Energy Retrofit Studies in Diethyl Thiophosphoryl Chloride (DETC) Plant

Y. P. Bhalerao, S. V. Patil, P. V. Vijay Babu, and S. J. Kulkarni

***Abstract*—The industrial application of detailed heat integration to a Di Ethyl Thiophosphoryl Chloride (DETC) plant has been addressed using Pinch design method. The calculated minimum energy targets are found to be very close to utility loads demanded by the existing process. This analysis shows that present plant is well integrated and small saving in energy was observed through a process-to-process energy integration. Alternatively, the retrofit study provides a general guideline for better placement and proper utilization of available utilities.**

***Index Terms*—Pinch design, minimum energy targets, Di ethyl thiophosphoryl chloride (DETC) plant**

I. Introduction

During the last decades, chemical industry has had to face growing competition driven by rapid globalization, rising public concern for the environment, and increasing regulatory efforts of national governments concerning the environment, health, and safety. In response to these conditions and with regard to the capital intensive nature of chemical industry, constant optimization through redesign of existing production plants has emerged as a key strategy.

Pinch technology presents a simple methodology for systematically analyzing chemical processes and the surrounding utility systems with the help of the First and Second Laws of Thermodynamics. The First Law of Thermodynamics provides the energy equation for calculating the enthalpy changes (ΔH) in the streams passing through a heat exchanger. The Second Law determines the direction of heat flow. That is, heat energy may only flow in the direction of hot to cold. This prohibits 'temperature crossovers' of the hot and cold stream profiles through the exchanger unit.

In a heat exchanger unit neither a hot stream can be cooled below cold stream supply temperature nor a cold streams can be heated to a temperature more than the supply temperature of hot stream. In practice the hot stream can only be cooled to a temperature defined by the 'temperature approach' of the heat exchanger.

The temperature approach is the minimum allowable temperature difference (ΔT_{min}) in the stream temperature profiles, for the heat exchanger unit. The temperature level at which ΔT_{min} is observed in the process is referred to as "*pinch point*" or "*pinch condition*". The pinch defines the minimum driving force allowed in the exchanger unit.

The basic concepts of Pinch Analysis are: Pinch Analysis is used to identify energy cost and heat exchanger network (HEN) capital cost targets for a process and recognizing the pinch point. The procedure first predicts, ahead of design, the minimum requirements of external energy, network area, and the number of units for a given process at the pinch point. Next a heat exchanger network design that satisfies these targets is synthesized. Finally the network is optimized by comparing energy cost and the capital cost of the network so that the total annual cost is minimized. Thus, the prime objective of pinch analysis is to achieve financial savings by better process heat integration (maximizing process-to-process heat recovery and reducing the external utility loads).

Pinch originated in the petrochemical sector and is now being applied to solve a wide range of problems in mainstream chemical engineering. Wherever heating and cooling of process materials takes places there is a potential opportunity. Thus initial applications of the technology were found in projects relating to energy saving in industries as diverse as iron and steel, food and drink, textiles, paper and cardboard, cement, base chemicals, oil, and petrochemicals.

Early emphasis on energy conservation led to the misconception that conservation is the main area of application for pinch technology.

The technology, when applied with imagination, can affect reactor design, separator design, and the overall process optimization in any plant. It has been applied to processing problems that go far beyond energy conservation. It has been employed to solve problems as diverse as improving effluent quality, reducing emissions, increasing product yield, debottlenecking, increasing throughput, and improving the flexibility and safety of the processes.

Since its commercial introduction, pinch technology has achieved an outstanding record of success in the design and retrofit of chemical manufacturing facilities. Documented results reported in the literature show that energy costs have been reduced by 15-40%, capacity debottlenecking achieved by 5-15% for retrofits, and capital cost reduction of 5-10% for new designs.

Pinch Technology is a methodology, comprising a set of structured techniques, for systematic application of the first

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and second laws of thermodynamics. The application of these techniques enables process engineers to gain fundamental insight into the thermal interactions between chemical processes and the utility systems that surround them. Such knowledge facilitates optimizing the overall utility consumption and setting process and utility system configurations prior to final detailed simulation and optimization.

This task is known as retrofitting and is especially carried out on continuous processes for the production of bulk products. While other techniques involve trial and error methods to achieve a better design, pinch technology enables the design engineer to fix targets and then set out to achieve it. Starting point for an energy integration analysis by pinch technology is to calculate the minimum heating and cooling requirements for a heat exchanger network.

These calculations can be performed without having to specify a heat exchanger network. Similarly, we can calculate the minimum energy requirements without having to specify a network, and then the minimum energy requirements and the minimum number of exchangers provide targets to subsequent design of a heat exchanger network. The basic data required for optimization are the input and output temperatures of the hot and cold streams along with their mass heat capacity values. These data are easily available from energy and material balances for any process.

This work mainly deals with energy integration and retrofit case study of an existing DETC plant, using recent advances in Pinch technology. Retrofit designs involve revamping of an existing flow scheme to debottlenecking plant to increase capacity, decrease energy consumption, reduce emissions or change the process to introduce a new technology. Unlike a new design that starts with a clean sheet of paper, a retrofit study starts with an existing, previously optimized process. Haitham *et al.* [1] studied retrofit analysis in selected ammonia plant, and not much saving is reported through process-to-process energy integration. Alternatively, the retrofit study concentrated on better placement of available utilities. Two promising options have been investigated. Total benefit claimed amounted to 17.6% reduction in combustion fuel consumption. Seviae *et al.* [2] presented how the application of pinch technology can lead towards great energy savings. The heat exchanger network of a nitric acid plant has been studied and it was found that it is possible to reduce requirements for cooling water and medium pressure steam. However, the result is a reduction of energy costs and a payback time of 14.5 months.

Bagajewicz [3] proposed a technique to calculate energy retrofit horizons in process plants. In particular, it focuses on crude fractionation units. They have developed the well-known sequential technique of performing pinch analysis after fixing operating conditions, particularly including heating and cooling targets. Linnhoff *et al.* [4] suggested the problem table algorithm, composite curves, minimum utility, cost targeting, grand composite curves, pinch design method, CP-matrix with remaining problem analysis, stand-alone column optimization, shaft work targeting, and energy analysis

Pinch technology, a term introduced by Linnhoff and Vredeveld [5], originated from the concept that it is possible to establish design targets for minimum number of heat exchangers and minimum heat transfer area without committing to a heat exchanger network structure. Linnhoff and Flower [6] built upon this concept and proposed the ``problem table" representation for the temperature vs. enthalpy data and introduced the idea of a fixed minimum temperature difference for a given problem, now referred to as the ``pinch". A number of basic principles and tools were then added and have become the foundation of Pinch technology.

Ebrahim and Kawari [7] reported the employment of process energy-integration technology is an important approach for reducing energy consumption in the chemical process industries. In the process energy integration, pinch analysis has been proved to be efficient in developing the best integrated process designs for both new plants and retrofits.

Yu *et al.* [8] shows that decrease of pressure in distillation column, the temperature of both the condenser and the reboiler are also decreases leading to energy saving opportunities under the assumption that the product temperatures have little or no effect on rest of the flow sheet.

Duran and Grossmann [9] proposed a systematic procedure for simultaneously handling the problem of optimal heat integration while performing the parameter optimization of reactors into the process flow sheet.

The prediction of area requirements, on the other hand, is not as reliable. The algorithm based on the Bath formula Linnhoff *et al.* [10] is the method most widely used for that purpose. The method assumes vertical heat transfer between the composite curves, and the prediction of a minimum value for area requirements is valid only if all film heat transfer coefficients for the streams are equal Linnhoff and Ahmad [11] studied that no vertical heat transfer was required to achieve a minimum area for the network. The new network thus developed has lower capital and operating cost, i.e. the number of heat exchangers as well as the steam requirement is reduced largely. The use of pinch technology, energy cost savings of 40-50 % in new designs and six months payback in retrofits was achieved. This technology is widely used in western countries and it has great scope in Indian industries. It can definitely bring a revolution in the field of optimization of energy in the years to come.

Nielsen *et al.* [12] studied the practical industrial heat exchanger network (HEN) synthesis problem. The new framework is based on a new object oriented representation of the HEN synthesis that allows handling of models of different complexity. The proposed framework is implemented as the software tool HEN explorer that successfully is tested on problems of varying complexity.

Wang *et al.* [13] proposed novel design approach for the retrofit of HEN based on intensified heat transfer. The development of a mathematical model to evaluate shell-and-tube heat exchanger performances, and identification of the most appropriate heat exchangers requiring heat transfer enhancements in the heat exchanger network.

Yoon *et al.* [14] studied pinch analysis for an industrial ethylbenzene after analysis, an alternative HEN is proposed to save the energy. The alternative HEN is achieved by adding a new heat exchanger and changing operating conditions. This study benefited to reduce the annual energy cost by 5.6%.

Khorasany and Fesanghary [15] proposed a new hybrid methodology for synthesis of cost-optimal heat exchanger networks (HENs). The problem is solved in a two-level approach. The upper level generates the structure of HENs using harmony search (HS) algorithm. To evaluate the minimum cost of each structure, it is sent to the lower level in which the heat load of units and stream-split fractions are optimized by a combination of the HS and sequential quadratic programming (SQP). The results predicted from this study were able to find more economical networks than those generated by other methods.

Yerramsetty and Murty [16] studied the problems in process synthesis based on heat exchanger network synthesis (HENS). Nevertheless, the complexity of the HENS problem provides enough scope for the development of novel algorithms involving the application of specialized optimization techniques. The proposed model has been applied to some case studies available in the literature and the results of these studies are very encouraging.

Piacentino [17] presented a procedure for retrofit and relaxation of existing HENs. The existing HEN and a MER design were preliminarily diagnosed to assess energy targets. The innovative diagrams and indicators were proposed to identify improvement in directions. The Energy targets, heat transfer area and number of shells were simultaneously examined and relaxation paths were pursued at a limited extent, to minimize total costs.

Nordman and Berntsson [18] proposed a cost effective graphical method for heat exchanger network (HEN) retrofit design. The method uses information about the placement of heaters/coolers in the existing HEN to identify the potential for cost-effective retrofit. They have presented a detailed matrix calculation and same were compared with the results from the graphical method, and the graphical method is compared with earlier published work. The results obtained from this study showed that the pay back period increased by a factor of four, when heat saving increased from the level suggested by the advanced curves to the maximum possible heat recovery.

The objective of this work is to reduce consumption of energy with minimum capital investment in a Di Ethyl Thiophosphoryl Chloride (DETC) plant, by applying energy integration analysis. This is accomplished by minimizing the use of utilities and maximizing process-to-process heat transfer between existing hot and cold streams. It also satisfies the important constraint of maximum utilization of available heat transfer areas as far as possible with retrofit technology.

II. Operating Pinch Technology

This section presents the determination pinch, development of PTA, Grand composite curve and cascade diagram to determine minimum energy requirements.

A. Determination of the Pinch

Maximum energy recovery (MER) implies the minimum amount of utilities. If Q_{hu} is the heat supplied by hot utility and Q_{cu} is the heat removed by cold utility, then computation of energy targets involves determining the minimum values of Q_{hu} and Q_{cu} .this must be achieved subject to thermodynamic constraints Linnhoff et.al [4].

The thermodynamic data of hot and cold utilities is presented in Table 1. The maximum load of hot and cold utility requirement were calculated by summing the enthalpy changes of all cold streams ($\sum Q_{c)}$ and similarly for all hot streams ($\sum Q_{h)}$ respectively, then maximum hot and cold utility load were computed as:

Maximum Hot Utility = $\sum Q_h$ = 23.28 kW
Maximum Cold Utility = $\sum Q_c$ =19.06 kW

The above values maximize external utility usage, only for heaters and coolers in the network. The reduction in hot and cold utility loads mainly utilized for heat exchanged in the match.

TABLE I: TOTAL STREAMS INVOLVED IN DETC PLANT

Stream	T^{in} (K)	T^{out} (K)	C (MCp) Kj/S. K	Q Kj/S
H1	337	318	1.97	37.43
H2	318	303	1.94	29.10
H3	303	293	1.91	19.10
H4	323	293	0.18	5.40
H5	348	318	0.62	18.60
H6	323	293	0.05	1.50
H7	348	308	0.22	8.80
C8	293	310	3.25	55.25
C9	312	322	2.99	29.90
C10	290	340	0.78	39.00

In this contest, the first law of thermodynamics may be stated as:

Heat available in hot streams / utilities = heat required by cold streams / utilities.

Mathematically, it can be written as:

$$\sum Q_h + \sum Q_{hu} = \sum Q_c + \sum Q_{cu} \tag{1}$$

Eq. 1 gives computed value of heat load as:

$$\sum Q_{hu} - \sum Q_{cu} = \sum Q_c - \sum Q_h = 124.53 - 119.93 = 4.22 \text{ kw}$$

The minimum hot and cold utility requirement satisfying this equation is $\sum Q_{hu} = 23.28$ kw and $\sum Q_{cu} = 19.06$ kw , which assumes that heat can be transferred from any hot stream to any cold stream

This is not necessarily feasible as the second law of thermodynamics states that heat transfer can occur only from higher temperature to lower temperature, there must be a positive temperature difference. This positive driving force is always expected between hot and cold streams, for calculations of energy targets. The maximum amount of heat transfer possible with a stipulated minimum positive temperature difference (ΔT_{min}) must be determined and the remaining heat must be supplied by external utilities. The Problem Table Algorithm (PTA) represents the algebraic calculations of energy interactions within various temperature intervals.

B. Problem Table Algorithm (PTA)

Development of PTA is essential to identify pinch temperatures and minimum energy targets. The minimum hot utility and minimum cold utility requirement were calculated by assuming $\Delta T_{\min}=10^{O}C$. The results on implementing the PTA are compactly tabulated in Table 2.

The methodology of development of PTA is described as follows with known inlet temperature, outlet temperature and heat capacity flow rates.

1) Determination of temperature intervals (T_{int} in column A)

First, $\Delta T_{\min}/2$ subtracted from the hot stream temperature and $\Delta T_{\min}/2$ added to the cold stream temperatures respectively. These temperatures were arranged in descending order, omitting temperatures common to both hot and cold streams, which form the limits for various temperature intervals. This step ensures that an adequate driving force of $\Delta T_{\min}$ between the hot and cold streams for possible heat transfer within each interval Linnhoff et.al [4].

2) Calculation of net MC_P in each interval ($MC_{p,\text{int}}$ in column B)

The sum of MC_P values of hot streams were subtracted from the sum of the MC_p values of cold streams present in each temperature interval and entered in column B against the lower temperature limit of the interval. Thus, for any interval MC_P was calculated as follows

$$MC_{p,\text{int}} = \sum MC_{p,c} - MC_{p,h} \qquad (2)$$

3) Computation of net Enthalpy in each interval ($Q_{,\text{int}}$ in column C)

The values of $MC_{P,\text{ int}}$ (calculated in step 2) are multiplied by the temperature difference of respective interval to get a heat requirement in the interval.

4) Estimation of Cascaded Heat (Q_{cas} in column D)

The net enthalpy of an interval, subtracted from the enthalpy of previous interval to obtain the cascaded heat in that interval.

$$Q_{cas},_{I} = Q_{cas},_{i-1} - Q_{cas},_{i} \qquad (3)$$

5) Revision of Cascaded Heat (R_{cas} in column E)

The most negative Q_{cas} in column D, subtracted from each value in that column to obtain the revised cascaded heat in column E, thus

$$R_{cas},_{I} = Q_{cas,i} - \min(Q_{cas}) \qquad (4)$$

The cascaded heat needs to be revised since a negative heat transfer is thermodynamically infeasible

6) Determination of Energy Targets

First and last value of column E represents the minimum hot and cold utility requirements respectively.

The results are presented as follows:

Minimum hot utility ($Q_{h,\min}$) = 23.28 kW
Minimum cold utility ($Q_{c,\min}$) = 19.06 kW
Pinch point occurs at (T pinch) = 298 ^{o}K (25 ^{o}C)
Hot pinch temperature = 303 ^{o}K (30 ^{o}C)
Cold pinch temperature = 293 ^{o}K (20 ^{o}C)

TABLE II: PROBLEM TABLE ALGORITHM (PTA)

A	B	C	D	E
T int	MCp,int	Q int	Q cas	R cas
345	0	0	0	23.28
343	0.78	1.56	-1.56	21.72
332	-0.06	-0.66	-0.90	22.38
327	-2.03	-10.15	9.25	32.53
318	0.96	8.64	0.61	23.89
317	0.73	0.73	-0.12	23.26
315	-2.26	-4.52	4.4	27.68
313	0.99	1.98	2.42	25.70
303	1.64	16.4	-13.98	9.30
298	1.86	9.3	-23.28	0
295	-1.36	-4.08	-19.2	4.08
288	-2.14	-14.98	-4.22	19.06

C. Development of Grand Composite Curve (GCC)

A plot of column A vs. column E yields the Grand composite curve (GCC), as presented in Table 1.The figure 1.shows variation of temperature with heat flow. It is seen from same figure that increasing temperature increases enthalpy of heat source and decreases heat sink enthalpy. Figure 1 also indicate that heat interactions between both heat source and heat sink approaches to zero at corresponding temperature of 298 K.

The sign convention used for development of Grand composite curve is according to the guidelines of Shenoy [19].

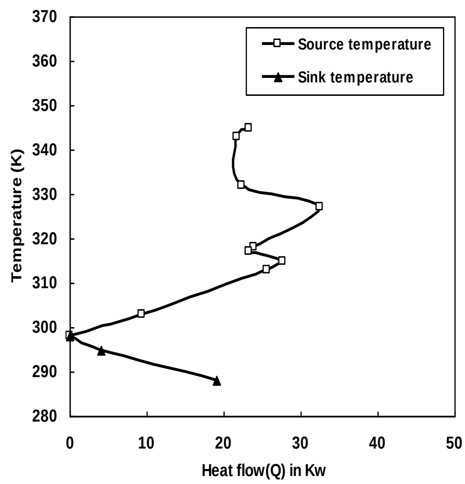

Fig. 1. Grand composite curve (GCC)

D. Development of Cascade Diagram

Figure 2.shows a Cascade diagram, it presents the heat flow information from different temperature interval, useful to identify the minimum energy requirement and pinch region.

The net heating and cooling requirement in each temperature interval indicates that transfer of excess heat to cold utility and supply of heat requirement from a hot utility.

Figure 2 depicts minimum energy requirements for hot and cold utilities. The corresponding values of minimum energy requirements for hot and cold utilities are found to be 23.28 kW and 19.06 kW respectively. The difference between those values corresponds to the first law analysis. The minimum heating and cooling loads determined from cascade diagram satisfy the second law analysis. This figure also provides the information of pinch temperature region, and observed to be between the eighth and ninth temperature intervals. This pinch temperature provides a guideline for decomposition of the design problem, above this pinch temperature shows only supply of heat, whereas below the pinch the rejection of heat to a cold utility.

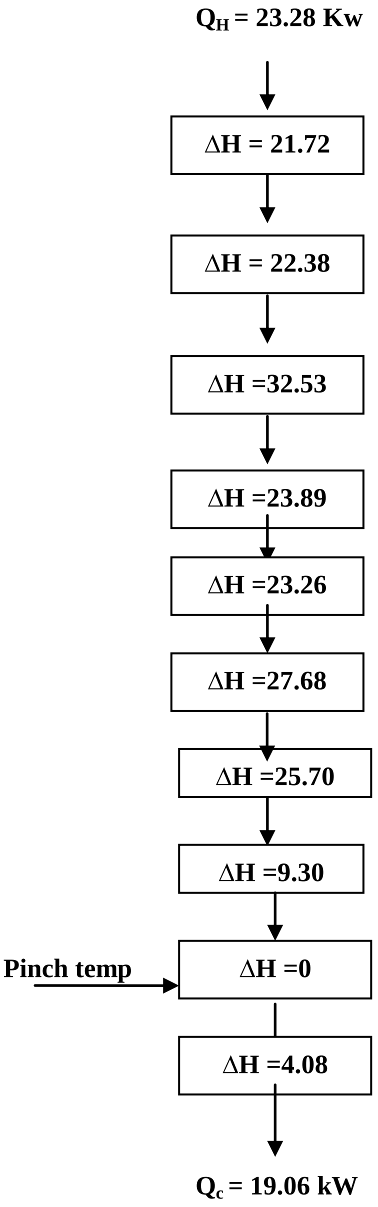

Fig. 2. A cascade diagram

III. Results and Discussion

The total enthalpy (heat content) of hot stream and cold stream are found to be 119.93 kW and 124.15 kW respectively. The first and last row of Table 2. shows similar values for minimum hot utility and minimum cold utility. This confirmed that results obtained from PTA analysis are matching satisfactorily with those obtained from the cascade diagram.

The reported values of minimum energy requirements for hot and cold utilities are 23.28 kW and 19.06 kW respectively. The PTA also confirmed that the potential to save energy from the current plant is very low, thus this analysis proved that the current utilization of the energy is at its optimal level.

IV. Conclusion

This paper addresses the application of retrofit design in a Diethyl Thiophosphoryl Chloride (DETC) plant to systematic application of the first and second laws of thermodynamics. The application of these techniques enables process engineers to gain fundamental insight into the thermal interactions between temperature intervals and the utility systems. The following conclusions were drawn from present work:

- In the present study pinch technology is found to be ineffective to save energy. The reason is that a present plant already running at optimum level and operates at maximum possible extent to save energy.
- The present plant awarded highly prestigious award from Energy conservation department, for excellence in energy savings and management. Hence, results reported in present paper confirmed that the application of pinch technology in retrofitting, support the truth that the plant is running at its best efficiencies.

Appendix

Cp	specific heat of fluid, kJ /kg K
GCC	grand composite curve
M	mass flow rate, kg/s
MER	Minimum energy requirement
HEN	Heat exchanger network
ΔH	Change in enthalpy, kW
PTA	problem table algorithm
Q	heat capacity, kW
R	revised
W	work done, kW
T^{in}	inlet temperature, K
T^{out}	outlet temperature, K
ΔT_{min}	minimum temperature difference, K
T_C, T_H	cold and hot stream temperature, K
T_{in}, T_{out}	temperature at inlet and outlet, K
subscript	
h,c	hot and cold streams
hu, cu	hot and cold utility
Q_{int}	intermediate heat capacity
Q_{cas}	cascade heat capacity

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