Application of Composition Interval Diagram for Cost Minimization in Mass Exchanger Networks

A.O.Akeem[1] Ismaila I. Paiko[2], U. D. Sule[2], N.A. Jipo[2]

[1]Department of Chemical Engineering, Federal University of Technology, Minna
[2]Department of Chemical Engineering, Federal Polytechnic Bida
Ismaeel.xcal@gmail.com

Abstract : This article presents a technique of reducing the Total Annual Cost (TAC) in mass exchange network synthesis (MENS). The method can minimize the pollutants getting into the environment through selective transfer of such wastes from rich process stream to lean process stream. It also enables the product to be obtained in their pure form. The method was applied to two problems with the aim of reducing the total annual cost (TAC) of production. The results obtained in this study demonstrate that the approach adopted in this paper is capable of giving costs that are comparable with other techniques in literature.

Key words: Total annual cost, mass exchanger networks, process streams, wastes, transfer

1.0 INTRODUCTION

Mass exchange unit is a system of that can selectively transfer certain species from a set of rich streams to a set of lean streams. The notion of mass exchange network was first introduced by [6]. They exploited the analogy between heat transfer and mass transfer and developed methods based on Pinch Technology for targeting the minimum cost of mass separating agents required. This is analogous to the minimum utility target in a heat exchanger network. They also showed how to design mass exchange networks to meet these targets exactly. However, until now, it was recommended to use the minimum number of units in an attempt to minimize the capital cost. However, this does not necessarily give a minimum cost. The absence of capital cost targets also meant that complete screening of design options could not be achieved by targeting alone [8].

1.2 Problem Statement

Stated the task of MENS as follows:
Given a number N_R of rich streams and a number N_S of MSAs (lean streams), it is desired to synthesize a cost-effective network of mass exchangers that can preferentially transfer certain species from the rich streams to the MSAs. Given also are the flowrate of each rich stream, G_i, its supply (inlet) composition, y^s_i, and its target (outlet) composition, y^t_i, where i = 1, 2,..., N_R. In addition, the supply and target compositions, x^s_j and x^t_j, are given for each MSA where j = 1, 2, ... ,N_S. The mass transfer equilibrium relations are also given for each MSA. The flowrate of each MSA is unknown and is to determined as part of the synthesis task. The candidate MSAs (lean streams) can be classified into N_{SP}

process MSAs and NSE external MSAs (where $N_{SP} + N_{SE}$ = N_S). The process MSAs already exist on the plant site and can be used for a low cost (often virtually free). The flowrate of each process MSA, L_J, is bounded by its availability in the plant and may not exceed a value of L^C_J the other hand, the external MSAs can be purchased from the market and their flowrates are to be determined by economic considerations.
The target composition of the transferred species in each MSA is determined by the specific circumstances of the application. The nature of such circumstances may be physical (e.g. maximum solubility), technical, (e.g., to avoid excessive corrosion, viscosity or fouling), environmental (e.g., to comply with environmental regulations), safety (e.g., to stay away from flammability limits) or economic (e.g., to optimise the cost of subsequent MSA regeneration)

2.0 METHODOLOGY

The methodolog adopted for the determination of minimum MSAs and cost is the use of comosition interval diagram of [6] and [7] where *y* is always the composition in the rich phase and *x* is always the composition of the lean stream. Also, G and *L* always refer to rich and lean stream flowrates.
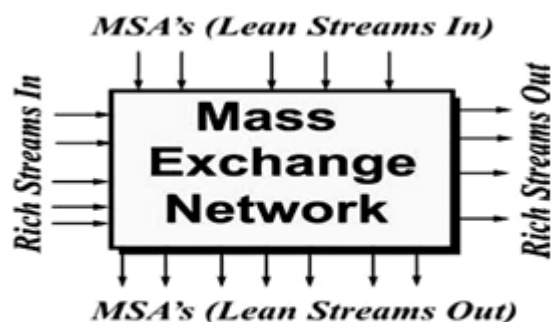

Figure 1: Mass Exchange Network [12].

2.1 Minimum MSA Cost Targets

The first task of targeting phase start by defining the quantitative relationships between the concentrations of all streams (process streams and MSAs). This tool established a one-to-one correspondence among the compositions of all streams for which mass transfer is thermodynamically feasible. By that way several composition scales (one for all the rich streams and one for each process MSA) are established and thermodynamic and other constraints are incorporate into the stream data [12]. If the relation between the process MSA

scales, x_j, and the rich stream concentration scale, y is linear this can be expressed as :

$$y = m_j x_j \qquad (1)$$

In order to ensure feasible mass transfer throughout the networks (similar to ΔT_{min} used in HENS) a *minimum approach concentration (MAC)* for mass transfer, ε_j, have to be defined.

$$y = m_j(x_j + \varepsilon_j) \text{ Or } x_j = \frac{y}{m_j} - \varepsilon_j \qquad (2)$$

A more general form of the linear equilibrium expression given in Equation including the equilibrium constant b_j:

$$y = m_j(x_j + \varepsilon_j) + b_j \qquad (3)$$

2.2 Targeting phase-Minimum Number of Mass-Exchange Units

Another useful target in MENs synthesis is the theoretical minimum number of mass exchange units. This is done by the use of Euler's graph theory, which identifies the number of contaminant-rich process streams and MSAs [8]. For systems where the pinch divides the design in to two separate regions the minimum number of units is:

$$N_{units} = (N_R + N_S - 1)_{above pinch} + (N_R + N_S - 1)_{below pinch} \qquad (4)$$

This target attempts to minimise indirectly the capital cost of the network, since the cost of each mass exchanger is usually a function of the unit size [8]

3.0 The Composition Interval Diagram

Concentrations are sorted in ascending order to form the composition interval boundaries y_k^* (where k = 1, 2, 3,.). Once the composition intervals have been defined, then the process follows:

1. For a given concentration interval, k, the mass load of contaminant to be removed from each process stream i, within the interval, $m_{i,k}$ is calculated from equation below:

$$m_{i,k} = G_i[y_{k+1}^* - y_k^*] \qquad (5)$$

Where, y_{k+1}^* and y_k^* are the upper and lower interval boundaries and G_i is the capacity flowrate of process stream i. Then, the total mass load transferred, m_k, in interval k, is calculated as the sum of mass loads for each rich process stream i, in the interval, $m_{i,k}$:

$$m_{i,k} = (y_{k+1}^* - y_k^*)\Sigma_i \, G_i \qquad (6)$$

2. The cumulative mass load at the end of each interval is calculated knowing that the intervals in ascending order (i.e., at concentration-interval boundary k+1), by summing the mass loads, m_k, to the concentration-interval boundary k+1:

$$\Delta m_{k+1} = \Sigma_k \, m_k \qquad (7)$$

3. For a system with i process streams, column 1 contains the concentration interval boundaries, in ascending order or descending order; columns 2 ($i + 1$) represent each

process streams in the system with respect to their target and supply concentrations (also in ascending order or descending order according to y_i^{target} and y_i^{supply}); column $i + 2$ contains the mass load of contaminant transferred within each interval; and column $i + 3$ contains the cumulative mass load of the system for process streams.

4. The process-MSA data is generated in a similar manner. However, the mass load of contaminant transferred within each interval is calculated through equation below.

$$m_k = (y_{k+1}^* - y_k^*)\Sigma_j \left(\frac{L}{m}\right)_j \qquad (8)$$

Where y_{k+1}^* and y_k^* are the concentration-interval boundaries of interval k on the concentration scale associated with process streams and $\left[\frac{L}{m}\right]_j$ is the capacity flowrate of the jth process MSA.

5. The cumulative mass load column for process MSAs is then calculated in the same way as the cumulative mass load column for rich process streams.

To determine the minimum utility targets (external MSA duty) using the concept of the pinch once the composition interval diagram (CID) for a given system has been constructed [7]. Thus;

1. Within each concentration interval, the difference between the available mass load from process streams and the capacity of the process MSAs is evaluated to get the net mass load of contaminant to be transferred as

$$m_k = (y_{k+1}^* - y_k^*)\sum_i G_i - \sum_j L_j[x_{j,k+1}^* x_{j,k}^*]$$
$$= (y_{k+1}^* - y_k^*)\left\{\Sigma_i \, G_i - \Sigma_j \left[\frac{L}{m}\right]_j\right\} \qquad (9)$$

2. Cascade the net mass load to be removed starting with zero at the highest concentration-interval boundary (bottom). The most negative of the minimum value from the cascaded mass load column at the bottom concentration-interval boundary is placed in the final column of the CID. Again, the net mass load to be removed is cascaded starting with that value at the highest concentration-interval boundary (bottom right). Where zeros are found in this column, lies the pinch concentration. The minimum external MSA duty and the excess process-MSA capacity are found at the top and bottom of the last column, respectively.

3. 3.1 EXCHANGER COSTING

The TAC of a network mainly consists of its operating cost and capital cost. Given that the unit price of the lean stream j is known, c_j, and assume the operating cost of a MEN mainly depends on the cost of MSAs used, then the operating cost can be formulated as follows:

$$C_{operating} = \Sigma_j \, c_j L_j \qquad (10)$$

The capital cost another part of the TAC. For simplicity, it is assumed that the capital cost is a function of the mass exchangers which can be classified into two main categories:

stage-wise exchangers and continuous-contact exchangers [4].The most common types are plate and packed columns. For the plate columns, there capital costs are related to the number of plates and column size, which can be calculated by the Kremser equation as follows:

$$N = \frac{ln\left[\left(1-\frac{1}{A}\right)\left(\frac{y_{in}-m_j x_{in}-b_j}{y_{out}-m_j x_{in}-b_j}\right)+\frac{1}{A}\right]}{ln(A)} \qquad (11a)$$

For $A \neq 1$.

$$N = \frac{y_{in}-y_{out}}{y_{out}-m_j x_{in}-b_j} \qquad (11b)$$

For $A = 1$.

Where $A = \frac{L_j}{m_j G_i}$, y_{in}, y_{out}, x_{in} denote the inlet and outlet compositions of the corresponding component of the rich and lean streams passing through the mass exchanger. Then this type of capital cost can be expressed as follows;

$$C_{capital} = \Sigma_i \Sigma_j C_{ij} \times N_{ij} \qquad (12)$$

Where C_{ij} is annual cost of each column plate and its value depends on the mass exchanger's type and size.
The capital cost of packed columns can be calculated by the packed height of the ith rich stream and the jth lean stream match, and it is calculated by equation

$$H_{i,j} = HTU_{i,j} \times NTU_{i,j} \qquad (13)$$

and characterized by

$$NTU_y = \frac{y_i^{in}-y_i^{out}}{(y_i-y_i^*)_{log\ mean}} \qquad (14)$$

$$(y_i - y_i^*)_{log\ mean} = \frac{\left(y_i^{in}-m_j x_j^{out}-b_j\right)-\left(y_i^{out}-m_j x_j^{in}-b_j\right)}{ln\left(\frac{\left(y_i^{in}-m_j x_j^{out}-b_j\right)}{\left(y_i^{out}-m_j x_j^{in}-b_j\right)}\right)} \qquad (15)$$

If $C_{i,j}^{''}$ denotes the annual cost of the unit height, which is the function of the mass exchanger type, packed types, and size, then this type of capital cost can be calculated as follows:

$$C_{capital} = \Sigma_i \Sigma_j C_{i,j}^{''} \times H_{ij} \qquad (16)$$

So the formulation of the whole mathematical model from the analysis above, a model is built up to solve the design problems, so as to obtain the optimal MEN. The model takes the TAC as the objective, which is expressed as follows:

$$\Sigma_j C_j L_j + \Sigma_i \Sigma_j C_{ij} \times N_{ij} + \Sigma_i \Sigma_j C_{i,j}^{''} \times H_{ij} \qquad (17a)$$

$$TAC = C_{operating} + C_{capital} \qquad (17b)$$

4.0   CASE STUDIES AND DISCUSSION

This problem is adapted from [2]. It involves the simultaneous removal of Hydrogen Sulphide from two gas streams; Sour coke oven gas (COG) (R_1) and Tail gas (R_2). Where two MSAs are available: Ammonia (S_1), which is a process MSA and

Methanol (S_2), which is an external MSA. Stream data are given in the table below.

Table 1: Data for the streams of case study 1

Rich stream

Stream	G_i(kg/s)	y_i^{in}	y_i^{out}
R_1	0.9	0.07	0.0003
R_2	0.1	0.051	0.0001

Lean stream

Stream	L_j(kg/s)	x_j^{in}	x_j^{out}	m_j	b_j	C_j (\$.sec/kg.yr)
S1	2.3	0.0006	0.0310	1.45	0	117360
S2	∞	0.0002	0.0035	0.26	0	176040

The equilibrium solubility data for hydrogen sulphide in aqueous ammonia and methanol may be correlated by the following relations respectively:

Aqueous ammonia $\qquad y = 1.45x_1$

Methanol $\qquad y = 0.26x_2$

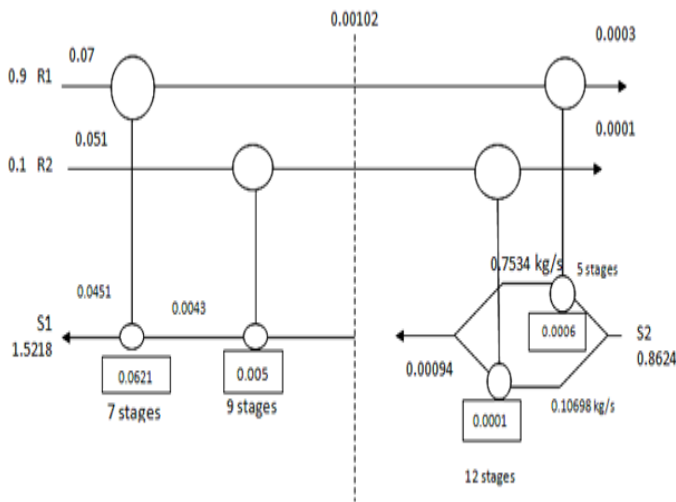Where j=1,2 corresponds to the aqueous ammonia and chilled methanol, respectively.
Perforated plate columns are considered for both solvent and the annualized investment cost of such a column is considered to be \$4552/yr (i.e cost per equilibrium stage per year) x Ns.

Table 2: CID including the minimum external MSA

S/N	Concentration Y*	R_1 (kg/s) 0.9	R_2 (kg/s) 0.1	Mass load (kg/s)	Cumulative mass load (kg/s)	S_1 (kg/s) $L_1 \leq 1.586$ m	Available capacity (kg/s)	Cumulative capacity (kg/s)	Net mass load (kg/s)	Cascade mass load (kg/s)	Adjusted mass load (kg/s)
1	0.0001		▲		0				0	-0.00209	0.00074
				0.00002				0	0.00002		
2	0.0003	▲			0.00002				0	-0.00211	0.00072
				0.00072				0	0.00072		
3	0.00102				0.00074				0	-0.00283	0.0000
				0.04408				0.06991	-0.02583		
4	0.0451				0.04482	▼		0.06991		0.023	0.02583
				0.00590				0	0.0059		
5	0.051				0.05072			0.06991		0.01710	0.01993
				0.01710				0	0.01710		
6	0.070				0.06782			0.06991		0	0.00283

Table 3: CID after reducing the capacity flowrate of process MSA

S/N	Concentration y^*	R_1 (kg/s) 0.9	R_2 (kg/s) 0.1	Mass load (kg/s)	Cumulative mass load (kg/s)	S_1 (kg/s) $L_1=1.5218$ m	Available capacity (kg/s)	Cumulative capacity (kg/s)	Net mass load (kg/s)	Cascade mass load (kg/s)	Adjusted mass load (kg/s)
1	0.0001				0			0		0.00074	0.00074
				0.00002			0		0.00002		
2	0.0003			0.00002				0		0.00072	0.00072
				0.00072			0		0.00072		
3	0.00102			0.00074				0		0	0.0000
				0.04408			0.06708		-0.023		
4	0.0451			0.04482				0.06708		0.023	0.023
				0.00590			0		0.0059		
5	0.051			0.05072				0.06708		0.01710	0.01710
				0.01710			0		0.01710		
6	0.070			0.06782				0.06708		0	0

Figure 2: Grid design for Coke Oven Gas.

$$C_{Total} = \$298{,}446 + \$150{,}216 = \$448{,}662$$

Table 4: comparison and Summary of TAC for case study 1

Method	Splits: rich/lean	No. of units	Total cost ($/yr$)	Diff (%)
Hyperstructure technique of Papalexandri et al (1994) [13]	0/1	3	917,880	113.61
Rich based IBMS of Isafiade (2008) [10]	0/0	4	530,471	23.45
T&SBS [2]	0/2	4	526,471	22.52
S&TBS (Type 1) [2]	0/2	4	524,244	22.00
S&TBS (Type 2) [2]	0/2	4	524,244	22.00
SBS of Azeez et al (2011) [1]	0/0	5	469,968	9.37
Present work	0/1	4	448,662	4.41
Lean Based IBMS of Isafiade (2008) [11]	0/2	4	446,840	3.99
Pinch technique of Hallale and Fraser (2000) [9]	0/1	5	431,613	0.44
'SWS' of Cheng and Huang (2005) [3]	0/2	4	429,700	0.00

Case study 2: An oil recycling plant

This problem is adapted from [7]. In an oil recycling plant, two types of waste oil are handled: gas oil and lube oil. The two streams are first deashed and demetallized. Next, atmospheric distillation is used to obtain light gases, gas oil, and a heavy product.

The heavy product is distilled under vacuum to yield lube oil. Both the gas oil and the lube oil should be further processed to attain desired properties. The gas oil is steam stripped to remove light and sulphur impurities, then hydrotreated. The lube oil is dewaxed/deasphalted using solvent extraction followed by steam stripping.
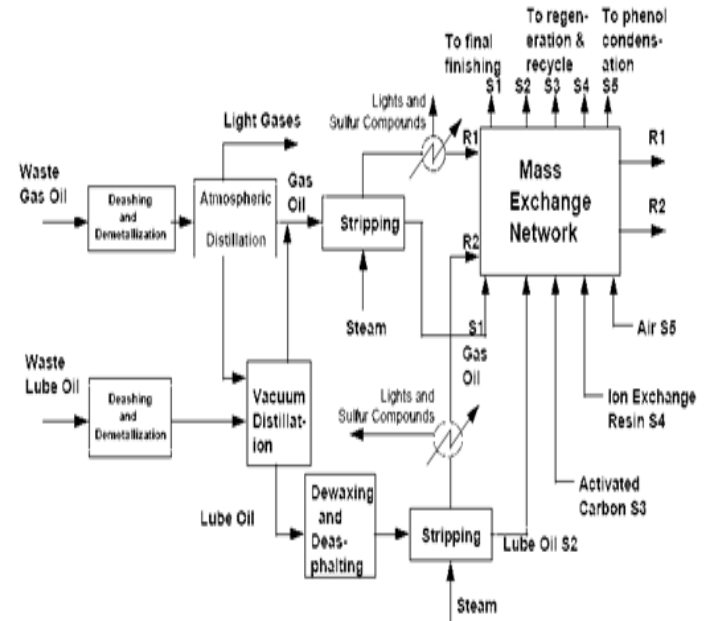
Figure 2: Schematic representation of an oil recycling plant [7]

The process has two main sources of waste water. These are the condensate streams from the steam strippers. The principal pollutant in both wastewater streams is phenol. Phenol is of concern primarily because of its toxicity, oxygen depletion, and turbidity. In addition, phenol can cause objectionable taste and odour in fish flesh and potable water

Table 5.1: Data of Waste Streams for the Dephenolization

Stream i	G_i (kg/s)	y_i^{supply}	y_i^{target}
R1	2.0	0.05	0.010
R2	1.0	0.030	0.006

Several techniques can be used to separate phenol. Solvent extraction using gas oil or lube oil (process MSAs: S1 and S2, respectively) is a potential option. Besides the purification of wastewater, the transfer of phenol to gas oil and lube oil is a useful process for the oils. Phenol tends to act as an oxidation inhibitor and serves to improve colour stability and reduce

sediment formation. The data for the waste streams and the process MSAs are given in Table.

Table 5.2: Data of Process MSAs for the Dephenolization

Stream j	L_j (kg/s)	x_j^{supply}	x_j^{target}	m_j	b_j	Cost ($/kg)
S1	5.0	0.005	0.015	2	0	0
S2	3.0	0.010	0.030	1.53	0	0
S3	∞	0.0013	0.015	0.71	0.001	0.01

Three external technologies are also considered for the removal of phenol. These processes include adsorption using activated carbon, S3, ion exchange using a polymeric resin, S4, and stripping using air, S5. In this paper we will consider only a S3 as an external MSA, which is available for purchase at an unlimited flow rate.

Using the corresponding concentration scales, the equilibrium data for the transfer of phenol to the jth lean stream is given by

$$y = m_j x_j$$

Thermodynamic and other constraints are incorporated into the stream data by including *a minimum approach concentration (MAC)* for mass transfer, ε_j. In order for mass transfer to occur from a process stream, at concentration y, to MSA j, the concentration of the contaminant in the MSA, x_j, must be ε_j below that defined in the equivalent rich stream concentration y that just allows mass transfer to a MSA at a concentration x_j.

A minimum allowable composition difference, $\varepsilon_j = 0.001(kg\ Phenol/kg\ MSA)$ is taken .

Table 6: CID including the minimum external MSA duty

S/N	Concentration Y"	R_1 2kg /s	$R_2$1 Kg/s	Mass load (kg/s)	Cumulative mass load (kg/s)	S_1 2.5 kg/s	S_2 1.691 kg/s	Available capacity (kg/s)	Cumulative capacity (kg/s)	Net mass load (kg/s)	Cascade mass load (kg/s)	Adjusted mass load (kg/s)
1	0.00600	▲			0				0	-0.00600		0.01242
				0.00400				0			0.00400	
2	0.01000	▲			0.00400				0	-0.01000		0.00842
				0.00600				0			0.00600	
3	0.01200				0.01000				0	-0.01600		0.00242
				0.01449				0.01208			0.00242	
4	0.01683				0.02449				0.01208	-0.01842		0
				0.03951				0.05875			-0.01924	
5	0.03000				0.06400				0.07082	0.00082		0.01924
				0.00400				0.00892			-0.00492	
6	0.03200				0.06800	▼			0.07975	0.00575		0.02416
				0.03086				0.03025			0.00061	
7	0.04743				0.09886		▼		0.11000	0.00514		0.02356
				0.00514				0			0.00514	
8	0.05000				0.10400				0.11000	0		0.01842

5.0
5.1
5.2
5.3
5.4
5.5
5.6

Table 7: CID after reducing the capacity flowrate of process MSA S₂ to eliminate the excess capacity of the process MSAs

S/N	Concentration Y"	R_1 2kg /s	$R_2$1 Kg/s	Mass load (kg/s)	Cumulative mass load (kg/s)	S_1 2.5 kg/s	S_2 1.359 kg/s	Available capacity (kg/s)	Cumulative capacity (kg/s)	Net mass load (kg/s)	Cascade mass load (kg/s)	Adjusted mass load (kg/s)
1	0.00600	▲			0				0		0.01242	0.01242
				0.00400				0			0.00400	
2	0.01000	▲			0.00400				0		0.00842	0.00842
				0.00600				0			0.00600	
3	0.01200				0.01000				0		0.00242	0.00242
				0.01449				0.01208			0.00242	
4	0.01683				0.02449				0.01208		0	0
				0.03951				0.05082			-0.01131	
5	0.03000				0.06400				0.06290		0.01131	0.01131
				0.00400				0.00772			-0.00372	
6	0.03200				0.06800	▼			0.07062		0.01503	0.01503
				0.03086				0.02097			0.00989	
7	0.04743				0.09886		▼		0.09159		0.00514	0.00514
				0.00514				0			0.00514	
8	0.05000				0.10400				0.09159		0	0

The number of stages is calculated using Kremser equation:

$$N = \frac{ln\left[\left(1 - \frac{1}{A}\right)\left(\frac{y_{in} - m_j x_{in} - b_j}{y_{out} - m_j x_{in} - b_j}\right) + \frac{1}{A}\right]}{ln(A)}$$

For $A \neq 1$.

$$N = \frac{y_{in} - y_{out}}{y_{out} - m_j x_{in} - b_j}$$

For $A = 1$.

The total number of stages $\sum_{i,j} N_{ij} = 24 stages$.

$$C_{Total} = 261,012 + 109,248 = \$370,260/yr$$

The table below shows the comparison of this work with those that have solved the same problem previously.

Table 8: comparison and Summary of TAC for case study 2

Method	Splits: rich/lean	No. of units	Total cost ($/yr)	Diff (%)
S&TBS of Azeez et al, (2012) [2]	0/1	5	421.147	26.85
Present Work	0/2	6	370,260	11.53
Lean based IBMS of Isafiade and Fraser(2008) [10]	0/0	5	358292	7.92
Pinch technique of Hallale and Fraser (2000)[9]	0/2	7	345,416	4.04
SBS of Azeez et al, (2012) [2]	0/0	6	339,579	2.28
Rich based IBMS of Isafiade and Fraser (2008) [12]	0/0	6	338,168	1.80
First option of insight based technique of Comeaux (2000) [5]	0/2	7	333.300	0.39
Second option of insight based technique of Comeaux (2000)[5]	0/2	8	332.000	0.00

CONCLUSIONS

The results demonstrate that it is a simplified and convenient way of optimization for the synthesis of MEN. Comparison of the results obtained in this paper with those of previous researchers shows that CID technique is also a practicable way of synthesizing cost effective MEN. This is because the technique produces results that fall within the range of those of other researchers.

REFERENCES

i. Azeez, O.S. (2011). Supply and target-based superstructure synthesis of heat and mass exchange networks, Ph.D. Thesis, Chemical Engineering Department, University of Cape Town, South Africa.

ii. Azeez, O. S., Isafiade, A.J and Fraser.D.M. (2012). Supply and target based superstructure synthesis of heat and mass exchanger network. Chem. Eng. Res. Des .IChemE, pp 266-287.

iii. Cheng-Liang, C. and Ping-sung, H. (2005). Simultaneous synthesis of mass exchange network for waste minimization. Retrieved from Elsevier, 1561-1576.

iv. Chen Li, Gao. Z., Du J. and Yao P. (2007) A Simultaneous Optimization Method for the Structure and Composition Differences of a Mass Exchange Network. Chin. J. Chem. Eng., $15(2)$ 254—261.

v. Comeaux, R. G. (2000). Synthesis of mass exchange networks with minimum total cost. Manchester, UMIST. MPhil Thesis.

vi. EI-Halwagi, M. M. and Manousiouthakis, V. (1989). Synthesis of Mass Exchange Networks, Retrieved from A.I.C.h.E. J., $35(8)$, 1233-1244.

vii. EI-Halwagi, M. M. (1997). Pollution Prevention through Process Integration: Systematic Design Tools, Academic Press, San Diego.

viii. Hallale, N. (1998). Capital cost targets for the optimum synthesis of mass exchange networks, Ph.D. Thesis, Chemical Engineering Department, University of Cape Town, Cape Town, South Africa.

ix. Hallale, N. and Fraser, D.M. (2000). Capital and total cost targets for mass exchange networks. Part 1: Simple capital cost models, Comp. Chem. Eng., 23:1661 – 1679.

x. Isafiade, A. J. and Fraser, D.M. (2008). Interval based MINLP superstructure synthesis of heat exchange networks. Chem Eng Res Des $86(3)$:245-257.

xi. Isafiade, A. J. and Fraser, D.M. (2008). Interval based MINLP superstructure synthesis of Mass exchange networks. Chem Eng Res Des $86(8)$:909-924.

xii. Rašković, P. (2007). Water Pinch Technology for Designing Wastewater Reduction and Water Conservation Systems. Faculty of Technology Engineering, Leskovac, Serbia.

xiii. Papalexandri, K. P., Pistikopoulos, E. N., and Floudas, C. A. (1994). Mass Exchange Networks for Waste Minimisation: A Simultaneous Approach, Trans IChemE (Part A), 72, 279-294.