Retrofit of Distillation Columns in a Methanol Plant

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ABSTRACT

Through its 'Column Targeting Tools' the Aspen plus simulator performs the 'Thermal Analysis' for rigorous column (RadFrac) calculations and produce Column Grand Composite Curves (CGCC) and exergy loss profiles. The CGCC displays the net enthalpies for the actual and ideal operations at each stage, and the cold and hot heat utility requirements, while the exergy loss profiles indicate the level of irreversibility at each stage including the condenser and reboiler. Therefore, the thermal analysis can identify the targets for restructuring and modifications, and may be helpful in suggesting retrofits. Some of the retrofits consist of feed conditioning (preheating or precooling), feed splitting, reflux adjustments, and adding side condensers and reboilers. These retrofits target a practical near minimum thermodynamic loss and suggest modifications for existing distillation columns by increasing the efficiency in energy utilization. This study uses the CGGC and the exergy loss profiles to assess the performance of the existing distillation columns, and reduce the costs of operation by appropriate retrofits in a methanol plant. Effectiveness of the retrofits is assessed by means of thermodynamics optimum and economics. The methanol plant is based on steam reforming and utilizes two distillation columns to purify the methanol in its separation section. The first column operates with 51 stages, has a side heat stream to the last stage, a partial condenser at the top and a side condenser at stage 2, and no reboiler. The second column operates with 95 stages, has a side heat stream to stage 95, a total condenser, and high reflux ratio. For the first column, the retrofits consisting of a feed preheating and a second side condenser at stage 4 have reduced the total exergy loss by 21.5%. For the second column, the retrofits of two side reboilers at stages 87 and 92 have reduced the total exergy loss by 41.3%. After the retrofits, the thermodynamic efficiency has increased to 55.4% from 50.6% for the first column, while it has increased to 6.7% from 4.0% for the second. The suggested retrofits have reduced the exergy losses and hence the cost of energy considerably, and proved to be more profitable despite the increases fixed capital costs of the distillation columns of the methanol plant.

Key Words: Thermodynamic analysis, Column grand composite curves, Exergy loss, Retrofitting, Thermodynamic efficiency

INTRODUCTION

Retrofits suggest modifications for existing distillation columns to reduce the costs of operations by increasing the efficiency in energy utilization [1-7]. Thermodynamic Analysis (TA) is one the methods for the retrofits by reducing the thermodynamic losses due to heat and mass transfer, pressure drop, and mixing in an existing design and operation. As a result, for example in a binary distillation, operating curves come closer to the equilibrium curve, and reflux ratio approaches to its minimum value. To analyze the performance of an existing column quantitatively for exploring the energy-saving potential, it is customary to construct the temperature enthalpy, called the Column Grand Composite Curves (CGCC), and the stage exergy loss profiles [1,2,7]. The CGCC displays the net enthalpies for the actual and ideal operations at each stage, and the cold and hot heat utility requirements [1,3], while the exergy loss profiles indicate the level of irreversibility at each stage including the condenser and reboiler [4,8-10]. Therefore, the area between the actual and the ideal operations in a CGCC should be small, and exergy losses should be lower for a thermodynamically efficient operation. The CGCC is constructed by solving the mass and energy balances for a reversible column operation. The stage exergy loss profiles are generated by the stage exergy balance calculations with a reference temperature.

The CGCC and stage exergy loss profiles are becoming readily available even for multicomponent, complex distillation column operations such as crude oil distillation by a suitable simulation package. For design and retrofit purposes, the CGCC and exergy loss profiles can identify the targets for restructuring and modifications, and suggest retrofits. Some of the retrofits consist of feed conditioning (preheating or precooling), feed splitting, reflux adjustments, and adding side condensers and reboilers. These retrofits target a practical near minimum thermodynamic loss [1,3]. This study presents the use of the CGCC and exergy loss profiles generated by the Aspen Plus simulator to assess the existing operations, and suggest retrofits, for the distillation columns in the separation Section of a methanol production plant.

THERMODYNAMIC ANALYSIS (TA)

Distillation columns operate with inevitable thermodynamic losses due to mixing, heat and mass transfer, pressure drops, internal stage design, and configuration of columns, such as the numbers of feeds and side products. TA combines the first and second laws of thermodynamics, and determines the net enthalpy deficits as well as the losses of available energy called the exergy losses due to irreversibilities at each stage of a column. The distributions of the enthalpy deficits and exergy losses can identify the scope and extent of retrofits required [10-12,14,17-19]. The Column-Targeting tool of Aspen Plus based on TA performs the thermal analysis, and produces the CGCC and the exergy loss profiles for rigorous column calculations based on the practical near-minimum thermodynamic condition [1]. This condition targets reversible column operation with negligible entropy production (or loss of exergy). To achieve that, heaters and coolers with appropriate duties would operate at each stage; reflux ratio would be close to its minimum, and hence the operating lines approaches to the equilibrium curve. Whether a retrofit is economical or not would only be known after an overall optimization, which seeks the best solution for a whole plant under specific constraints. Therefore, the relations between the energy efficiency and capital cost must be evaluated [11,12]. In a simpler approach, one may estimate the trade offs between the costs of retrofits and savings due to the reduced exergy loss equivalent of fuel or electricity.

Column Grand Composite Curve (CGCC) - Temperature-enthalpy profiles of CGCC represent the theoretical minimum heating and cooling requirements over a temperature range. Using the equilibrium compositions of light *L* and heavy *H* key components, minimum vapor and liquid flow rates leaving the same stage with the same temperatures can be estimated from the following mass balances

$$V_{\min} = \frac{1}{y_L^*}(D_L + L_{\min} x_L^*) \tag{1}$$

$$L_{\min} = \frac{1}{x_H^*}(V_{\min} y_H^* - D_H) \tag{2}$$

The enthalpies for the minimum vapor and liquid flows are obtained from the molar flow ratios

$$H_{\text{Vmin}} = H_V^* \left(\frac{V_{\min}}{V^*} \right) \tag{3}$$

$$H_{\text{Lmin}} = H_L^* \left(\frac{L_{\min}}{L^*} \right) \tag{4}$$

where V^* and L^* are the molar flows of equilibrium, and H_V^* and H_L^* are the enthalpies of equilibrium vapor and liquid streams leaving the same stage, respectively. From the enthalpy balances at each stage, the net enthalpy deficits are obtained

$$H_{\text{def}} = H_{\text{Lmin}} - H_{\text{Vmin}} + H_D \qquad \text{(before the feed stage)} \tag{5}$$

$$H_{\text{def}} = H_{\text{Lmin}} - H_{\text{Vmin}} + H_D - H_{\text{feed}} \qquad \text{(after the feed stage)} \tag{6}$$

After adding the individual stage enthalpy deficits to the condenser duty, the enthalpy values are cascaded, and plotted in the CGCC [1,3]. At the feed stage, mass and energy balances differ from a stage

$$H_{\mathrm{def,F}} = Q_C + D[H_D + H_L(x_D - y_F^*)/(y_F^* - x_F^*) - H_V(x_D - x_F^*)/(y_F^* - x_F^*)] \tag{7}$$

The values of y_F^* and x_F^* may be obtained from an adiabatic flash for a single phase feed, or from the constant relative volatility estimated with the converged compositions at the feed stage and feed quality. In a CGCC, a pinch point near the feed stage occurs for nearly binary ideal mixtures. A horizontal distance between the CGCC pinch point and the vertical axis represents the excess heat, and therefore the scope for reduction in reflux ratio [1-3,16]. For smaller reflux ratios, the CGCC will move towards the vertical axis, and hence reduce the reboiler and condenser duties, which may be estimated by [3]

$$Q_R - Q_{R,\min} = Q_C - Q_{C,\min} = D\lambda[R - (x_D - y_F^*)/(y_F^* - x_F^*)] \tag{8}$$

where λ is the heat of vaporization. The horizontal distance of the CGCC from the temperature axis, however, determines the targets for installing a side reboiler or side condenser at suitable temperatures [1,2,16,17]. On the other hand, a sharp change in the enthalpy represents inappropriate feed conditioning, such as feed quality or temperature; a sharp change on the reboiler side may be due to a subcooled feed. Feed conditioning is usually preferred to side condensing or reboiling, since the side heat exchangers are effective at suitable temperature levels or stages only [18].

Exergy Loss Profiles- Exergy Ex ($Ex = H - T_oS$) shows the available energy that can be converted into a useful work in a reversible process based on a reference temperature T_o, which is usually assumed as the environmental temperature of 298.15 K. Exergy balance for a steady state system shows that exergy is not conserved

$$\sum_{\substack{\text{into}\\\text{system}}} \left[\dot{n}Ex + \dot{Q}\left(1 - \frac{T_o}{T_s}\right) + \dot{W}_s\right] - \sum_{\substack{\text{out of}\\\text{system}}} \left[\dot{n}Ex + \dot{Q}\left(1 - \frac{T_o}{T_s}\right) + \dot{W}_s\right] = \dot{X}_{\text{loss}} \tag{9}$$

where $\dot{W}_s$ is the shaft work. The rate of loss exergy $\dot{E}x_{\text{loss}}$ represents the overall thermodynamic imperfections, and directly proportional to the rate of entropy production due to irreversibilities in a column operation. As the exergy loss increases, the net heat duty has to increase to enable the column to achieve a required separation. Consequently, smaller exergy loss means less waste heat or thermodynamic imperfections. For distillation columns, the difference between the exergies of products and feed streams determines the minimum exergy (separation work) necessary for a required separation

$$\dot{E}x_{\min} = \sum_{\text{out}} \dot{n}Ex - \sum_{\text{in}} \dot{n}Ex \tag{10}$$

A conventional column receives heat at a higher temperature level in the reboiler, and discharges about the same amount in the condenser at a lower temperature. Therefore, it resembles a heat engine that produces the separation work. When $\dot{E}x_{\min} > 0$, thermodynamic efficiency becomes

$$\eta = \frac{\dot{E}x_{\min}}{\dot{E}x_{\text{loss}} + \dot{E}x_{\min}} \tag{11}$$

The denominator in Eq. (11) is the total exergy input. The values of efficiencies before and after the retrofits can quantify the improvements, and help assessing the effectiveness of retrofits.

METHANOL PLANT

The methanol plant uses natural gas, carbon dioxide, and water as the basic feed streams, and produces 62000 kg/hr and 99.95% pure methanol. The plant operates with five Sections connected to each other by the material and heat streams, as shown in Figure 1. Section 1 prepares the feeds of 24823 kg/hr carbon dioxide at 1.4 bar and 43 ^{o}C, and 29952 kg/hr natural gas containing 95.39 mole% methane at 21.7 bar and 26 ^{o}C. Also, there are the circulation water of 410000 kg/hr at 26 bar and 195 ^{o}C, and the makeup steam at 26 bar. By adjusting the steam flow rate, the steam to methane ratio of 2.8 is achieved in the reactor. The reactor outlet contains small amounts of dimethylether, n-butanol, and acetone, beside the main product of methanol. The outlet is flashed and the methanol rich liquid stream 407 is fed to the separation Section 4, which consists of two complex columns in series. The columns operate with multicomponent feeds and multiple side products, and use process heats as side heat streams from the other Sections of the plant. The first column operates with a side condenser, and has no reboiler. Separation of the methanol starts with flashing of stream 407. The feed to the first column is the mixture of the liquid outlet of the flash drum and the makeup water at 5 bar and 40^{o}C. Flow rate of the makeup water is adjusted in order to minimize the methanol loss at the bottoms of the second column. The stages are numbered from the top to the bottom. The first column has 51 stages, a partial condenser at the top, and a side condenser at stage 2. It receives the feed at stage 14, a side heat stream of 15.299 MW at stage 51, and operates without rebolier. A pumparound connects the liquid flow between stage 1 and 3. The second column has 95 stages and a total condenser at the top. It receives the feed at stage 60, a side heat stream of 18.9 MW at stage 95, and operates with high reflux ratio. The methanol is a side product of the second column drawn from stage 4. The side heat streams come from Section 2 (Figure 1). Section 5 is the furnace Section, where the offgas from Section 4 is burned.

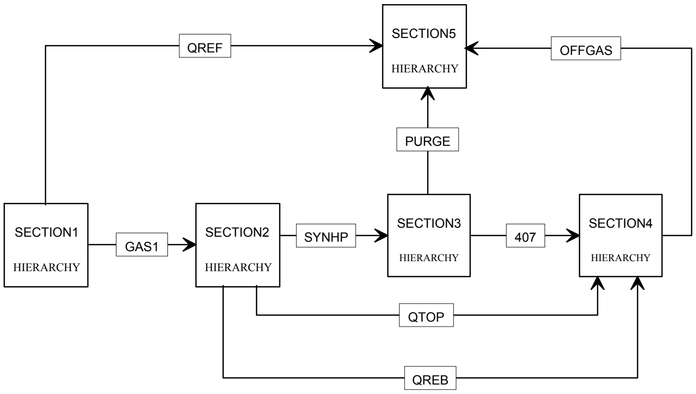


Figure 1. Connection of the Sections of the methanol plant with material and heat streams.

RESULTS AND DISCUSSION

Stream 407 containing 73.45 mole% of methanol and the makeup water are the feed streams to the separation Section. Tables 2 and 3 describe the existing base case columns operations for the columns 1 and 2. The simulations use the thermodynamic method of Redlich-Kwong-Soave (RKW) to estimate the vapor properties, while the activity coefficient model NRTL and Henry components method are used for predicting the equilibrium and liquid properties.

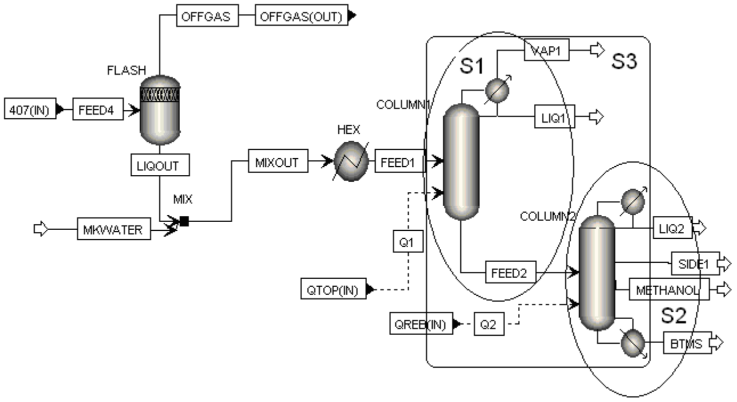


Figure 2. Separation Section of the methanol plant with subsystems: S1-column 1; S2-column 2; S3-column 1 and 2.

Column 1- As the base case design in Table 1 shows, column 1 has 51 stages, and operates with a partial condenser with a duty of 1.371 MW at the top, and a side condenser with a duty of 8.144 MW at stage 2. It has no reboiler, however, it receives a side heat stream with a duty of 15.299 MW to the last stage from Section 2 of the plant (Figure 1).

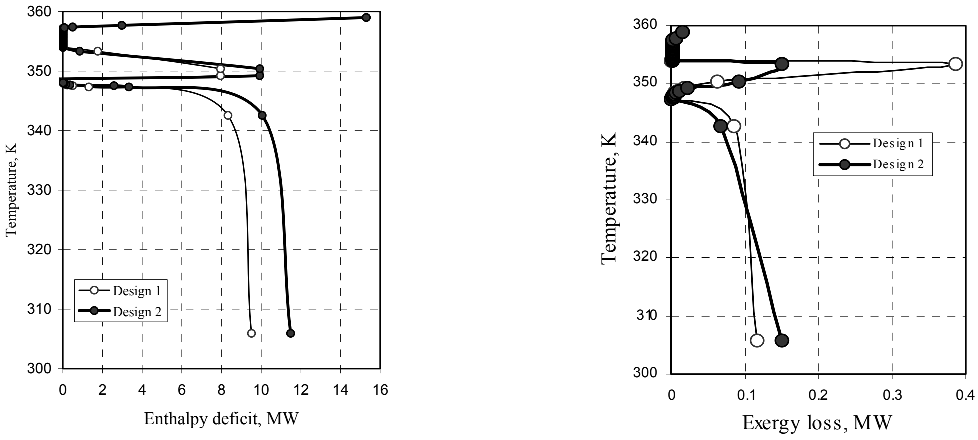
Table 1 Comparison of operating parameters of base case and retrofitted case for column 1

Parameter	Design 1 (Base case)	Design 2 (Retrofitted case)
No. of stages	51	51
Feed stage	14	14
T (Feed), ^{o}C	43.7	65.0
Reflux ratio	3.7	4.5
Condenser duty, MW	1.372	1.691
Distillate rate, kmol hr^{-1}	34.14	34.14
T (Condenser), ^{o}C	32.7	32.7
Side condenser 1 stage	2	2
Side condenser 1 duty, MW	8.144	7.700
T (Stage 2), ^{o}C	69.4	70.3
Side condenser 2 stage	-	4
Side condenser 2 duty, MW	-	2.100
T (Stage 4) ^{o}C	74.4	74.4
Heat stream (Q1) duty, MW	15.299	15.299
Heat stream (Q1) stage	51	51
T(Heat stream) (Q1), ^{o}C	104.0	104.0
Boilup rate, kmol hr^{-1}	1551.28	1551.56
Bottom rate, kmol hr^{-1}	2995.14	2995.14
Bottom temperature, ^{o}C	85.8	85.8

Within the rectification Section of column 1, there exists a significant area difference between the ideal and actual enthalpy profiles, which identifies the scope for side condensing [21]. As the temperature change after stage 3 is very small, and a side condenser at stage 2 already exists, it has been decided to install second side condenser at stage 4 with a duty of 2.1 MW. Figure 3a compares the base case and retrofitted designs for column 1; the side condenser has reduced the area between the ideal and actual enthalpy profiles. The duty of 2.1 MW is in the range of enthalpy difference between the hot duty of 15.299 MW and the total cold duty of 9.51 MW (side condenser + partial condenser). The existing side condenser duty is reduced to 7.7 MW from 8.144 MW, so that the new total duty of 11.49 MW is close to the previous total of 9.51 MW. The total costs due to retrofits would not change too much, and the need for extra stages would be negligible as the heat changes sharply below the first side condenser.

Figure 3a also displays a sharp change of the enthalpy on the reboiler side. The extent of the change determines the approximate feed preheating duty required [18] as the feed at 43.74^{o}C is highly subcooled. Therefore, a new heat exchanger with a duty of 1.987 MW is used as the second retrofit for the column, and the feed temperature has increased to 65.0^{o}C from 43.74^{o}C. The difference between the hot and cold duties is lower, and the actual and ideal profiles are closer to each other after the retrofits.

The suggested retrofits also aim at reducing the irreversibility due to mixing of the streams at different temperatures on the feed stage, which is at 80.18^{o}C, and throughout the column. The exergy loss profiles (Figure 3b) show that the reduction in exergy loss at the feed stage is about 60% with the values of 0.3865 MW in design 1 and 0.1516 MW in design 2 [21]. However, the exergy loss at the partial condenser increases by 28%, and becomes 0.150 MW in design 2 instead of 0.117 MW in design 1. As Table 3 shows, the reduction in the total exergy loss or the recovered available energy is 21.5 % with the total column exergy losses of 0.837 MW and 0.656 MW in design 1 and 2, respectively.



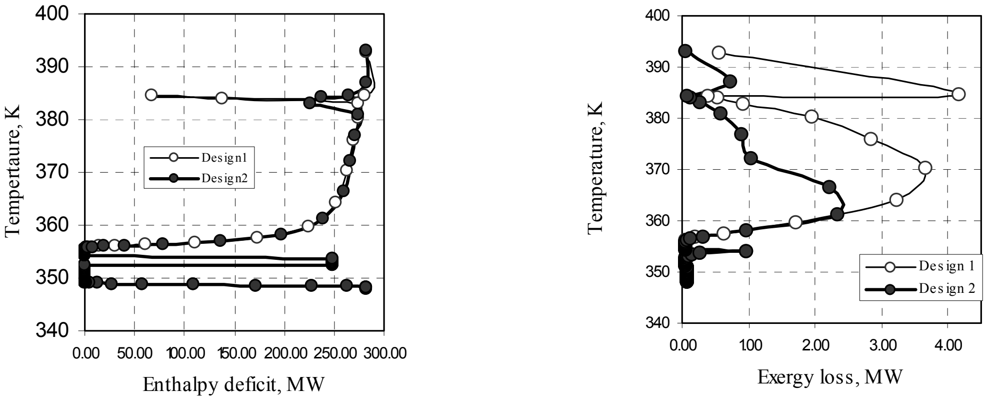
(a) (b)

Figure 3. (a) Temperature-enthalpy deficit curves (CGCC) and (b) exergy loss distribution for column 1.

Column 2- Column 2 has 95 stages, and a total condenser with a duty of 281.832 MW. It operates with a high reflux ratio, and receives a side heat stream of 18.9 MW to the last stage from Section 2 of the plant. One of the side products is the methanol stream and drawn at stage 4 at 348.3 K. The second side product is drawn at stage 86 at 361.2 K. The CGCC of column 2 shows a significant area difference between the ideal and the actual enthalpy profiles above the feed stage representing the pinch, and hence suggests side reboiling at appropriate temperature levels to decrease the difference [19-21]. The existing reboiler duty is 282.28 MW (Table 2). There is a side product at stage 86 and a side heat inlet of 18.9 MW at stage 95. Therefore, it has been decided to install two side reboilers at stages 87 and 92 with the duties of 180 and 50 MW, respectively. Figure 4a compares the base case and retrofitted designs for column 2.

Table 2. Comparison of operating parameters of designs 1 and 2 for column 2.

Parameter	Design 1 (Base case)	Design 2 (Retrofitted case)
No. of stages	95	95
Feed stage	60	60
T (Feed), ^oC	85.8	85.8
Reflux ratio	188765.0	188765.0
Condenser duty, MW	281.832	281.832
Distillate rate, kmol hr^{-1}	0.15	0.15
Condenser temperature, ^oC	74.8	74.8
Reboiler duty, MW	282.283	52.292
Boilup rate, kmol hr^{-1}	24890.68	4633.93
Bottoms rate, kmol hr^{-1}	1050.96	1049.66
T (Reboiler), ^oC	119.7	120.0
Side reboiler 1 stage	-	87
Side reboiler 1 duty, MW	-	180.000
Stage 87 temperature, ^oC	90.9	93.3
Side reboiler 2 stage		92
Side reboiler 2 duty, MW		50.000
Stage 92 temperature, ^oC	110.9	110.9
Heat stream (Q2) duty, MW	18.900	18.900
Heat stream (Q2) stage	95	95
Heat stream (Q2) temperature ^oC	136.0	136.0



(a) (b)

Figure 4. (a) Temperature-enthalpy deficit curves (CGCC) and (b) exergy loss distribution for column 2.

With the two side reboilers, the duty of the reboiler decreases to 52.3 MW from 282.3 MW. Extra stages due to the side reboilers would be minimal since the enthalpy rises sharply at each stage after stage 84. The retrofits reduce the area between the ideal and actual enthalpy profiles [21].

The base case design operates with rather large exergy losses at the feed stage and around the reboiler. The retrofits reduce the total exergy losses by about 41.3 %, and hence save a considerable amount of the available energy (Figure 4b). The minimum values of exergy for the required separation and the thermodynamic efficiencies for designs 1 and 2 are estimated using Eqs. (10) and (11), and compared in Table 3. The estimations are based on the value T_o = 298.15. The reductions in the exergy losses range from 21.5% to 41.35%. The thermodynamic efficiencies have increased considerably, although the low efficiencies are common for industrial column operations [8]. For column 1 the efficiency increases to 55.4% from 50.6%, while it increases to 6.7% from 4.0% in column 2.

An approximate economic analysis has compared the fixed capital costs (FCC) of the retrofits with the savings in electricity due to the retrofits. FCC consists of equipment, materials, construction, and labor cost. Table 4 shows the approximate values of FCC for the heat exchangers needed in the retrofits. The costs are estimated by using the current chemical engineering plant cost index of 420, and the approximate areas of the exchangers are obtained from the individual duties. Estimations of the energy saving are based on the unit cost of electricity of \$0.060/kW-hr and a total 8322 hours/year of the plant operation. The costs of retrofits and the saved electricity for each subsystem are compared in Table 4, which shows that the retrofits are effective and save a considerable amount of energy per year.

Table 3. Assessment of the effectiveness of the retrofits: The subsystems S1 to S3 are shown in Fig. 2

	Design 1 (base case)			Design 2 (retrofitted case)						
System	$\dot{E}x_{\min}$ (MW)	$\dot{E}x_{loss}$ (MW)	η %	$\dot{E}x_{\min}$ (MW)	$\dot{E}x_{loss}$ (MW)	η %	Saved $\dot{E}x_{loss}$ (MW)	Change $\dot{E}x_{loss}$%	FCC*of retrofits, \$	Electricity Saving** (\$/year)
S1										
Column 1	0.856	0.837	50.6	0.815	0.656	55.4	0.179	21.5	183,500	89,578
S2										
Column 2	1.136	26.98	4.0	1.135	15.85	6.7	11.133	41.3	409,000	5,558,829
S3										
Column 1+2	1.992	27.82	6.7	1.950	16.51	10.6	11.312	40.7	592,500	5,648,407

$\dot{E}x_{loss}$: Total column exergy loss from the converged simulation by Aspen Plus with SRK, NRTL.

* FCC: Fixed capital cost.

** Electricity equivalent of energy saving is based on a unit cost of electricity of \$0.060/kW-hr.

Table 4. Approximate fixed capital cost calculations for the retrofits

Heat exchanger	Type	Duty (MW)	*P* (bar)	Material	Area (m^2)	FCC** ($)
Preheater (HEX) Column 1	S/T* Fixed Tube sheet	1.9	5.0	Carbon Steel	130	90,500
Side condenser Column 1	S/T* Fixed Tube sheet	2.1	1.5	Carbon Steel	130	93,000
Total cost for column 1						183,500
Side reboiler 1 Column 2	Floating head	180.0	2.0	Carbon Steel	600	294,000
Side reboiler 2 Column 2	Floating head	50.0	2.0	Carbon Steel	170	115,000
Total cost for column 2						409,000

* S/T: Shell and tube.

** Approximate fixed capital cost (FCC) with the chemical engineering plant cost index = 420 [20].

SUMMARY and CONCLUSIONS

This study has used thermodynamic analysis for retrofitting the distillation columns within the separation Section of a methanol production plant. The suggested retrofits consist of an additional side condenser at stage 4 and feed preheating for column 1, and two side reboilers at stages 87 and 92, respectively for column 2. Effectiveness of the retrofits has been assessed by the improved column grand composite curves and exergy loss profiles as well as by an approximate economical analysis. The range of reductions in the total exergy losses is 21.5% to 41.3%, which causes a considerable saving in the available energy losses. The thermodynamic efficiencies also increased considerably, and the columns operate with less thermodynamic imperfections. The savings in electricity can payback the initial cost of retrofits in a short time of operation.

Column grand composite curves and exergy loss profiles are becoming readily available through a simulator package. This enables engineers to assess an existing operation and suggest retrofits or design thermodynamically optimum processes. Therefore, Thermodynamic analysis is emerging as retrofitting and optimization tools for existing and new processes.

NOMENCLATURE

D	Distillate, (kmol hr^{-1})
Ex	Exergy (MW)
H	Enthalpy (J mol^{-1})
$\dot{Q}$	Heat flow (W)
L	Liquid flow rate (kmol hr^{-1})
$\dot{m}$	Mass flow rate, (kg hr^{-1})
$\dot{n}$	Molar flow rate, (kmol hr^{-1})
Q_C	Condenser duty (MW)
Q_R	Reboiler duty (MW)
S	Entropy (J mol^{-1}K^{-1})
T	Temperature (K)
x	Liquid mole fraction
y	Vapor mol fraction

V	Vapor flow rate (kmol hr^{-1})
η	Efficiency
λ	Heat of vaporization (J mol^{-1})

subscripts

def	Deficit
D	Distillate
F	Feed
V	Vapor
H	Heavy
L	Light
min	Minimum
R	Reboiler
s	Stream, shaft

REFERENCES

1. Dhole, V.R. and Linnhoff, B. Distillation column targets. Comput. Chem. Eng., 1993, *17*, 549-560.
2. Ognisty, T.P. Analyze distillation columns with thermodynamics. Chem. Eng. Prog., 1995, *91*, 40-46.
3. Bandyopadhyay, S. Malik, R.K. and Shenoy, U.V. Temperature-enthalpy curve for energy targeting of distillation columns. Comput. Chem. Engng., 1998, *22*, 1733-1744.
4. De Koeijer, G.M. and Rivero, R. Entropy production and exergy loss in experimental distillation columns. Chem. Eng. Sci., 2003, *58*, 1587-1597.
5. Al-Muslim. H. and Dincer, I.; Zubair, S.M. Exergy analysis of single-and two-stage crude oil distillation units. J. Energy Resource Tech., 2003, *125*, 199-207.
6. Al-Muslim, H. and I. Dincer, I. Thermodynamic analysis of crude oil distillation systems. Int. J. Energy Res., 2005, *29*, 637-655.
7. Demirel, Y. Thermodynamic analysis of separation systems. Sep. Sci. Technol. 2004, *39*, 3897-3942.
8. Seider, W.D.; Seader, J.D. and Lewin, D.R. *Product & Process Design Principles*; 2nd Ed.; Wiley: New York, 2004.
9. Demirel, Y. *Nonequilibrium Thermodynamics Transport and Rate Processes in Physical, Chemical and Biological Processes*; Elsevier: Amsterdam, 2007.
10. Demirel Y. and Sandler, S.I. Nonequilibrium thermodynamics in engineering and science. J. Phys. Chem. B, 2004, *108*, 31-43.
11. Chang, H. and Li, Jr-W. A new exergy method for process analysis and optimization. Chem. Eng. Sci., 2005, *60*, 2771-2784.
12. Rivero, R.; Garcia, M. and Urquiza, J. Simulation, exergy analysis and application of diabatic distillation to a tertiary amyl methyl ether production unit of a crude oil refinery. Energy, 2004, *29*, 467-489.
13. Demirel, Y. and Sandler, S. I. Linear nonequilibrium thermodynamics theory for coupled heat and mass transport. Int. J. Heat Mass Transfer, 2001, *44,* 2439-2451.
14. Doldersum, A. Exergy analysis proves viability of process modifications. Energy Convers. Mgmt., 1998, *39*, 1781-1789.
15. Liu, Y.A. *Process and Product Design I: Hands-on Training Course on Process Simulation, Retrofit and Optimization Using ASPEN PLUS;* Virginia Tech: Virginia, 2003.
16. Aspen Plus V11.1. Aspen Technology: Cambridge, MA.
17. Agrawal, R. and Herron, D.M. Efficient use of an intermediate reboiler or condenser in a binary distillation. AIChE J., 1998, *44*, 1303-1315.
18. Bandyopadhyay, S. Effect of feed on optimal thermodynamic performance of a distillation column. Chem. Eng. J., 2002, *88*, 175-186.
19. Rivero, R. Exergy simulation and optimization of adiabatic and diabatic binary distillation. Energy, 2001, *26*, 561-593.
20. Turton, R.; Bailie, R.C.; Whiting W.B. and Shaeiwitz, J.A. *Analysis, Synthesis and Design of Chemical Processes*; 2nd Ed.; Prentice Hall: New Jersey, 2003.
21. Demirel, Y., Retrofit of distillation columns using thermodynamic analysis, Sep. Sci. Tech., 2006, *41*, 791-817.