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A MODEL TO OPTIMIZE A CRYOGENIC SEPARATION SYSTEM WITH INNOVATIVE HYBRID DISTILLATION MEMBRANE IN SERIES

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Abstract

The study developed a model for hybrid distillation membrane that optimized the energy usage in binary cryogenic separation. In separating air mixture components, distillation columns are often used and these columns consumes very large energy during operation. From analysis, the exergy efficiency and heat transfer of a cryogenic air separation double diabatic column in the distillation process is greater than that of the conventional adiabatic double columns. There is need to discover alternative separation technologies with lesser energy consumption such as membrane separation. However, use of membrane separation alone is constrained to small separation due to large areas needed with the attendant costs. Thus, a hybrid system comprising of distillation column and membrane separator offers the best compromise. To optimize the process, the overhead product from the distillation column was fed to a membrane separator in series in this study.

A mathematical Model approach was proposed to improve a hybrid separation system comprising of a distillation column and a Serial novel membrane separation unit. First, a model was introduced that validated if the hybrid system could optimize the process and the order of magnitude of energy that can be expected. Secondly, a superstructure optimization approach was applied and it uses rigorous models for both the column and the membrane. A process simulator, excel and visual basic were used to solve and program the equations. The result showed that significant energy savings was achieved using a novel hybrid separation system with a material membrane.

Keywords: *Cryogenic distillation; Separation; Petrochemical industry; Hybrid separation system; Membrane separation unit*

1. Introduction

The most common operation in process industries and distillation is separation of mixtures (liquids / fluids) into various components and achieving it is an important oil refining operation. The demand for clean products, as well as the need for processing efficiency, allowed further research on the technology of distillation. Since the 1960s, a new technology has been developed that uses the process of synthesis of the rapid-separation membrane [1]. These membrane separations are widely applied to various conventionally difficult separation operations. The ultimate membrane structure is a combination of phase separation and a variable mass transfer of production conditions to produce membranes with different separation characteristics.

Currently separation of light binary hydrocarbon mixtures (ethylene-ethane/propylene-propane) used as petrochemical feedstocks is performed almost exclusively by cryogenic distillation. It is a known fact that energy consumption in conventional distillation processes is quite significant since the process is thermally driven and has low energy efficiencies. This is even more pronounced in cryogenic systems where the mixtures have close relative volatilities (near unity), thus making separation difficult thereby necessitating the use of large number of theoretical plates/stages, with the attendant increased energy consumptions [2].

However, use of membrane separation alone is constrained to small separation due to large areas needed with the attendant costs. Thus, a hybrid system comprising of distillation column and membrane separator offers the best compromise [3].

In Nigeria, most of the existing plant utilizes distillation column only for the separation of light hydrocarbon such as ethylene and ethane separations which in turn requires so much energy. However, because of inherent limitations in each method, there is a need to find the best configuration for the hybrid system that will minimize the costs/energy spending or maximize energy savings, hence this study. This study proposed a novel distillation membrane hybrid that will optimize energy usage in binary super-fractionation/cryogenic separations while still achieving the same desired degree of purity.

2. Theory/Literature

The technology, Cryogenic air separation has been applied successfully over the years in providing oxygen in gasification of some feedstocks (hydrocarbons) in generating synthesized gas for fuel production and other products [4]. In the hydrocarbon downstream processing, demands have been made by different quarters to optimize the efficiency and cost of the process by introducing and developing an oxygen production process unit in the stream [4].

Burdyny and Henning [5] established that in the combustion chamber of oxy-fuel combustion process, there is need to separate oxygen from air on a huge scale. They studied the use of O_2/N_2 permeable membrane to develop air with high quantity of oxygen. It was observed that the vacuum pump applied in drawing air has the ability to reduce the required energy from the current process in-use. Also the proposed hybrid system can be profitable in small to medium scale application. But, it will not be very effective in large scale because of the decreased irreversibilities in the cryogenic process at large scale.

Li *et al.*, [6] analyzed the mixture of CO_2/H_2 and CO_2 transition phase characteristic. They adopted two stages of refrigeration, compression, separation and optimum recovery of cryogenic energy; which reduced the refrigeration operation of the system. From the experimental analysis, it was observed that the proposed cryogenic liquefaction using CO_2 and two stages separation was effective in liquid CO_2 separation from gas systems where CO_2 concentration are huge. This is an opportunity to reduce CO_2 significantly since it's largely blamed for global warming [7].

Researchers have tried to develop and design a model that will simulate the cryogenic separation process, this resulted in a rigorous and complex equations. Zhu *et al.*, [8] simulated a cryogenic separation process using a multi scenario approach. The initial result was a non-linear equation with multiple variables. With the aid of a computer program, the unknown was resolved and applied. The study concluded that the proposed approach was more conservative.

In 1999, Tessendorf *et al.* [11] simulated and modeled an optimized gas separation system that is membrane-based. The model was designed to simulate multicomponent mixtures and consider the drop in pressure.

In separating air mixture components, distillation columns are often used. These columns consumes very large energy during operation. Rizk *et al.*, [9] analyzed the energy consumption of a cryogenic air separation distillation column and concluded that, the exergy efficiency and heat transfer of the double diabatic column in the distillation process is greater than that of the conventional adiabatic double columns.

3. Methodology

This study was limited to a single distillation column, single vapor-liquid-equilibrium (VLE) membrane hybrid in series as shown in the figure 1. The fluid leaving the condenser are returned into the column as reflux and the remaining feed are pumped into the membrane separator. The major task is to determine which combinations of process / design parameters between the two units that will optimize the energy.

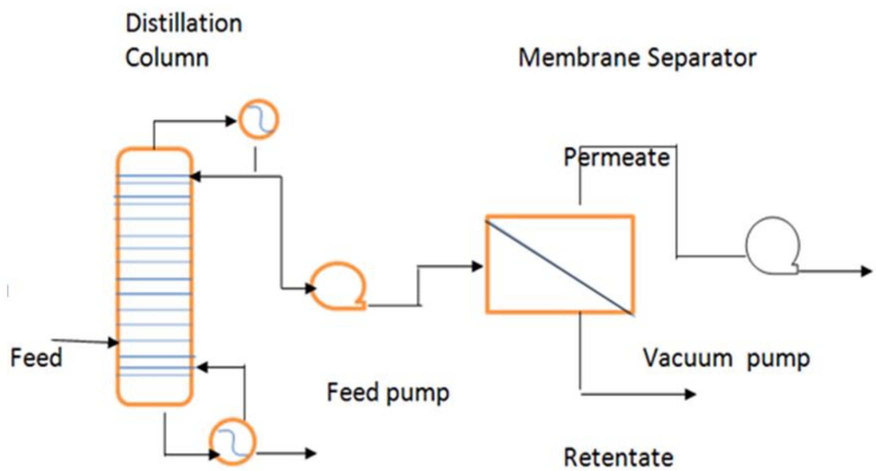

Figure 1. Distillation-Membrane Hybrid System

3.1. Developing the models

In developing the model for the system, the framework adopted was as follow:

- First, a method was adopted to test the viability of the configuration and to specify the process/design parameters that will serve as an energy saving hybrid (by comparing the total energy spending with the pure conventional distillation method).
- Once the potentiality was established, then rigorous mathematical process according to Zhu *et al.*, [8] and Rizk *et al.*, [9] were deployed in this case to determine the actual values.

For the first step/ method, the number of stages for the distillation column to function was determined by the Fenske-Underwood-Gilliland Correlations. In this approach, Fenske's equation was used to calculate *N*, which is the number of plates required to make a specified separation at total reflux, i.e., the minimum value of N_{min}.

$$N_{min} = \frac{log\left[\left(\frac{X_d}{1-X_d}\right)\left(\frac{1-X_b}{X_b}\right)\right]}{log\alpha_{avg}} \quad (1)$$

where, N_{min} is the minimum number of theoretical plates required at total reflux (including the reboiler), X_d is the mole fraction of more volatile component in the overhead distillate, X_b is the mole fraction of more volatile component in the bottoms, and α_{avg} is the average relative volatility of the more volatile component to the less volatile component.

Underwood's equations was used to estimate the minimum-reflux ratio R_m or R_{min}. The empirical correlation of Gilliland was applied to determine the actual *N* for any specified *R* or actual *R* for any specified *N.*

Molokanov *et al.*, [10] developed equation that satisfies the end points and fits the Gilliland equation (1940) curve reasonably well. The final model was;

$$\frac{(N-N_{min})}{N+1} = 1-\exp\left[\left(\frac{1+54.4(R-R_{min})/(R+1)}{11+117.2(R-R_{min})/(R+1)}\right)\left(\frac{(R-R_{min})/(R+1)-1}{[(R-R_{min})/(R+1)]^{0.5}}\right)\right]$$

If, N_m=N_{min}, the minimum number of stages needed (implying total reflux) was given by:

$$N_{min} = \frac{log[(x_{LK}/x_{HK})_D(x_{HK}/x_{LK})_B]}{\log\alpha} \quad (2)$$

where, N_{min} is the minimum number of stages, *x* is mole fraction, mole percent, or actual number of moles, *α* is relative volatility of the light key (in this case ethylene) with respect to the heavy key (in this case ethane), and the subscripts *LK*, *HK*, *D*, and *B* refer to light key, heavy key, overhead product or distillate.

It should also be noted that, as the number of stages is decreasing, the molar feed to the membrane, N_i, which is by implication the mole fraction, x_i increases. Hence, more feed pressure requirement which implies more power consumption in the membrane. The algorithm can be visualized in the table 1 below.

Table 1. The study algorithm

No of Stages, i	Reflux ratio for I stages, $R_i = f(i)$	$L_i=F(R_i)$	Heat consumption by distillation column, $H_c = F(R_i)$	$P_o = f(L_i)$	Heat consumption by membrane separator, $H_m = f(P_0)$	Total heat requirement $H_t = H_c + H_m$
N	R_N	$L_{i,N}$	$H_{c,N}$	0	0	$H_{c,N}$
N-1	R_{N-1}	$L_{i,N-1}$	$H_{c,N-1}$	$P_{o,N-1}$	$H_{m,N-1}$	$H_{c,N-1} + H_{m,N-1}$
N-2	R_{N-2}	$L_{i,N-2}$	$H_{c,N-2}$	$P_{o,N-2}$	$H_{m,N-2}$	$H_{c,N-2} + H_{m,N-2}$
: .		: .	: .	: .	: .	: .
2	R_2	$L_{i,2}$	$H_{c,2}$	$P_{o,2}$	$H_{m,2}$	$H_{c,2} + H_{m,2}$
1	R_1	$L_{i,1}$	$H_{c,1}$	$P_{o,1}$	$H_{m,1}$	$H_{c,1} + H_{m,1}$
0	0	0	0	P_o	$H_{m,0}$	$H_{m,0}$

Plots of the total energy requirement as a function of the number of stages and the membrane feed pressure to determine the optimum can now be made**.** Once it is seen that there is an energy savings in the serial hybrid configuration, rigorous simulations which is the main modeling process can now be implemented; this will determine the actual values using Sorel and Lewis-Matheson algorithm for the distillation column. For the membrane separator, solution thermodynamics involving activity/fugacity coefficients/Henry's Law and Ficks' diffusion models are applied for the actual (non-ideal) system. The results obtained will be compared with the previous works for validation.

4. Results and discussion

The underlying principle is energy optimization (analogous to cost optimization). The task is to determine the serial hybrid combination, that is, the number of column stages and the membrane area/ feed pressures that will give an overall minimum energy while achieving the same required degree of purity / separation.

By incorporating a membrane in series to draw the overhead distillate, the number of theoretical stages will obviously be reduced, since membrane will supplement the separation. This translates to reduced energy spending in the distillation column but will increase throughput to the membrane which implies increased feed pressure; hence increased energy spending in the membrane. Thus in the serial hybrid system, the more the number of stages is reduced, the more the energy reduction in the column but the higher the throughput and hence; an increased energy requirement on the membrane (Fig. 2). To determine the actual number of stages and the corresponding total energy required for the hybrid arrangement, we fit a model to the data and optimize.

To fit a 4th Order polynomial to the data: Y = a0 + a1 X + a2 X^2 + a3 X^3 + a4 X^4: by regression analysis (least-square method), the resulting matrix is:

Table 2. Regression analysis and the proposed model

69	2415	111895	5832225	3.24E+08	a0 = 2.6E+08
2415	111895	5832225	324249331	1.88E+10	a1 = 9.14E+09
111895	5832225	3.24E+08	18777820425	1.12E+12	a2 = 4.29E+11
5832225	324249331	1.88E+10	1.11851E+12	6.8E+13	a3 = 2.26E+13
324249331	1.8778E+10	1.12E+12	6.80109E+13	4.2E+15	a4 = 1.27E+15
Solving: Y = 4455647 + -90510.82 X + 3344.308 X^2 + -54.23164 X^3 + 0.35059 X^4					

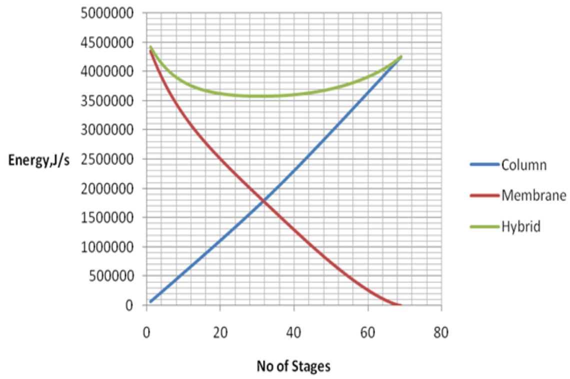

Fig. 2. Optimal energy consumption in a column-membrane hybrid

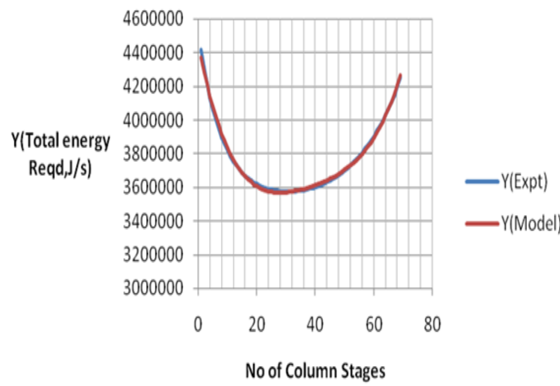

Figure 3. Total energy required vs column stages for a column-membrane hybrid confi-guration

To validate the model results with the experimental data, the correlation coefficient, R was calculated for the regression. It gave correlation coefficient; R = 0.9983742. Generally, R = 0.95 corresponds to 95% statistical confidence interval and it is usually accepted; but for high accuracy in engineering analyses, R = 0.99 is usually accepted and is adopted in this case.

Table 3. Validation of the model using field data

X	Y(EXPT.)	Y(MODEL)	X	Y(EXPT.)	Y(MODEL)
1	4415508.93	4368427	16	3669512.68	3664460
2	4309260.33	4287575	17	3654205.26	3646310
3	4216328.75	4212778	18	3640806.14	3630533
4	4134962.78	4143732	19	3629099.88	3616951
5	4063654.27	4080141	20	3618913.16	3605395
6	4000599.28	4021718	21	3610085.8	3595704
7	3945523.44	3968183	22	3602481.8	3587723
8	3896965.4	3919266	23	3595994.97	3581310
9	3854319.49	3874704	24	3590522.91	3576328
10	3816844.4	3834244	25	3585983.63	3572649
11	3783898.87	3797640	26	3582302.39	3570154
12	3754811.14	3764655	27	3579419.71	3568732
13	3729244.44	3735061	28	3577282.74	3568281
14	3706731.51	3708637	29	3575850.12	3568707
15	3686922.59	3685171	30	3575086.98	3569923

The total number of stages for the column and energy required for the field and simulated process are presented in figure 3.

Thus the required model is:

$Y = 4455647 + -90510.82\,X + 3344.308\,X^2 + -54.23164\,X^3 + 0.35059\,X^4$

$dY/dX = -90510.82 + 6688.616X + -162.6949X^2 + 1.40236X^3$

Optimizing the Model

The Newton's gradient method was applied in this case, which is given as:

$$X_{n+1} = X_n - {}^{(dY(X_n)/dX)}\!\big/_{Y(X_n)} \qquad (3)$$

Table 4. The convergence scheme (showing the first and the last 10 iterations)

Iteration Number	X_n	$Y[X_n]$	$(dY[X_n]/dx)$	Solution
1	100	9675010	353761.6875	99.96343231
2	99.96343231	9662084	353168.875	99.92687988
3	99.92687988	9649186	352577	99.89034271
4	99.89034271	9636314	351986.0938	99.85381317
5	99.85381317	9623467	351395.9688	99.81729889
6	99.81729889	9610647	350806.7813	99.78079987
7	99.78079987	9597854	350218.5313	99.74430847
8	99.74430847	9585084	349631.0938	99.70783234
9	99.70783234	9572342	349044.5938	99.67137146
10	99.67137146	9559626	348459	99.63491821
:	:	:	:	:
43395	28.0013752	3568280.75	3.419129372	28.00137329
43396	28.00137329	3568280.75	3.417458773	28.00137138
43397	28.00137138	3568280.75	3.415787935	28.00136948
43398	28.00136948	3568280.75	3.414117336	28.00136757
43399	28.00136757	3568280.75	3.412446499	28.00136566
43400	28.00136566	3568280.75	3.4107759	28.00136375
43401	28.00136375	3568280.75	3.409105301	28.00136185
43402	28.00136185	3568280.75	3.407434464	28.00135994
43403	28.00135994	3568280.75	3.405763865	28.00135803
43404	28.00135803	3568280.75	3.404093027	28.00135612

One of the ways to optimize the converging point is by changing the initial starting point to a lower one, the convergence scheme is:

Table 5. The convergence scheme for lower value as starting point (showing the first and the last 10 iterations)

Iteration Number	X_n	$Y[X_n]$	$(dY[X_n]/dx)$	Solution
1	1	4368426.5	-83983.5	1.019225121
2	1.019225121	4366813	-83861.14063	1.03842926
3	1.03842926	4365204	-83739.03906	1.057612538
4	1.057612538	4363598.5	-83617.17969	1.076774955
5	1.076774955	4361997.5	-83495.57031	1.09591651
6	1.09591651	4360400.5	-83374.21094	1.115037322
7	1.115037322	4358807.5	-83253.10156	1.134137273
8	1.134137273	4357218.5	-83132.23438	1.153216481
9	1.153216481	4355633.5	-83011.61719	1.172274947
10	1.172274947	4354052.5	-82891.24219	1.191312671
:	:	:	:	:
31555	27.99357224	3568280.75	-3.418437481	27.99357414
31556	27.99357414	3568280.75	-3.416765451	27.99357605

Iteration Number	X_n	$Y[X_n]$	$(dY[X_n]/dx)$	Solution
31557	27.99357605	3568280.75	-3.415093422	27.99357796
31558	27.99357796	3568280.75	-3.413421392	27.99357986
31559	27.99357986	3568280.75	-3.411749363	27.99358177
31560	27.99358177	3568280.75	-3.410077333	27.99358368
31561	27.99358368	3568280.75	-3.408405304	27.99358559
31562	27.99358559	3568280.75	-3.406733274	27.99358749
31563	27.99358749	3568280.75	-3.405061245	27.9935894
31564	27.9935894	3568280.75	-3.403389215	27.99359131

The observation from the iterations in tables 4 and 5 was that for the lower and higher starting points, there must be a converging point. Thus, implying one optimum point which occurred in this case at 28 column stages, with a corresponding total energy spending of 3568280 J/S.

5. Conclusion

In this paper, it has been shown through the simulation of the model developed that a distillation column-membrane separator hybrid system, offers a better advantage in terms of energy savings than individual units in the purification of light hydrocarbon mixtures. By incurporating a membrane in series to draw the overhead distillate, the number of theoretical stages was obviously reduced, since the membrane supplemented in the separation operation. This was what translated to reduction in energy spending in the distillation column but increased throughput to the membrane.

The model simulation results was validated with experimental data and the correlation coefficient, R calculated for the regression gave 0.9983 which was adopted for this study. The Newton's gradient method was used to optimize the Model and after the iterations using both lower and higher starting values; the optimum point occurred at 28 column stages with a corresponding total energy spending of 3568280 J/S.

From the foregone analysis using this study, it has been shown that using a novel column-membrane hybrid configuration consumes lesser energy than using individual units alone to achieve the same degree of purification, thus more economical.

References

[1] Lacey RE. In Handbook of Separation Techniques for Chemical Engineers, SCHWEITZER, P. A. (ed.) 2nd edn. McGraw-Hill, New York, 1988.
[2] Steinigeweg S and Gmehling J. Transesterification processes by combination of reactive distillation and pervaporation. Chemical Engineering and Processing, 1992; 43, 447 - 456.
[3] Kookos IK. Optimal Design of Membrane/Distillation column Hybrid Processes. Industrial & Engineering Chemistry Research, 2003; 42, 1731-1738.
[4] Smith AR and Klosek J. A review of air separation technologies and their integration with energy conversion processes. Fuel Processing Technology, 2001; 70(2): 115-134.
[5] Burdyny T and Struchtrup H. Hybrid Membrane/Cryogenic Separation of Oxygen from air for use in the Oxy-Fuel Process. Energy, 2010; 35(5): 1884 – 1897.
[6] Xu G, Li L, Yang Y, Tian L, Liu T and Zhang Ki. A novel CO_2 cryogenic liquefaction and separation system. Energy, 2012; 42(1): 522-529.
[7] Zangareh KE., Shafeen A and Salvador C. CO_2 Capture and Development of an Advanced Pilot-Scale Cryogenic Separation and Compression Unit. Energy Procedia, 2009; 1(1): 247-252.
[8] Zhu Y, Legg S and Laird CD. Optimal design of cryogenic air separation columns under uncertainty. Computers & Chemical Engineering, 2010, 34(9): 1377-1384.
[9] Rizk J, Nemer M and Clodic D. A real column design exergy optimization of a cryogenic air separation unit. Energy, 2012; 37(1): 417-429.

[10] Molokanov YK, KorablinaTP, Mazurina NI, Nikiforov GA. An approximation method for calculating the basic parameters of multicomponent fraction. Int. Chem. Eng., 1972; 12(2), 209-212.

[11] Tessendorf S, Gani R, Michelsen ML. Modeling, simulation and optimization of membrane-based gas separation systems. Chemical Engineering Science, 1999; 54(7): 943-955.

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