit using hydrophilic membranes to produce an alcohol mixture with less than 0.5% wt of water.[21]

- Feed: 34,000 kg/day, 12% wt water
- Product (retentate): < 0.5% wt water
- Permeate: rich in water and recycled in the distillation column.

Capex: -31% compared to a two-column azeotropic distillation process with hexane as entrainer. Opex estimated as a percentage of investment costs (including membrane replacement costs):-15% / -16% lower than azeotropic distillation.

3.3.2.2 Schema 2

The hybrid pervaporation-distillation process to dehydrate IPA consists of a hydrophilic pervaporation unit installed between two distillation columns.[22]

- Feed Column 1: 36.4% mol of IPA.

- Feed pervaporation: Overhead product from column 1 + overhead product from column 2
- Bottom product column 1: removed from the process
- Permeate: 97% mol water recycled to the first column
- Retentate: 96% mol of IPA = Feed Column 2
- Bottom product column 2: dehydrated IPA

Production costs (Hybrid process): -5% compared to azeotropic distillation with benzene as entrainer.

Production costs (simplified process layout: one distillation column and one pervaporation unit): -36% compared to the conventional process.

3.3.2.3 Schema 3

Pervaporation-distillation hybrid process is used to produce dehydrated ethanol modified to produce isopropanol (*Figure **3.3.3***).[23]

- Feed Column 1: IPA 5% mol
- Feed pervaporation: overhead product from column 1 (62% mol IPA) + overhead product from column 2 (73% mol IPA)
- Permeate 45.4% mol water recycled to the first column.
- Retentate = Feed Column 2
- Bottom product column 2: IPA concentration of 99.5% mol

No indications of costs were included for this schema.

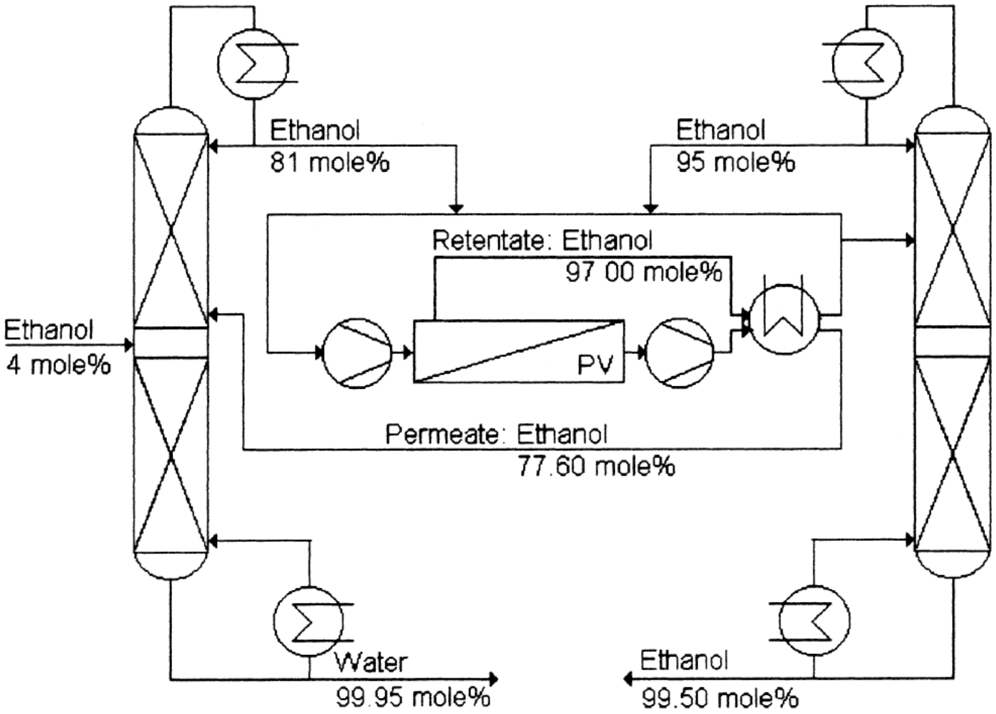


Figure 3.3.3 Dehydrated ethanol production: process layout of a pervaporation-distillation hybrid process integrating the PV unit between two distillation columns (a process then modified to dehydrate IPA: schema 3)

3.3.2.4 Schema 4

This distillation-pervaporation hybrid process is used to dehydrate an IPA-water mixture (50% wt) to a final IPA concentration of 99.5% wt using a hydrophilic membrane.[24][25][26]

- Feed: IPA 50% wt
- Overhead product: IPA 86% wt (azeotropic concentration)
- Retentate: IPA 99.5% wt

Capex:

- The feed of 500 kg/h: about - 10% compared with single rectification or PV alone
- The feed of 2000 kg/h: about - 20% lower compared with single rectification or PV alone.

Opex:

- Feed of 500 kg/h: about - 25%
- Feed of 2000 kg/h: about - 45%

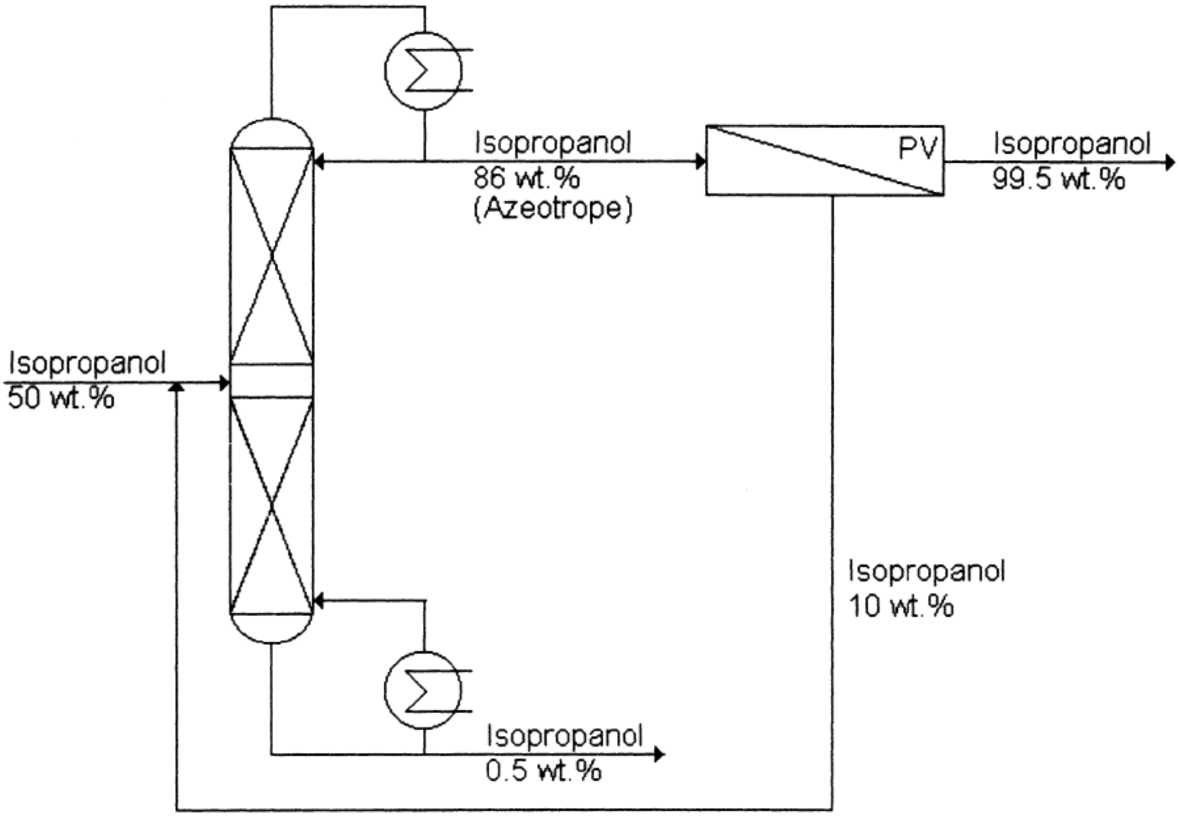


Figure 3.3.4 Schema 4: Dehydrated isopropanol production process: pervaporation-distillation hybrid process

3.3.2.5 Schema 5

Another optimized hybrid process includes a pervaporation unit with a hydrophilic plasma-polymerized membrane placed between two distillation columns to split the IPA-water azeotrope.[27] This process was compared with conventional extractive distillation with ethylene glycol as entrainer giving the following results:

- Capex: 92% of the conventional process
- Opex: 54% of the conventional process.

This led to annual overall cost savings of 27%. More in detail, the cost analysis has revealed that the pervaporation unit accounted for about 22% of the overall costs.

Furthermore, a sensitivity analysis showed that the hybrid process may be economically unfavorable only if the membrane replacement becomes more frequent, whilst an increase in steam prices would further advantage the hybrid process. Finally, scaling-up from 5000 to 20 000 kg/h, the advantages of the hybrid process may further increase due to its lower energy requirement.

3.3.2.6 Schema 6

Finally, another pervaporation-distillation hybrid process consists of a pervaporation unit placed between the azeotropic and extractive distillation columns. In this way, the pervaporation unit concentrates the IPA from 85% wt to 95% wt and this leads to a lower water load in the extractive distillation column and enables the use of an alternative entrainer other than benzene.[28]

3.4 Adsorption

The adsorption dehydration process is not typically used for the dehydration range required for the removal of water from the water-isopropanol azeotrope.[17] The basic difference in membrane processes and molecular sieves used for dehydration is that the productivity of a membrane system increases with water concentration, while the productivity of molecular sieves decreases with water concentration.[29] Furthermore, processes for the dehydration of isopropanol by adsorption are not yet present in the literature. However, this technique is widely used for the dehydration of the water-ethanol azeotrope. A brief presentation of adsorption dehydration will then be made.

The elimination of water from the water-ethanol couple takes place by adsorption/desorption of water on molecular sieves. The terms molecular sieves are used to describe microporous solids used as adsorbents in the purification and separation processes of fluids. The main and most abundant class of microporous absorbents are zeolites. Electrostatic interactions and polarity between adsorbent and ethanol-water mixture are the basis for operation.

The main problem faced when breaking down the water-ethanol azeotrope by adsorption on molecular sieves is that ethanol and water are both highly polar compounds, so both compounds are highly adsorbed to normal adsorbents. It is, therefore, necessary to use molecular sieves which preferentially adsorb water. One of the most potential materials for preferentially adsorbing water is 3Å molecular sieves as they have a very small pore diameter, greater than the diameter of water molecules (2.6Å), and smaller than that of ethanol (5.2Å).

The separation, therefore, occurs based on differences in molecular size and polarity (water slightly more polar than ethanol).[30]

As for the technique used to perform dehydration, fixed bed adsorption dehydration can be performed as temperature swing adsorption (TSA) or pressure swing adsorption (PSA). The main phases of both processes are the same, adsorption and desorption. However, they differ in the driving force used in the desorption/regeneration phase. In industrial applications both PSA and TSA, processes have been used for the dehydration of ethanol.

In a PSA process, the adsorption and regeneration steps are performed at a constant temperature. As for the pressure, on the other hand, the adsorption phase is carried out at relatively high pressure while the regeneration phase is carried out at low pressure or under vacuum. On the other hand, the TSA process operates at constant pressure (atmospheric pressure) during adsorption and regeneration while employing low temperatures during the adsorption phase and higher temperatures during the regeneration phase.

In *Figure **3.4.1*** it is possible to see a scheme used to dehydrate ethanol using a PSA process. During the adsorption phase the water molecules are adsorbed in the pores of the molecular sieves while an unabsorbed, dehydrated ethanol vapor leaves the column and after being condensed is collected as dehydrated liquid ethanol. After a certain time, the column under adsorption becomes saturated with water molecules. This column is then subjected to desorption for the regeneration of molecular sieves.

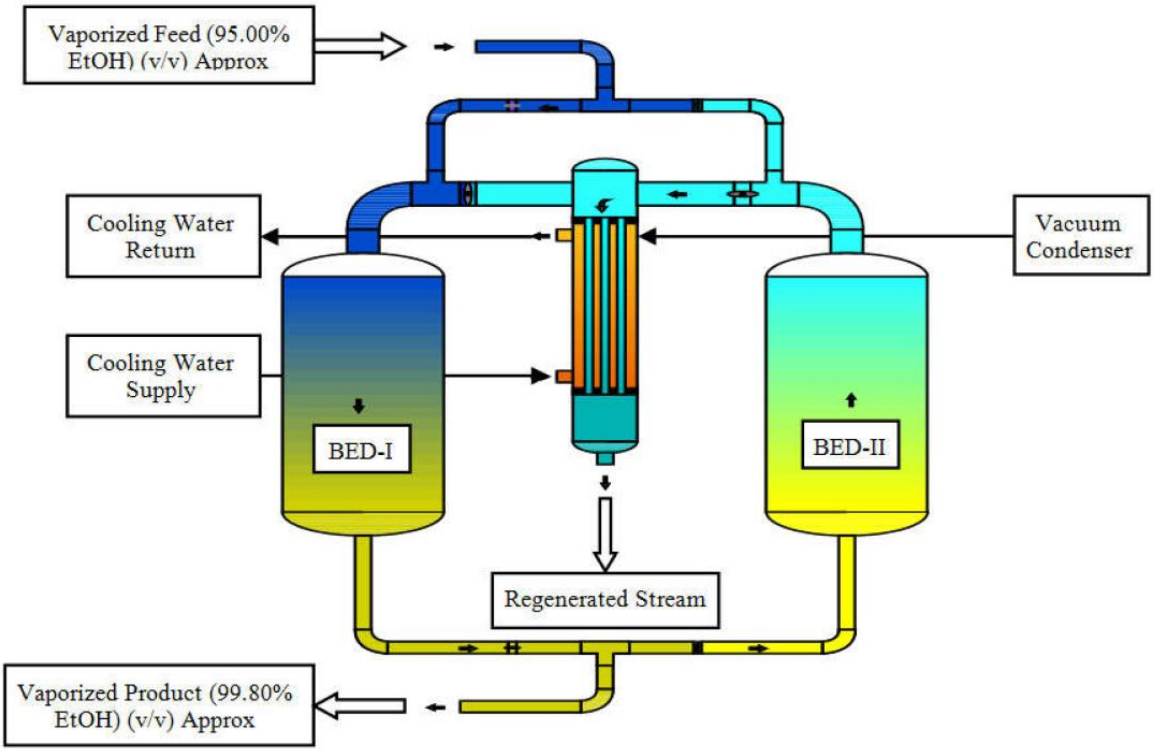


Figure 3.4.1 Scheme of a PSA process for ethanol dehydration

According to many researchers, PSA is energy efficient as it does not involve heating. However, in the current PSA process heating of the molecular sieves is usually required at the time of regeneration. Therefore, PSA cannot be considered a greater energy saving than the

TSA process as both processes include heating in the regeneration phase. TSA is therefore preferred in the ethanol dehydration process as it is more suitable for desorbing strongly adsorbed components as a slight change in temperature results in a large change in the liquid / gas-solid adsorption equilibrium. Therefore, in the ethanol dehydration process, it is recommended to use a TSA process to ensure complete and efficient regeneration for the adsorbents used.

4 Conclusions and future perspectives

The optimization of both the classic distillation scheme and the Mikitenko scheme for the production of IBEA has allowed reducing the separation cost of the two schemes. The optimization was mainly done on the beer column. The optimization of the number of plates, of the feed plate, and of the feed temperature allowed to reduce the energy consumption, so the separation cost of the two schemes. In particular, optimizing the feed/effluent exchanger and its technology the separation cost of the classic scheme has been reduced by about 28.8%. However, the shell and tube exchanger technology turned out to be not optimal from a practical point of view, given the high exchange areas involved. In this case, plate exchangers prove to be a better technology from a practical point of view. With their higher heat exchange coefficients, these exchangers allow obtaining much lower exchange surfaces compared to classic shell and tube. A more in-depth study must therefore be made on this technology to be able to size these exchangers and to be sure of their use for this type of application. However, in the end, the best scheme is the Mikitenko energy-optimized scheme which allows a cost reduction of 34.3 % compared to the reference case, even though using classical shell and tube exchanger technology.

Moreover, the effect of the quality of the vinasses (in terms of IBEA ppm) on the separation cost has been highlighted. It will be necessary to verify the possibility of having a higher IBEA concentration in the vinasses. While the increase in IBEA concentration in the vinasses allows reducing the separation cost, the limits allowed for the vinasses treatment are still not well known. Furthermore, an increase of IBEA in the vinasses leads to a loss of production in IBEA. The literature also talked about the possibility of recycling part of the vinasses in the fermenter without treating them. This would therefore allow obtaining an advantage in terms of water treatment and terms of production loss, as part of the lost IBEA is recycled back into the fermenter. On the other hand, the species in the vinasses mustn't exceed the toxicity limits of the microorganisms in the fermenter. A study on the vinasses that can be recycled could be the subject of future studies for the optimization of the IBEA production scheme.

Furthermore, the IBEA concentration in the distillation feed has not a negligible effect on the separation cost. Also, in this case, it is necessary to consider a wider perimeter to be able to optimize the scheme. If the increase of IBEA concentration in the feed allows a decrease in the separation cost, it is not known if this decrease offsets the increase in the cost of obtaining more concentrated IBEA from the fermenter.

Two alternative schemes to the beer column for IBEA concentration were presented in this study. As for the ELL scheme, this turned out not to be advantageous compared to the beer column. Nevertheless, further optimizations can be carried out on this scheme. For example, a study could be carried out on the feeding temperature of the feed and the solvent. The variation of the temperature would modify the solubility equilibriums, therefore the quantity of solvent needed. The reduction of the solvent flow rate may require only one column to perform the liquid-liquid extraction. Furthermore, the sizing of the extraction column was done roughly and just a few data were available. More precise sizing of this column and the use of a column with a different technology could be studied.

Furthermore, both the ELL scheme and the Diaz scheme resulted in the production of a more concentrated IBEA. Currently, the classical scheme and the Mikitenko scheme involve separating the alcohols and subsequently eliminating the water from the isopropanol-water azeotrope. Given the low concentrations of water in the streams produced by the ELL and Diaz schemes, it might be interesting to check the possibility of eliminating the water before proceeding with the separation of the various alcohols. This, therefore, necessitates a more in-depth study of dehydration techniques. In particular, it is necessary to study dehydration techniques such as adsorption and pervaporation. This very last is presented as the most promising dehydration technique. However, little data is available for sizing and evaluating this technology.

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