

Distillation Operation Modification with Exergy Analysis

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Abstract

In this work, an approach based on thermodynamic analysis was proposed to assess and improve the energy efficiency of a debutanizer column. The approach is hinged on the application of exergy analysis. Use is made of the exergy loss profiles obtained from Aspen Plus to assess the performance of the debutanizer and suggest suitable modification for improvement in the column's energy efficiency. An assessment of the converged base case simulation indicated the need for more efficient operations. The scheme proposed for improvement is the splitting of the feed, preheating one and placing the two feeds at different stages in the column. The range of reduction in the total exergy losses is 12 to 21%. The range of thermodynamic efficiency for these retrofits is 63 to 66% as compared to the base case value of 58%. The retrofits thus provide less thermodynamic imperfections and a reduction in energy cost.

Keywords: exergy loss, distillation, thermodynamic efficiency, two-enthalpy feed, feed preheating and splitting

INTRODUCTION

Distillation is the single most important method of separating mixtures in the chemical process industries. Unfortunately, distillation processes are both energy intensive and inefficient especially in their conventional mode where heat is supplied to a single reboiler at the highest temperature and, an almost equal amount of heat, rejected in a condenser at the lowest temperature. There has been an endless quest over the years to improve the economics and efficiencies of distillation columns. The present trend tends towards the use of the principles of thermodynamics; a combination of the first and second laws of thermodynamics which can identify and quantify the energy dissipation and define targets for energy consumption (Demirel, 2004).

Thermodynamic analysis is an important tool for synthesizing and developing energy-efficient distillation processes. Targets can be set that reduces the thermodynamic losses due to heat and mass transfer, pressure drop, and mixing in the column. As a result, the distillation condition approaches that for a reversible operation as reported by Dhole and Linnhoff, (1993). Distillation columns can be analyzed thermodynamically through the stage exergy loss profiles (Dhole and Linnhoff, 1993; Zemp et al, 1997). The exergy loss profiles indicate the level of irreversibility at each stage, measures can thus be taken to even out these irreversibilities (Chang and Li, 2005; Santana and Zemp, 2005). Zemp et al. (1997) generated the exergy loss profile of the distillation column and used it to identify beneficial column modifications. De Koeijer and Rivero (2003) described the entropy production rate on both adiabatic and diabatic experimental

water/ethanol rectifying column by applying the theory of irreversible thermodynamics (de Koeijer and Kjelstrup, 2004). As a benchmark for the description, an exergy analysis of the two columns was used. Rivero et al. (2004) carried out a detailed exergy analysis of a tertiary amyl methyl ether (TAME) unit of a crude oil refinery; Faria and Zemp (2005) also used the exergy loss profiles and enthalpy-temperature profiles for the evaluation of the thermodynamic efficiency in distillation column. Column optimization involves options such as feed conditioning, which include preheating and/or precooling of the feed (Dhole and Linnhoff, 1993), feed splitting (Wankat and Kessler, 1993, Agrawal and Herron, 1997, Bandyopadhyay, 2002), feed stage location, reflux adjustments and the addition of side condensers/reboilers. Exergy loss profiles can identify targets for the distillation process optimization. Douani et al. (2007) used exergy analysis to analyze the performance of a distillation column. Their results showed that the exergetic output is relatively low and that the produced irreversibility fluxes are distributed throughout the whole column in a non-uniform manner. They are particularly significant in the condenser, reboiler and feed tray. Le Goff et al. (1996), in their study on the exergy analysis of distillation processes described distillation unit as an exergy converter, converting thermal exergy to chemical exergy. Due to high exergy losses in distillation operation, they proposed a new type of distillation (diabatic column) in which the condenser and reboiler are replaced by two heat exchangers integrated in the column itself. This arrangement, according to their study, minimizes the creation of entropy in the column and therefore

maximizes the exergetic effectiveness. The diabatic column from energy and economic points of view has shown large reduction in the consumption of heat carrier fluids for heating and cooling, and also a reduction in capital investment respectively. Several works have also been carried out on the diabatic column optimization, (Kjelstrup and Rosjorde, 2005, Rivero, 2001, Sauar et al., 1991, Schaller et al., 2001). Huang et al. (2008) used the high-pressure vapour distillate to pre-heat the feed to be separated, thereby giving rise to a totally heat-integrated distillation column, (THiDiC). The THiDiC is self-regulating and therefore leads to further improvement of thermodynamic efficiency of the distillation column.

The objective of this paper is to illustrate the advantages in terms of performance that can be derived from using the two-enthalpy feed modification to analyze the debutanizer column operation of the fluid catalytic cracking (FCC) unit of Kaduna Refining and Petrochemical Company (KRPC). The exergy profile of the column will be generated using the Aspen Plus simulator to identify sources of low thermodynamic efficiency and scope for column improvement.

THEORY

Exergy loss profiles

Application of the first law of thermodynamics to a distillation column yields:

$$\frac{d(MU)}{dt}_{cv} = \sum (mH)_i + \sum q_j + \sum w_k \quad (1)$$

where m_i and H_i are respectively the molal flow rate and enthalpy of an input or output stream i to the system; q_j is the rate of heat exchange with the environment through an auxiliary heat reservoir maintained at a temperature T_j , and w_k is the work done by a part of the system. M_{cv} is the mass of the control volume, U_{cv} is the internal energy averaged over the control volume and the accumulation term reflects the usual assumption that kinetic and potential energy contributions may be neglected.

The second law of thermodynamics applied to the control volume gives:

$$\frac{d(MS)}{dt}_{cv} = \sum (mS)_i + \sum \frac{q_j}{T_j} + \sigma \quad (2)$$

where S_{cv} denotes the entropy averaged over the control volume and S_i is the entropy of the material in stream i . The magnitude of $\sum(q_j/T_j)$ represents the rate of entropy change of the heat reservoirs at various temperatures of T_j . The additional term σ accounts for the rate of entropy production due to irreversibility. Multiplying Equation (2) by the temperature of the environment T_o and subtracting the result from Equation 1 yields Equation 3.

$$\frac{d[M(U-T_oS)]_{cv}}{dt} = \sum [m(H-T_oS)]_i + \sum \left(1 - \frac{T_o}{T_j}\right) q_j - \sum w_k - T_o\sigma \quad (3)$$

The term " $H - T_oS$ " is known as the availability " A " or exergy: that is, $A = H - T_oS$. A change in availability represents the maximum useful work a system can deliver when it is brought to equilibrium with the environmental conditions in reversible mode. Conversely, it also represents the minimum work required to achieve a change in the process. The term $(1 - T_o/T_j)q_j$ is the Carnot cycle work required to restore q_j to the heat reservoir at T_j at the expense of the environment. In other words, it is the maximum theoretical work that can be extracted from the heat reservoir at T_j at the expense of the environment. The term $T_o\sigma$ is called the rate of lost work, or W_{LOST} . It is a measure of the irreversibility in a system. The lost work is that portion of the total work that is necessary to overcome thermodynamic inefficiency due to driving forces within the system.

For a steady state flow process and in the absence of mechanical work, Equation (3) becomes:

$$W_{LOST} = \sum (mA)_i + \sum \left(1 - \frac{T_o}{T_j}\right) q_j \quad (4)$$

The exergy loss W_{LOST} can be calculated for each stage in the column, considering that exergy is available from the temperature difference of the streams meeting at the stage, and exergy is required for the mass transfer. The result for the column is the exergy loss (or lost work) profile, which describes the driving force distribution in the column (Zemp et al, 1997). Sections with large changes in composition and temperature also show large exergy losses, and vice versa. Thus from the exergy loss profile, column sections or individual stages that operate under large thermodynamic inefficiency are so readily identified (Smith et al, 2003). The minimum separation work required to separate the products from the feeds in a distillation column is calculated as the net change in availability of the process streams, that is,

$$W_{MIN} = -\sum (mA)_i = \sum_{out} mA - \sum_{in} mA \quad (5)$$

In distillation columns, this work is supplied by heat being injected at the reboiler q_{reb} and rejected at the condenser q_{cond} . The net work available from the heat energy (or the net exergy from the heat transferred) is:

$$W_{HEAT} = q_{reb} \left(1 - \frac{T_o}{T_{reb}}\right) - q_{cond} \left(1 - \frac{T_o}{T_{cond}}\right) \quad (6)$$

The thermodynamic efficiency of the distillation process is defined as the ratio of the reversible work of separation (W_{MIN}) to the net available energy put into the system ($W_{LOST} + W_{MIN}$). Mathematically, it is written as:

$$\eta = \frac{W_{MIN}}{W_{MIN} + W_{LOST}} \quad (7)$$

This factor, η , identifies how efficient the distillation column is at converting thermal exergy to work of separation.

Thus the main emphasis in the thermodynamic analysis of distillation column is the minimization of lost work. The key to minimizing lost work is to

devise a process that is close to being reversible as is economical (Bandyopadhyay, 2002; Demirel, 2004; Fitzmorris and Mah, 1980; Ognisty, 1995; Ratkje and Arons, 1995; Smith et al, 2003).

Preheat Efficiency

The preconditioning efficiency is one way of analyzing the effect of feed thermal-condition optimization. In the case of feed preheating, a portion of the thermal energy given to the feed reduces the reboiler load and the rest increases the condenser load. Hence, there exists an efficiency associated with feed preconditioning. Feed preconditioning efficiency may be defined as the ratio of the decreases in reboiler duty (for feed preheating) or condenser duty (for feed precooling) to the total amount of heat exchanged with the feed:

$$\text{Preconditioning efficiency (\%)} = \frac{-dQ}{dH} \times 100 \quad (8)$$

where $-dQ$ is the reduction in reboiler or condenser duty as the case may be, and dH is the heat exchanged with the feed. Feed conditioning efficiencies are usually less than 100% for single feeds. However, by splitting the feed and altering the thermal condition of a part of the feed, it is possible to achieve 100% preconditioning efficiency (Wankat and Kessler, 1993, Deshmukh et al, 2005; Bandyopadhyay, 2006). The efficiency of preconditioning depends on the thermal energy exchanged, the initial thermal condition of the feed, the feed concentration, relative volatility of the light to heavy key and the reflux/reboil ratio (Liebert, 1993, Agrawal and Herron, 1997).

METHODOLOGY

The thermal analysis of the debutanizer was carried out using the Aspen Plus simulator Version 11.1 through its column targeting tool for rigorous column calculations. Exergy loss profiles obtained from Aspen Plus RadFrac was used in this study. For each of the simulations, the Peng-Robinson (PR) property package was used. The column analyzed has 30 trays with a feed preheater. The stages are numbered starting from the condenser, and each actual tray operates at an efficiency equivalent to about $\frac{2}{3}$ of a

theoretical tray, which is the usual value found for such columns in practice (Puglisi, 2002). For all simulations, the distillate purity was set at 4mol% C_5 while the bottoms product purity at 4mol% C_4 by varying the distillate rate and the reflux ratio respectively. The feed composition to the debutanizer as shown in Table 1 was used. The debutanizer operation was simulated in order to approximate the actual column operation to a simulated base case. In analyzing the thermodynamics of the debutanizer, the feed optimization parameter was studied. Various simulation runs were conducted to determine the effect of a single and two-enthalpy feed of various vapor fractions with varying feed inlet point on the thermal behavior of the debutanizer.

Table 1: Debutanizer Feed Composition

Component name	Formula	Mole fraction
Propylene	C_3H_6	0.0551
Propane	C_3H_8	0.0239
1-butene	C_4H_8	0.0933
Isobutene	C_4H_{10}	0.0606
n-butane	C_4H_{10}	0.0479
2-methyl-1-butene	C_5H_{10}	0.1592
2-methyl-1-pentene	C_6H_{12}	0.1374
2-methyl-1-hexene	C_7H_{14}	0.1346
2-methyl-1-heptene	C_8H_{16}	0.1381
2-methyl-1-octene	C_9H_{18}	0.0860
2-methyl-1-nonene	$C_{10}H_{20}$	0.0397
1-undecene	$C_{11}H_{22}$	0.0161
1-dodecene	$C_{12}H_{24}$	0.0081

Source: KRPC 2002; www.chevron.com, 2007

For a single feed case (Figure 1), the enthalpy of the feed was varied from that of the cold feed without preheating to a totally saturated vapor feed. For the two-enthalpy feed case, Figure 2, (feed splitted with one portion preconditioned), the flow rates of the cold and hot portions were also varied to optimize the column's thermal performance as reported by Wankat and Kessler, 1993.

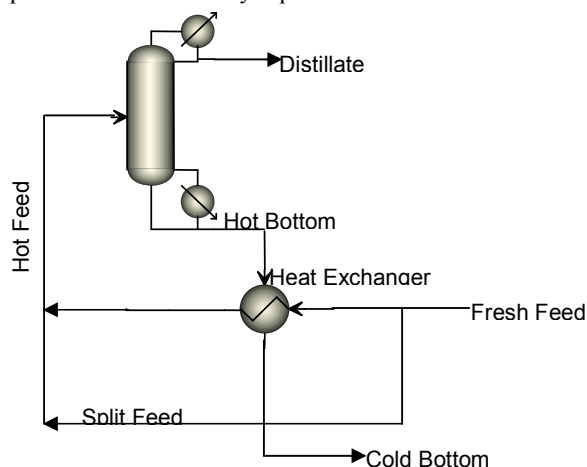


Figure 1. Single Feed Base Case Configuration

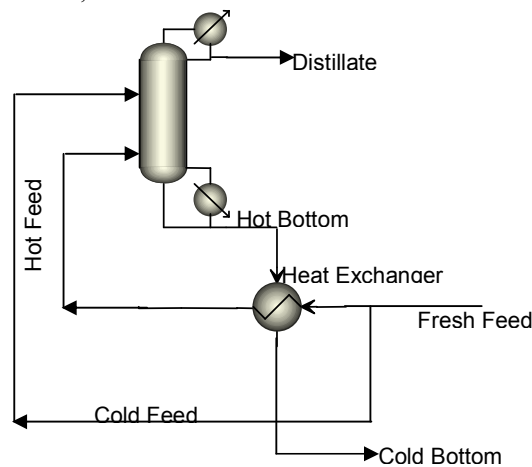


Figure 2. Two-Enthalpy Feed Case Configuration

Several simulation runs were also carried out by varying the split fraction of the preheated portion of the feed keeping constant the (base case) preheater duty.

RESULT AND DISCUSSION

Table 2 shows the column input specification and results. The match between the simulated base case results and its design values is reasonable.

Table 2: Column Specification and Results

	Simulation	Design
Number of real stages	32	32
Feed rate, kg/hr	83666	83666
Feed pressure, MPa gauge	1.389	1.389
Cold feed temperature, °C	111	111
Final column feed temperature, °C	132.85	136
Feed stage	15	14 or 16
Stage 1 pressure, MPa gauge	1.049	1.049
Stage 2 pressure, MPa gauge	1.089	1.089
Stage 32 pressure, MPa gauge	1.118	1.118
Stage 1 temperature, °C	56.62	53
Stage 2 temperature, °C	67.07	67
Stage 31 temperature, °C	156.49	162
Stage 32 temperature, °C	174.05	187
Reflux ratio (mass basis)	1.75639	1.79898
Distillate rate, kg/hr	23339	21839
Bottoms rate, kg/hr	60327	61827
Condenser duty, MW	5.76148	5.48928
Reboiler duty, MW	5.32446	5.23342
Feed preheater duty, MW	2.36750	2.73301
Final bottom temperature, °C	123	123

Figure 3 shows the exergy loss profile for the simulated single feed base case. The exergy loss profile shows large exergy losses in the vicinity of the feed and at the condenser and reboiler. This is as a result of the large driving forces for heat and mass transfer at these regions. The total exergy loss at 0.72354MW is also large. There are larger exergy losses in rectifying section than in the stripping section. This could be due to the larger concentration swings in the rectifying section than in the stripping section.

The minimum separation work, W_{MIN} , for the base case using Equation 5 was calculated as 1.04376MW, and the thermodynamic efficiency (Equation 7) was 58.469%. The not-too-high thermodynamic efficiency and significant exergy loss necessitate suitable modifications for improvement in column thermodynamic efficiency.

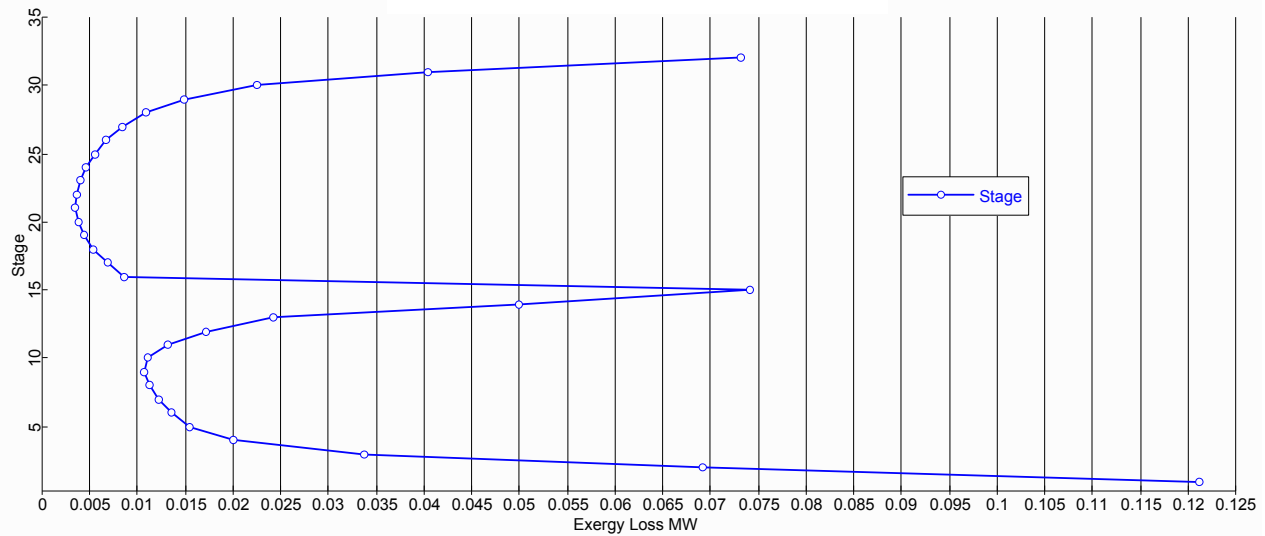
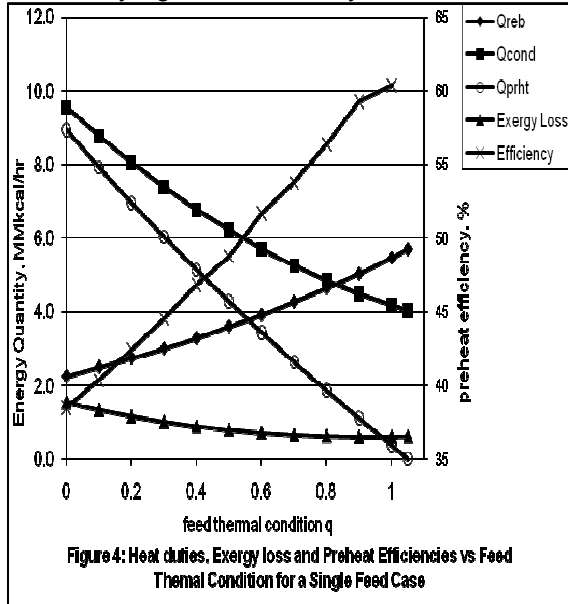


Figure 3: Exergy Loss Profile for the Base

Feed Optimization

As observed in Figure 4, the exergy loss for the single feed case goes through a minimum at about $q = 0.9$, with an exergy loss equal to 0.69MW – this represents the optimum in terms of exergetic performance. There is a continuous decrease and increase in reboiler and condenser duties respectively as the feed is increasingly preheated to saturated vapor. Some trade-off between a slightly higher-than-minimum exergy loss and a relatively lower reboiler duty can be tolerated for a preheated feed of about $q = 0.8$, even though this is at the expense of a relatively higher condenser duty.



Thus, the maximum heat, in some economic sense, is being extracted from the bottoms product stream; increasing the heat duty above this value will necessitate a larger exchanger area or even another heating fluid which might be uneconomical. The final feed stream thermal condition is equal to a “ q ” of about 0.78 for the base case; the exergy loss for the base case is 0.72354MW and this value is close to the minimum of 0.69MW. Thus, for a single feed, the base case could be the optimum in some economic sense and should be adopted. The base case column performance is summarized in Table 3.

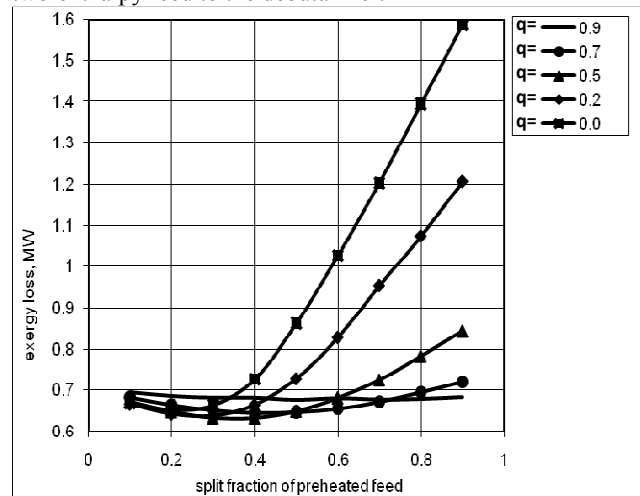
Table 3: Base Case Column Performance

split proportion of preheated feed	0.8
feed thermal condition q	0.78
Preheater duty, Q_{PRHT} , MW	2.36750
final temperature of feed, °C	132.85
condenser duty, Q_{COND} , MW	5.76148
reboiler duty, Q_{REB} , MW	5.32446
column exergy loss, MW	0.72354
preheat efficiency, $\eta_{PREHEAT}$, %	54.234

The preheat efficiencies decreases with increasing preheat. This implies that as the preheater duty increases, there is a lower reduction in reboiler duty and most of the heat added to the feed goes to increasing the condenser duty. The total heating requirement (preheater plus reboiler duty) increases with feed preheat; however, preheater and reboiler temperatures are different. Thus, it is unsuitable thermodynamically to preheat the feed totally to near saturated vapor conditions owing to the high exergy losses and low preheat efficiencies.

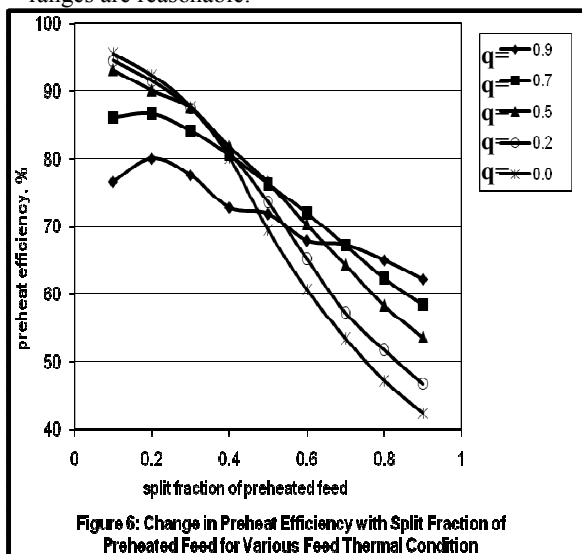
Two – Enthalpy Case

Generally, as seen from Figure 5, lower exergy losses down to about 0.63MW can be obtained by the use of a two-enthalpy feed. Thus, a higher exergetic performance can be obtained by the application of a two-enthalpy feed to the debutanizer.



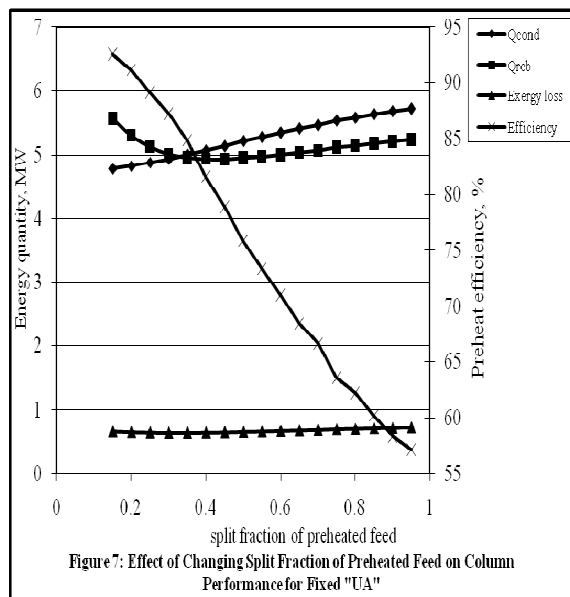
For a fixed preheated portion of the feed, the exergy loss seems to go through a minimum on increasing the vapor fraction of the preheated feed. The outlet temperature of the preheated feed at which this minimum exergy loss occurs appears to decrease with increasing portion of the preheated feed. At very high values of the preheated portion of the feed (0.8 to 0.9), the exergy loss continuously increases with increasing vapor fraction of preheated feed (preheater duty). For a fixed vapor fraction of the preheated portion of the feed and an increasing split fraction of the preheated feed, the exergy loss goes through a minimum between split fractions of 0.2 to 0.5. Specifically, $q = 0.5$ produced optimal exergy loss between split fraction 0.3 and 0.4, $q = 0.2$ and 0.6 produced optimal exergy loss between split fractions 0.2 and 0.3, while $q = 0.7$ and 0.9 produced optimal exergy loss at 0.5 and 0.9 split fractions respectively. The greater effect of the split fraction on exergy loss reduction is therefore higher between $q = 0.2$ and 0.4. The lowest exergy loss reduction actually occurred at $q = 0.4$ and split fraction of the preheated feed of 0.3.

The preheat efficiencies are generally higher for the two-enthalpy feed case (up to about 90%) as seen from Figure 6, than for the single feed case as shown in Figure 4. Thus, most of the heat added to the feed goes to reducing the reboiler duty. For low values of split fraction of preheated portion of the feed (0.1 to 0.3), the preheat efficiency generally increases with increasing vapor fraction of the preheated feed. For intermediate values of split fraction (0.4 to 0.6), the preheat efficiency goes through a maximum. For higher values of split fraction (0.7 to 0.9), the preheat efficiency continuously decreases with increasing vapor fraction of preheated feed. For a fixed vapor fraction of the preheated portion of the feed, the preheat efficiency generally decreases with increasing split fraction of the preheated portion of the feed as seen in Figure 6. Figures 5 and 6 show that some advantages in energy savings for the debutanizer can be achieved by splitting 30 to 50% of the feed and preheating this portion to about 50 to 70% vapor – the exergy losses and preheat efficiencies in these ranges are reasonable.



The preheat efficiency is observed to continuously decrease as the split fraction of the preheated portion of the feed is increased. The exergy loss goes through a minimum at about a split fraction of 0.3 with a value of 0.633MW on increasing the split fraction of the preheated portion of the feed (Figure 7). The bottom product stream cannot be used for preheating the feed above 175°C.

Thus if the bottoms product stream is to be used as the preheating fluid for the same preheater duty, it can be deduced from Figure 7 that relatively greater energy-efficient distillation could be obtained by splitting about 35 to 50% of the feed for preheating – the exergy losses (0.633 to 0.647MW) for these cases are close to the minimum and the preheat efficiencies (85 to 75%) are still reasonably good. The lower the split fraction of the preheated feed, the higher will be the required preheater area for the given duty and heating fluid.



The preheat efficiency continuously decreases on increasing the split fraction of the preheated portion of the feed. Also, on increasing the split fraction of the preheated feed, the exergy loss and the reboiler duty goes through a maximum at about split fractions of 0.3 and 0.45 respectively where they take values of 0.6298 and 4.9299MW respectively as seen in Figure 7. Thus for the same exchanger configuration, great advantages in energy savings can be obtained by splitting 30 to 45% of the feed for preheating with the bottoms product stream. The preheater duty for this case will vary between 1.831 to 2.128MW.

CONCLUSION

In conclusion, whether both the preheater duty and area can be allowed to vary widely, or the preheater duty fixed but the area varying, or even the area fixed and the duty varying, will depend on several factors viz.: the availability of other hot streams, the ease of routing these other hot streams to the debutanizer preheater, the types of exchangers in stock, blower energy cost, etc. However it seems that in all cases, the optimum split fraction of the preheated portion of the feed varies between 30 to 50% yielding reboiler and condenser duties as low as 4.93320 and 5.06744MW respectively (with preheater duty of 2.05383MW) and exergy loss of 0.63368MW for the fixed preheater configuration and similar respective values of 4.74371, 5.19341, and 0.64095MW for the fixed preheater duty case.

These values for either case are still significantly better than the base case with reboiler and condenser duties of 5.32446 and 5.76148MW respectively and exergy loss of 0.72354MW. Thus, the fixed preheater configuration case represents energy savings of 7.348 and 12.046% in reboiler and condenser duties (with a 13.248% reduction in preheater duty), and a 12.419% increase in energy utilization (decrease in exergy

loss) above the base case; while the fixed preheater duty case presents energy savings up to 10.907 and 9.860% in reboiler and condenser duties and 11.414% increase in energy utilization above the base case. The overall thermodynamic efficiency of the fixed exchanger configuration and the fixed preheater duty case (for each of their particular selected "optimum": which are split fraction of 0.4 for fixed exchanger configuration and 0.45 for fixed preheater duty) are found to be 63.384% and 63.410% respectively.

The overall thermodynamic efficiencies for these two cases of a two-enthalpy feed are higher than that for the base case; thus signifying a higher exergetic performance for the two-enthalpy case above the base case. Thus for the debutanizer column studied in this work, large mismatch of composition and temperature at the vicinity of the feed point and at the column's top and bottom, where reflux and reboil vapor were introduced, were identified as the major sources of thermodynamic inefficiencies. Large concentration swings in the rectifying section of the column also contributed to the thermodynamic inefficiencies.

The suggested modifications therefore are a two-enthalpy feed where 40 – 45% of the feed was split and preheated sufficiently to vaporize 45 – 55% of it. The cold (un-preheated) fraction of the feed was fed to about stage 13 while the preheated fraction to stage 23. The effectiveness of these modifications was assessed by improvements in energy utilization given by the reduction in exchanger loads and exergy losses, improvements in utility temperature levels and thermodynamic efficiency.

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