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A Novel approach on entropy production rate

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Abstract—We know diabatic distillation with heat exchangers in all trays increases the second law's energy efficiency compared to an adiabatic distillation. In this paper, our main purpose will be describing the entropy production rate in an adiabatic experiment with Water or Ethanol in columns using thermodynamic approach and analysis. We will find out that the entropy production rate in the diabatic column is less than the entropy production in the adiabatic column. Further on, we will analyze the reflux ratio showing that this ratio can be replaced with heat exchangers without infecting the diabatic distillation operation specially in the diabatic column.

Index Terms —Diabatic, Adiabatic, Entropy, Thermodynamic analysis, Reflux ratio.

1 INTRODUCTION

We understand that distillation is the most important and functional process used in chemical industries, also industries focusing on fluids such as alcohol, oil, gas, petroleum etc. Typically have more than one distillation column. With these distillation columns, the most important problem concerning us is the energy consumption. Therefore adiabatic column distillations are more applicable because they have a re-boiler at bottom, a condenser at the top trays and adiabatic trays. By adding heat exchangers to each tray, we can un-consider the adiabatic assumption, meaning a portion of the heat will be decreased or in other words, lost. These distillation columns having heat exchangers as explained are known as adiabatic columns.

Up to now, almost all publications on these types of distillation have been used on theoretical simulations assuming equilibrium conditions on all trays. There are two exceptions thou; Rivero and Rivero & Cachot & Le, whom published actual experimental data on diabatic distillations of ethanol and water . [123]

Also, the use of irreversible thermodynamics is relatively new to the study field of distillation and is still under development through research.The importance of this parameter is its effect on the correlation within the entropy production rates.

Therefore it is well suited for processes in which second law analysis and optimization are important. A diabatic distillation falls in this category, therefore irreversibility's can be considered in the transfer of heat and mass at equilibrium state in columns.

Many studies and research has been done on distillation columns, one of them being De Koejier research done at2003.In which they compared the entropy production in adiabatic and diabatic states through experiment held on water and ethanol

Distillation column's, holding the same conditions for both experiments. They managed to calculate the entropy production rate(with driving force?)

Another approach was done by Diego & et al which used non equilibrium equations and studied the second thermodynamic efficiency in adiabatic columns. Also many researches have been held focusing on energy optimization following distillation columns. For example Fredric studied on the binary distillation column, in which he tested a method to decrease the entropy production.

Demirel et al. shows distillation using heat and thermal difference is an important and applicable method. Also he shows that the work lost in separation systems which are based on irreversible process, mass and heat transfer directly generates entropy.

The main purpose of our work is the thermodynamics analysis of adiabatic and diabatic columns which Rivero and Koejier operated

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experimentally. Therefore in this paper, data from adiabatic and diabatic columns as published by Rivero and Rivero et al. will be used. (The managed to calculate entropy using driving force and experimentally).
We also will analyze the reflux ratio and find its effect on the diabatic column, which wasn't studied by Rivero or Koejier.

2 Experimental set up

The experimental column was a pilot-scale rectifying column and is a described in detail by Rivero (2003) which includes a complete flow-sheet and detail sketches. Rivero et al (1993) contains a brief summery on the topic. Thus only aspects relevant to our study purpose are mentioned in detail here. A scheme of single tray can be found in Fig.1 , and the design parameters are given in Fig.2.In Fig.1 we see that the coils are hanging 2 cm above the plate. In the experiment help, forty different temperature, 14 composition, 8 pressures, 13 flows and 10 valve positions were measured and considered. Of all these finding, the measured data mentioned in the table 1 is used in this paper. However the effect of heat exchanger and vapor mole fraction could not be measured directly, therefore they were calculated the molar and energy balances.

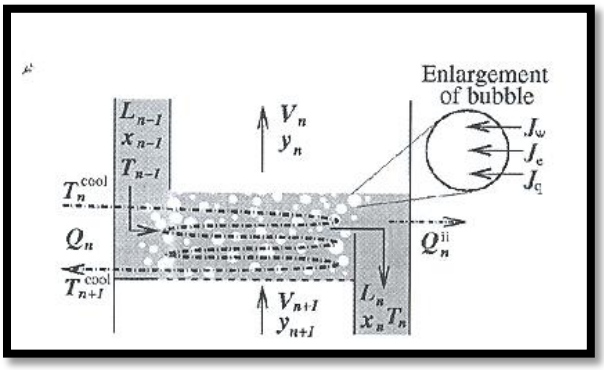

Fig.1 Scheme of a tray

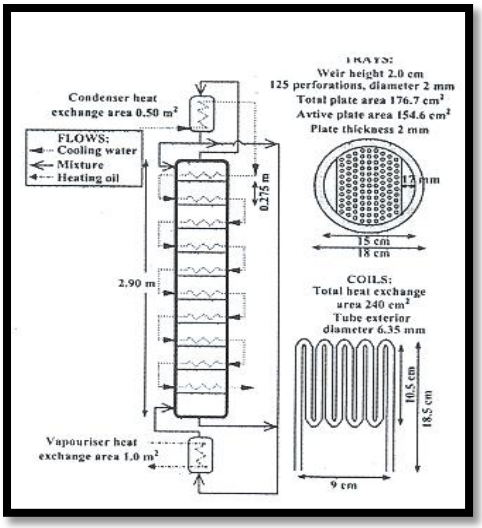

Fig.2 Schematic of a experimental set-up

Bearing in mind that heat exchanger vaporizing the feed is called the vaporizer; it is not a re-boiler since the distillation column contained only a single rectifying section.

Also we chose two runs (first and 9th run) of the total 68 held By Rivero (2003) to focus on. The first being adiabatic and the second adiabatic. The reason behind choosing this lies on the similarity of molar fraction and flows from the feed and its products which allow us to make comparisons. Thus the other runs were not as suitable for direct comparison.

3 Binary distillations

The simple distillation column has a single input feed, two products, a re- boiler and a condenser.

For the analysis of mass balance, column distillation must be divided in two sections: the rectifier and the stripper. The total mass balance around the system is shown in the Fig.3:

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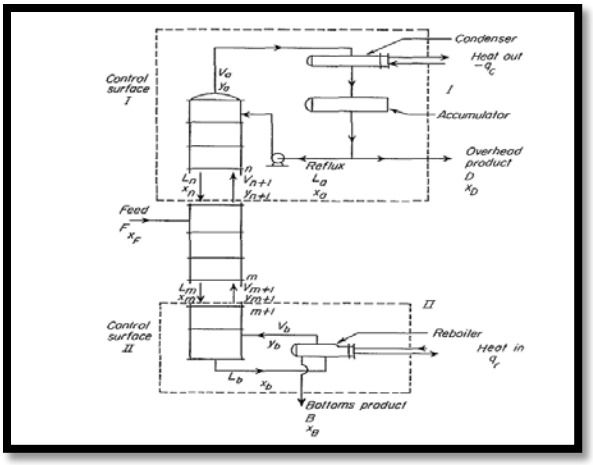

Fig.3 Total mass balance around the system

Total mass balance is:

$V_{n+1} = L_n + D$ (1)

Mass balance for each partial molar in the rectifier is:

$V_{n+1}\, y_{n+1,i} = L_n\, x_{n,I} + D\, x_{D,i}$ (2)

V&L are consecutively vapor and liquid.

With the assumption of $L_n = L$ and V_{n+1} it can be written:

$V = L + D$ (3)

Reflux ratio is written by (4):

$R = \frac{L}{D}$ (4)

The equation (3) and (4) substitute in (2) can be written as :

$Y_{n+1,i} = \frac{R}{1+R} x_{n,i} + \frac{1}{1+R} x_{D,i}$ (5)

Equation (5) can be plotted same as the following Figure. The slope of the line is $\frac{R}{1+R}$

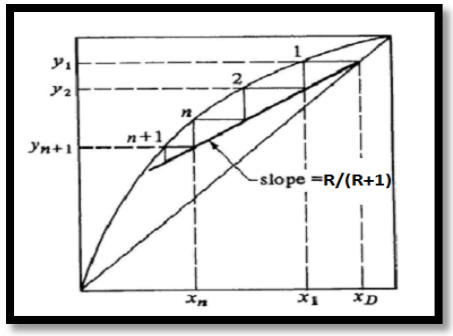

Fig.4 Operation line plot in the rectifier

Mass balance for each partial molar in the stripper is :

$L_m\, x_{m,i} = V_{m+1}\, y_{m+1,i} + B\, x_{B,i}$ (6)

With the assumption of $L_m = L$ and $V_{m+1} = V$ can be written :

$L = V + B$ (7)

$Y_{m+1} = \frac{L}{v} x_{n,i} - \frac{B}{V} x_{B,i}$ (8)

Equation (8) is plotted same as the following Figure . The slop line is $\frac{L}{V}$

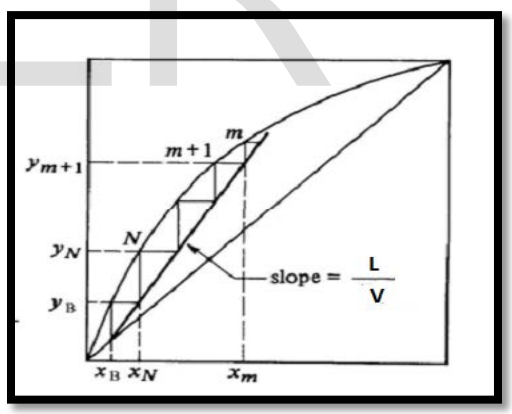

Fig.5 Operation line plot in the stripper

Reflux ration concept:

An important factor in each distillation column is the reflux ratio, so important that the distillation column cannot be analyzed without it. Thus the presence of this parameter is highlighted as extremely important.

We know that the feed is usually injected to the distillation column from beneath. The distillation being done, lighter parts are lifted to the top of the

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column. The reflux ratio is the section in the column which is transferred and cooled in the condenser and retuned back to the column. The reflux phenomena help where there are substances within the vapor which aren't distillated. This works as the fluid is being lifted to the top of the column, the unwanted substances inside the are returned to the lower trays of the distillation column. It's good to mention that in a diabatic distillation column R is zero.

There are 4 different approach methods for solving this case of problems:

1) The adiabatic column is analyzed using the temperature, pressure, feed and the condenser information at hand. With the conditions mentioned, R will be equal to 0.5 which has a great contrast with the adiabatic assumption in distillation column.
2) If the reflux ratio is small enough to be neglected so that there will be on reflux flow within the column. This is the assumption held in the diabatic distillation columns. In the case, R is taken to be 0.0001.
3) In order to decrease the heat from the condenser and to decrease the distillation rate, more heat is taken from the first tray.
4) The side steam method can be a suitable approach, however it is slightly difficult. Because in order for it to be done correctly, we have to ensure the equilibrium state is held in all trays. The analysis of the diabatic column and calculations of the entropy production and energy lost has been done using the second method.

4 The thermodynamic analysis

All equation used for steady state operation of the distillation column are MESH equations.

MESH abbreviates for the following words:

M: Mass equilibrium equations

E: Equilibrium equation that include dew point and bubble point

S: Summation of stoichiometric equations

H: Heat transfer equation

In this paper, we added two other words to the above list. We added two E's, first meaning entropy generation and the second meaning energy lost, making it MESHEE.

Fig.6 shows the total equilibrium of a distillation tower. This can be used for design purposes of distillation columns. In which a vapor stream flows from the bottom tray and a liquid phases fluid flows from the top tray into each part. These operations are held in each tray. Feed can be also been entered and the heat withdrawn in needed.

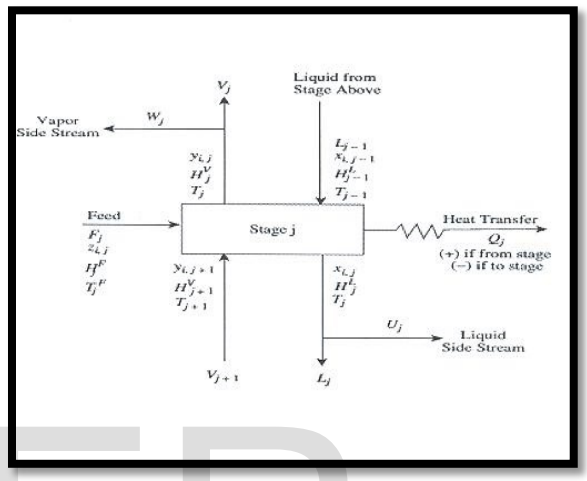

Fig.6 Total equilibrium part of the distillation tower

$$L_{j-1}x_{j-1}+V_{j+1}y_{i,j+1}+F_jZ_{i,j}-(L_j+V_j)x_{i,j}-(V_j+W_j)y_{i,j} \quad (9)$$

$$y_{i,j}-K_{i,j}x_{i,j}=0 \quad (10)$$

$$\sum x_{i,j}-1=0 \;\&\; \sum y_{i,j}-1=0 \quad (11)$$

$$L_{j-1}H^L{}_{j-1}+V_{j+1}H^V{}_{j+1}+F_jH^F{}_j-\left(L_j+V_j\right)H^L{}_j-\left(V_j+W_j\right)H^V{}_j-Q_j=0 \quad (12)$$

$$\dot{S}_{gen,j}=\left(V_j+W_j\right)S^V{}_j+\left(L_j+U_j\right)S^L{}_j-L^L{}_{j-1}-V^V{}_{j+1}-F_jS^F{}_j+\frac{Q_j}{T_0} \quad (13)$$

5 Discussion and results

5-1 Experimental results

In the table 1 shown below , experimental results from Rivero' paper (2003) are shown. It can be seen from these result that the operation of adiabatic and diabatic column is distillation doesn't differ much. However there is a distinction between them, the absence of reflux ratio and less entropy production inside the diabatic column in comparison to the presence of the reflux ration and higher entropy production in adiabatic column. Another focus point for our study was the

temperature of each tray shown in Fig3. Tables 2 and 3 show some parameters in the adiabatic and diabatic columns, the condenser being the first tray in them.

Table 1.Measurement result of the adiabatic and diabatic columns

	Diabatic	Adiabatic
Feed	0.318	0.331
Distillation (mol/s)	0.028	0.030
Bottom(mol/s)	0.291	0.301
Feed mole fraction ethanol	.0675	0.0710
Distillate mole fraction ethanol	0.6972	0.7073
B mole fraction ethanol bottom	0.0073	0.0074
Top pressure (10^5 Pa)	0.994	1.011
Bottom pressure (10^5 Pa)	0.995	1.021
Water flow into the condenser and heat exchanger (mol/s)	2.10	3.11
Oil flow into the vaporizer (Kg/s)	0.160	0.160
Measurement error in temperatures (K)	0.11	0.45
Measurement error in mole	0.012	0.008

Table 2. Calculate result of the adiabatic column

Tray number	Temperature (K)	Pressure (K.Pa)	Heat duty (Watt)	Liquid flow (mol/sec)	Vapor flow (mol/sec)
1	351.616	101.1	-13150145	0.301	0
2	352.029	101.2	0	0.299	0.331
3	353.167	101.3	0	0.293	0.329
4	358.028	101.4	0	0.286	0.323
5	368.047	101.5	0	0.290	0.316
6	370.960	101.6	0	0.291	0.320
7	371.305	101.7	0	0.291	0.321
8	371.362	101.8	0	0.291	0.321
9	371.392	101.9	0	0.291	0.321
10	371.420	102	0	0.291	0.321
11	371.447	102.1	0	0.301	0.321

Table 3 Calculate result of the diabatic column

Tray number	Temperature (K)	Pressure (K.Pa)	Heat duty (Watt)	Liquid flow (mol/sec)	Vapor flow (mol/sec)
1	352.672	99.40	-1734.296	4.27*10^(-6)	0
2	358.161	99.41	-2327.999	0.055	0.042
3	365.092	99.42	-1975.999	0.103	0.098
4	368.290	99.43	-1398.999	0.138	0.460
5	369.359	99.44	-1158.000	0.166	0.181
6	369.876	99.45	-1164.000	0.195	0.209
7	370.221	99.46	-1408.999	0.229	0.238
8	370.538	99.47	-1408.000	0.255	0.272
9	370.736	99.48	-370.999	0.264	0.298
10	370.808	99.49	-244.999	0.270	0.307
11	370.850	99.50	0	0.275	0.313

5-2 Heat load analysis in the diabatic column

We know there is a heat exchanger in each tray of the adiabatic column.

Analytical results are shown in table 3. For more accurate analysis of adiabatic columns, a re-boiler must be considered. As shown, in Fig. 3.The fluid flow enters the re-boiler, later exiting to the tray. This can have an effect on the operation of the column. It is clear that no single tray can have two different temperatures at the same time , because of this assumption to simplify the conditions and reduce the errors the heat load of the final two trays are added together and considered as the last tray's temperature. It is most suited in our analysis that the condenser is located in the first tray.

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5-3 Entropy production analysis

The most important analysis in the diabatic and adiabatic column is the entropy production analysis. In the Rivero and Koejier's paper, the focus only on the mass and heat transfer.
Therefore the pressure and mixing effects were never considered. Fig.1 gives a scheme of tray N with the variables including numbering. The enlargement of the bubble is shown and also the three flows through the interface causing the entropy production are displayed. Jw and Je are the number of moles of water and ethanol respectively transferred per second, from the liquid into the vapor.
Mass transfer rates through the interface.
Jp is the corresponding measure (or fourier tray) of heat flow through the interface, or alternatively the heat transfer rate.
The entropy production caused by the heat and mass transfer to the Nth tray through the interfaces are described by three flow-force production:

$$\frac{dS_n}{dt} = J_{q,n}X_{q,n} + J_{w,n}X_{w,n} + J_{e,n}X_{e,n} \quad (14)$$

In this equation the J's are the flows (or integrated flux or transfer rates) and the X's are the average driving forces between inlets and outlets of trays.

$$X_{q,n} = \Delta\left(\frac{1}{T}\right) = \frac{1}{2}\left(\frac{1}{T_{n+1}} - \frac{1}{T_{n-1}}\right) \quad (15)$$

For an equilibrium column separating and ideal mixture, Eq.14 can be simplified to a single force-flow product. The description for the entropy production rate is:

$$\frac{dS_n}{dt} = \left(J_{w,n} - \bar{y}_n J_{e,n}\right) X_n^{\nu} = \left(J_{w,n} - \sqrt{\frac{y_{w,n}y_{w,n+1}}{y_{e,n}y_{e,n+1}}}\right) R.Ln\frac{y_{w,n}}{y_{w,n+1}} \quad (16)$$

This equation contains only a single force-flow product, which is in agreement with the single thermodynamic degree of freedom in a column with equilibrium state condition on all trays.
Fig.7 and Fig.8 shows the entropy production rate in the two columns using the thermodynamic analysis and equation (13).Fig.(9) and Fig.10 shows the entropy production rate that Rivero & Koejier measured using equation (14) and its expansion's. Comparing Fig 8&9 and Fig10&11 we can find indications of entropy production rate using thermodynamic analysis which have acceptable results.

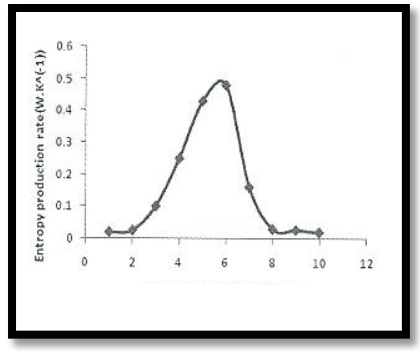

Fig.7 Tray number from condenser : result Eq. 14 and 16 (diabatic column) (a)

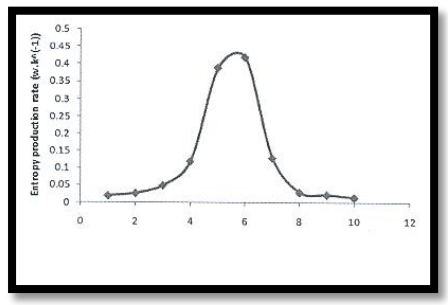

Fig.8 Tray number from condenser : result Eq. 14 and 16 (diabatic column) (b)

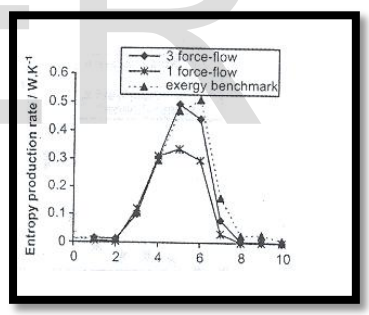

Fig.9 Tray number from condenser : result of Eq. 14 and 16 (adiabatic column)

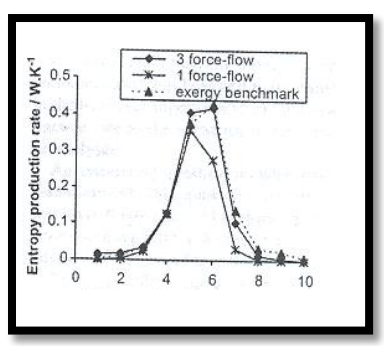

Fig.10 Tray number from condenser : result Eq. 14 and 16 (diabatic column)

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The role of heat exchangers in the diabatic column is extremely important. The main improvement by adding heat exchanger diabatisation, was on the temperature of the cooling water. In the adiabatic column, water exited at a temperature of 340K which is considers useless (in the shapes, the water outlets are shown by down facing arrows, showing their direction).
However in the diabatic column, water exited at 370K. This means an elevated 30K temperature difference, which gives it a potential usefulness. The cooling water outputs are used for heating other parts in the plant, resulting in reduced energy losses and therefore saving energy.

6 Conclusions

Our first conclusion in this study is that the entropy production rate calculated by thermodynamic analysis in the diabatic column is less than the entropy production rate in the adiabatic column. This is caused by the heat exchangers of the diabatic column, because the heat exchangers can withdraw more heat from the column cooling it down. Also this heat taken, could be used somewhere else to heat another part, saving dramatically in energy.
The second conclusion taken from this study is that the reflux phenomena can be replaced by heat exchangers in the diabatic column without great effects on the operation of the column. In fact, heat exchangers can execute the exact benefits of the reflux phenomena, with a greater entropy production rate.

Notations

B bottom, m/s

$\frac{ds}{dt}$ entropy production rate, $\frac{J}{sK}$

D distillation rate, $\frac{J}{sK}$

F feed, $\frac{mol}{s}$

H enthalpy, $\frac{J}{mol}$

J flow through interface, $\frac{mol}{s}$ or $\frac{J}{s}$

K constant, dimensionless

L liquid flow, $\frac{mol}{s}$

Q duty, $\frac{J}{s}$

R reflux ratio, $\frac{mol}{s}$

R (just in equ22,R is gas constant, $\frac{J}{mol.K}$)

S entropy, $\frac{J}{mol.K}$

T temperature,K

V vapor flow, $\frac{mol}{s}$

X force, $\frac{J}{mol.K}$

x liquid mole function, dimensionless

y vapor mole function, dimensionless

$\overline{y}$ average Gibbs-Duhem vapor mole function, dimensionless

Z mole partial of the feed, $\frac{mol}{s}$

Super-and sub-scripts

e ethanol

F feed

i component i

L liquid

n tray number n

m tray number m

j tray number j

V vapor

w water

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