Modification of an Absorption Column

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Abstract:
Energy management is becoming an important goal of entrepreneurial activity.The increasingly limited energy resources demand managers of organisational systems to perform alternative measures in managing organisational systems. This article discusses the use of solution heat in absorption, integrating absorption with distillation, and improving the distillation column, so that steam is unnecessary for heating the reboiler. This method of absorber modification is based on the use of solution heat. It is composed of two steps:

- First step - Analysing the existing heat integration of the process
- Second step - Modification of the absorption column, by usefully utilizing solution heat during the process.

This analysis of solution heat in an absorber requires profitable integration during the process, and energy efficiency. The technique is based on the pinch-analysis method by using a grand-composite curve. Pinch analysis does not guarantee a global optimum solution, but it quickly proposes good ideas for heat integration during the process.

Key words: solution heat, integration, pinch analysis, absorber, emission

1 Introduction

Modification of the processes can reduce energy usage, and emissions of important components. It can be performed either by pinch analysis or by mixed integer nonlinear programming, MINLP.

Pinch analysis can increase the energy efficiencies of individual chemical processes. It has established itself as a highly versatile tool for process design. Originally pioneered as a technique for reducing the energy costs of new plants, it was later adapted for retrofits [1]. Pinch analysis quickly proposes good ideas for heat integration during complex processes, e.g. by using grand-composite curve. Thermodynamic analysis does not guarantee a global optimum solution because it cannot be used simultaneously with the material balance, but it quickly proposes good ideas for heat and power integration during complex processes. Combined heat and power design adds degrees of freedom to the optimisation method [2].

Havelsky [3] analysed the problem of energy efficiency evaluation in a trigeneration system for combined heat, cooling, and power production. Equations were presented for energy efficiency and primary energy savings. Separate and combined energy production was compared.

H.M. Kvamsdal and coworkers [4] studied post-combustion concepts based on the absorption of CO_2 in aqueous amine solutions and are considered the most mature technologies for CO_2 capture from power plants. Several steady-state models of the absorption process exist. However, a dynamic model is required in order to study the behaviour of the absorption process downstream of a power plant operating at varying loads.

A. Sala and co-authors [5] presented a study of maximum possible assurance and precision, the quench water-flow rate, which at present is cooled down through cooling towers and in the future through an absorption cooler driven by the waste-heat present in the exhaust gases.

J. Fathikalajahi and co-workers studied [6] a mathematical model for gas absorption and particle collection in a spray tower. The model includes a mass balance for gas phase (continuous phase), liquid phase (discontinuous phase), and the liquid film formed along the walls of the tower. Including radial motion with axial motion for droplets, it makes it possible to predict the location and amount of film formed along the column's wall. The significance of this model is when considering the real location of distributors at top of the tower, droplets size distribution and uniformity in droplet dispersion from the pressure nozzles. The results from the model are in good agreement with the experimental data.

The NLP algorithm [7], which is based on mathematical programming, can be used for rigorous process and heat integration a process. Although simultaneous, it is difficult to converge for complex and energy intensive processes because the number of variables increases with the number of combinations.

This paper studies the modification of an absorption column by using the pinch method. The modification method includes the use of solution heat in the absorber and heat integration during the process.

1.1 Nafta Lendava

Nafta Lendava, d.o.o., whose 100% owner is Republic of Slovenia, is organised as a firm with six daughter firms:

- Eko Nafta, d.o.o.
- Nafta Geoterm, d.o.o.
- Nafta Petrochem, d.o.o.
- Nafta Strojna, d.o.o.
- Nafta Inženiring, d.o.o.
- Nafta Informatika, d.o.o.
- Nafta Biodizel, d.o.o.

The daughter firms are active in the fields of storing and sales of oil derivatives, maintenance and well drilling, geothermal energy research, production of methanol and other products based on methanol, production of energy media, waste water purification, production of specialised machines and devices for chemical, oil and wood industry, project engineering, supervision and development of new information technology.
The group employs 512 workers, who help achieve the set goals with their commitment and creativity. Managing authorities of the company are: assembly, supervisory board and director.

ASSEMBLY of the firm is active within Government of Republic of Slovenia, who is the founder as well as the 100% owner of the firm [15].

As one of the daughter company's of Nafta Lendava d.o.o. , Nafta - Petrochem d.o.o. is the leading economic operator in petrochemical industry in Republic of Slovenia. Our production program is based on production of methanol as the basic raw material for production of formaldehyde and other petrochemical products.

The firm employs 225 people. The firm is divided in 11 organizational units:

1. Management
2. Methanol production
3. Formaldehyde production
4. Resins production
5. Energy sector
6. Waste water treatment
7. Quality control
8. Development
9. Economic and financial sector
10. Marketing
11. Logistics department [15].

1.2 Production

Principal activity of Manufacturing programme of Nafta Petrochem is:

- production of methanol
- production of 37% and 40% formaldehyde and Lendaform 70 (urea formaldehyde precondensate)
- production:
- urea formaldehyde (UF) adhesives
- melamine-urea-formaldehyde (MUF) adhesives
- phenol formaldehyde (PF) resin
- production and distribution of electric energy
- production of industrial and demineralized water, industrial air and vapour
- treatment of waste water from production processes

Methanol plant (presents figure 1) was built in 1979 after German technology LURGI and has the capacity of 165.000 t/a. We produce 99,99% methanol, which can also be used by some pharmaceutical firms.

Figure 1: Methanol plant [15]

In the formaldehyde department (presents figure 2) we have two plants for production of formaldehyde, with total capacity of 120.000 t/a of 37% formaldehyde, based on silver method. We produce various concentrations of formaldehyde from 37% through 40% to 60% solutions. In organisational unit Resins we produce urea-formaldehyde adhesives after our own procedures and technological processes developed within our firm. Joint capacity of technological processes is 120.000 t/a [15].

Figure 2: Formaldehyde department [15]

1.3 Vision and Goals

Business strategy of development of all our products with special emphasis on glues as demanded by our business partners.

Our global goal is therefore to ensure all our customers and other business partners are satisfied by offering the best possible technical and technologic service for our products. The strategy is marketing oriented. It is of extreme importance for us to lower the operating costs by ensuring all our production capacities are occupied and our offer expands. Another important factor is also establishment of an efficient system which includes:

- clear mission, vision, strategy
- efficiency of investments
- establishment of strategic alliances
- development of employees' skills and their affinity to the firm[15].

1.4 Mission

Our most important mission is an ecologically clean production of organic chemicals and its derivatives. NAFTA - PETROCHEM continues the mission of Nafta Lendava at its care for a clean environment. This is how we have been solving our important ecologic problems for many years. The development and setup of purification facilities go back to 1980. Nevertheless, in the past years we have only intensified the concern for solving ecological problems.

The problems of formalin and phenol vapour emissions have already been solved. Through some technical and technological improvements we have managed to substantially improve the performance of the purification plant, so that waste waters of NAFTA – PETROCHEM comply entirely with the Decree on the emission of substances and heat in the discharge of waste water from pollution sources (Official Gazette of the Republic of Slovenia 35/96).

More than 1.4 million EUR has been invested in ecological projects in the past three years. All projects give excellent results, which also show in the quality of the waste water to flow into stream Kopica, the quality of air and soil. It can thus be seen that a large part of the turnover, which NAFTA - PETROCHEM devotes to environment protection investments, proves the positive attitude of the community towards our natural environment [15].

1.5 Quality policy, environment protection policy and health and safety at work policy

Mission of Nafta Petrochem is to become one of the most important producers of urea formaldehyde, melamine urea formaldehyde adhesives and phenol formaldehyde resins in central Europe. We at Nafta Petrochem understand quality as a set of activities which joined into a whole ensure a high quality level of products and operations, employee, public, partners and customer satisfaction through their synergistic effects. Among the mentioned activities the most important are quality in classical sense, environment protection and occupational health. We entrench our position as a leading manufacturer of polymers at central Europe markets with our knowledge and development, international connections, flexibility and efficiency.

In order to achieve our goals, the primary and strategic task of all employees is to ensure quality of products and services, correct choice of product, on time deliveries, competitive prices and excellent technical and technologic service. For a successful and long lasting functioning of Nafta Petrochem it is essential to consider environmental issues as well, so as to adapt the philosophy that developed world accepts where quality products are only those that are produced in an environment friendly way and where protection, safety and health at work are ensured.

Nafta Petrochem follows and complies with all provisions of environmental and labour legislation, safety legislation (SEVESO II) and safety and health at work, which affects our production, employees, products and services. To monitor increase in environmental performance we set ourselves precisely measurable objectives. We evaluate our results and give ourselves strategic and performable objectives to ensure excellence in environmental and safety responsibility. A strategic goal of Nafta Petrochem is responsible management of the environment and control over natural resources, emissions and waste. When dealing with environment, our basic approach is to prevent all kinds of accidents and pollution. We lowered environmental, medical and safety risks which could harm the environment, employees and the population to the minimum.

The management and the employees all strive for:

- permanent improvement of environmental, safety and health business aspects,
- economical use of energy and raw materials and rational use of outer resources,
- modern and efficient waste management which does not harm the environment.

All employees working at or for Nafta Petrochem d.o.o. or in the name of Nafta Petrochem d.o.o. are familiar with our quality policy as well as with our environment protection, safety and health policy [15].

2 Energy management

In efforts for the improvement of position on the purchaser's market the companies must also consider accordance of operation with valid environment protected prescriptions in field of energy consument. The inclusion of enterprises in the international market, the care for reputation, that the enterprise profit with the environment protection and permanent development, places the politics of environment protection to the base of the professional politics. The environment protection and permanent development is so a basic component of the basic politics and it is confirmed by the highest administration agency. It is about the important decisions about the basic goals of operating and development. It is about the acceptance of basic principles values and rules. More than constraint of the state, the system is important, that is founded on the volunteer offer and creative cooperation. In the contemporary circumstances the creating of teams is getting most important for the creative cooperation, because they search the opportunities, solve the problems and in the end they take decisions.

The planning of energy objective begins with market research, it continues with the preparational functions (development) and so on to packaging, delivery, use and after cessation of life period of the product it comprehends the elimination on the environment friendly way[9]. The innovative operation is operation that, according to the production and all other its components is found on innovations. That's why the following characteristics indicate it:

- Each cost is basically unnecessary. It gets really unnecessary when we know and want to work in more intelligent way.
- Each product or procedure falls sooner or later out of use. So we must incessantly doubt about all given habits, although we count them (still) for perfect and correct. Otherwise we cannot achieve the contemporary quality of life.
- Everyone is concerned about the quality of life and for this reason (as possible as perfect!) Everyone is also concerned for quality of the whole operation and its all components. That's why we have to develop our brains and activate the creativeness of everyone.
- We should search constantly and everywhere the possible novelties! Only rare of them will become innovations, but without intended search, there will be even less of them, probably not enough.
- For this reason we should work as clever people and not as crazy people [17].

Just the energy management become our every day’s care and more and more numerous people care for the environment we live in.

Numerous case studies regarding the drafting and implementation of efficient energy use measures point to the fact that enterprises and institutions approach them partially, attached from other potential measures, without a complex analysis of the entire issue of energy consumption and supply. Such a partial approach can lead to technically and economically inappropriate solutions. The foundation of an energy efficiency program for an enterprise or an institution must therefore be an energy audit, whereby the main component is represented by a proposal of an action plan with specified priorities, which provides guidelines for the following issues in entrepreneurial or institutional organization:

- organizational changes
- or quality investment decisions.

The basic aim of the energy audit is to increase the process efficiency or rather lower the loss of energy. This is why we determine where in the system the energy was used efficiently and where energy losses were made on the basis of mass and energy balances.

Possible measures, which the energy audit can encompass, include the fields of organizational measures, reconstruction of existing installations and buildings, the use of modern equipment and techniques as well as the introduction of new technologies. In data acquisition, the quality of the cooperation between the conductor of the energy audit and the expert team working for the entity requesting the audit is of vital importance. The authenticity of data is a key to the successful execution of an energy audit. The presentation of an energy audit is an event, whereby we are educating the customer, investor, business financier, the user and in fact all participants in the decision-making process with regard to efficient energy use and investments. A presentation of an energy audit is the first step to the implementation of organizational measures and establishment of favorable conditions for the implementation of investment proposals of the energy audit.

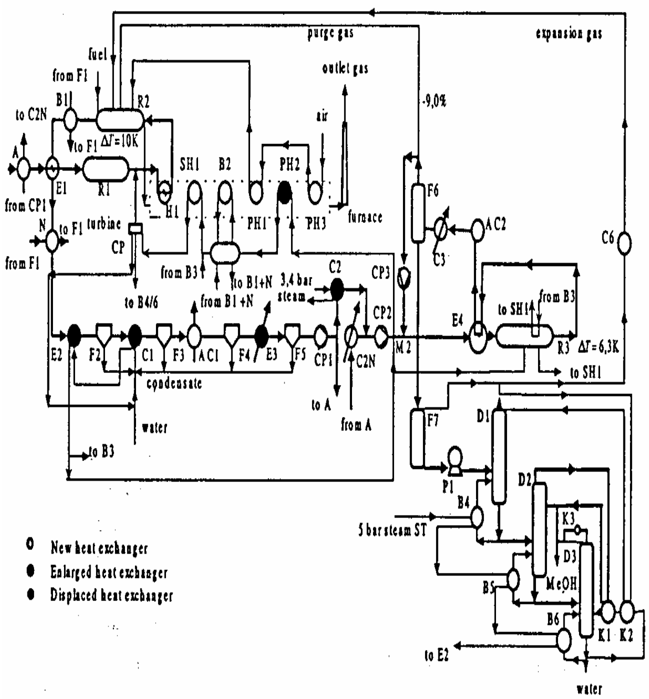

Figure 2: Methanol process flow diagram for optimal Retrofit [18]

The care for the enterprise and so the care for environment and permanent development claim (dialectic) system reflection:

- The creative collaboration enables the use of different viewpoints, so the totality of reality is better realized,
- The specialists are inevitable, but for themselves only partly useful, because they see and consider only that part of reality, that the chosen point of view enables them because of the specialisation
- Without collaboration they can not supplement to achieve the synergy, that they can not manage individually, but it is urgent,
- The environment protection is realized more successfully with the system of viewpoints, that many individually creatively enforce them.

3 Absorption column

Absorption is a process by which one or more components of a gas mixture are transferred to a liquid where it is soluble [8]. The operation of absorption can be categorized, on the basis that the interaction is natural between absorbent and absorbate (Fig. 1), into the following two types:

- physical absorption: the component being absorbed is more soluble in the liquid absorbent than the other gas components with which it is mixed, but does not react chemically with the absorbent.
- chemical absorption: is characterized by the occurrence of a chemical reaction between the gas component being absorbed and a component in the liquid to form a compound.

To date, absorption is still a powerful tool for gas separation and purification. However, current processes for the enhancement of gas liquid absorption rate are still limited to those chemical reactions, which occur in the liquid phase between gas component and liquid solution.

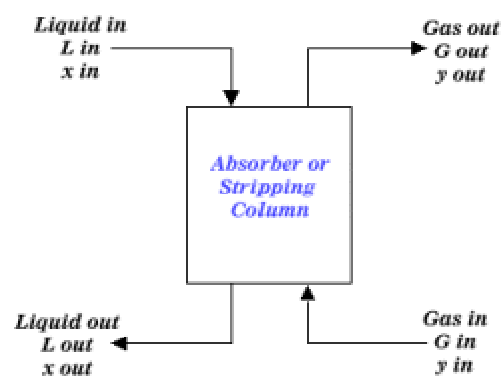

Figure 3: The absorber.

Adsorption is present in many natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins, and water purification. Adsorption, ion exchange, and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column [8, 10].

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding).

Adsorption is usually described through isotherms, that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials.

The first mathematical fit to an isotherm was published by Freundlich and Küster (1894) and is a purely empirical formula for gaseous adsorbates,

$$x_{ab}/m = kP^{1/n} \quad (1)$$

where x_{ab} is the quantity adsorbed, m is the mass of the adsorbent, P is the pressure of adsorbate and k and n are empirical constants for each adsorbent-adsorbate pair at a given temperature [8]. The function has an asymptotic maximum as pressure increases without bound. As the temperature increases, the constants k and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface.

If absorption is a physical process not accompanied by any other physical or chemical process, it usually follows the Nernst partition law: the ratio of concentrations of some solute species in two bulk phases in contact is constant for a given solute and bulk phases:

$$[c_1]/[c_2] = \text{constant} = K_N \quad (2)$$

The value of constant K_N depends on temperature and is called partition coefficient. This equation is valid if concentrations are not too large and if the species 'c' does not change its form in any of the two phases '1' or '2'. If such a molecule undergoes association or dissociation then this equation still describes the equilibrium between 'c' in both phases, but only for the same form - concentrations of all remaining forms must be calculated by taking into account all the other equlilibria. In many technologically important processes, chemical absorption is used in place of the physical process, e.g. absorption of carbon dioxide by sodium hydroxide - such processes do not follow the Nernst partition law.

Packed columns are most frequently used to remove contaminants from a gas stream (absorption). However, packed columns can also be used to remove volatile components from a liquid stream by contacting it with an inert gas (stripping). Raoult's Law can be used to estimate the equilibrium data for absorption or stripping applications. François-Marie Raoult, Raoult's law states: the vapour pressure of an ideal solution is dependent on the vapour pressure of each chemical component and the mole fraction of the component present in the solution [11].

Once the components in the solution have reached chemical equilibrium, the total vapor pressure of the solution is:

$$P_{\text{solution}} = P_{1,\text{ pure}}\, x_1 + P_{1,\text{ pure}}\, x_1\, P_{1,\text{ pure}} + \ldots \quad (3)$$

and the individual vapour pressure for each component is:

$$P_i = P_{i,\text{ pure}}\, x_1 \quad (4)$$

where

$P_{i,\text{ pure}}$ is the vapour pressure of the pure component
x_1 is the mole fraction of the component in solution

Consequently, as the number of components in a solution increases, the individual vapour pressures decrease, since the mole fraction of each component decreases with each additional component. If a pure solute which has zero vapour pressure (it will not evaporate) is dissolved in a solvent, the vapour pressure of the final solution will be lower than that of the pure solvent. This law is strictly valid only under the assumption that the chemical interaction between the two liquids is equal to the bonding within the liquids: the conditions of an ideal solution. Therefore, comparing actual measured vapour pressures to predicted values from Raoult's law allows information about the relative strength of bonding between liquids to be obtained. If the measured value of vapour pressure is less than the predicted value, fewer molecules have left the solution than expected. This is put down to the strength of bonding between the liquids being greater than the bonding within the individual liquids, so fewer molecules have enough energy to leave the solution. Conversely, if the vapour pressure is greater than the predicted value more molecules have left the solution than expected, due to the bonding between the liquids being less strong than the bonding within each.

4 Modification of absorption column using pinch analysis

Pinch analysis is a methodology for minimising the energy consumption of chemical processes by calculating thermodynamically feasible energy targets (or minimum energy consumption) and achieving them by optimising heat recovery systems, energy supply methods and process operating conditions. It is also known as process integration, heat integration, energy integration or pinch technology [11]. The process data is represented as a set of energy flows, or streams, as a function of heat load (kW) against temperature (^oC).
This data is combined for all the streams in the plant to give composite curves, one for all 'hot streams' (releasing heat) and one for all 'cold streams' (requiring heat). The point of closest approach between the hot and cold composite curves is the pinch temperature (pinch point or just pinch), and is where design is most constrained.

This analysis of solution heat in an absorber requires profitable integration in process and energy efficiency. The technique is based on the pinch-analysis method by using a grand-composite curve. Pinch analysis does not guarantee a global optimum solution, but it quickly proposes good ideas for heat integration during the process.

This method of absorber modification is based on the use of solution heat. It is composed of these two steps:

- First step - Analysing the existing heat integration during the process
- Second step - Modification of absorption column, by usefully using the solution heat during the process.

Figure 3: Oil plant [16]

Analysing the existing heat integration (first step) during the process includes all the energy streams in a grand composite curve, so the energy efficiency can be analysed (Fig. 2).

The fraction of the maximum possible internal integration during the process can be estimated using equation 5, using pinch analysis, and a grand composite curve [14]:

$$f_{MPI} = (\min\Sigma Q - Q_{HU}) / \min\Sigma Q \quad (5)$$

f_{MPI} being the fraction of the maximum possible integration in the process, $\min\Sigma Q$ the minimum sum of heat flow rates of hot (ΣQ_i) or cold (ΣQ_j) streams whichever is smaller, Q_{HU} the hot utility flow rate (of the heighest level; Fig. 2) in kW.

The maximum possible heat flow rate Q_{MPI} can be calculated using equations 5 and 6:

$$Q_{MPI} = f_{MPI} \cdot \min\Sigma Q \quad (6)$$

Step two includes modification of the absorption column, by usefully using the solution heat during the process. The stream of the existing solution heat in the absorber (stream - existing absorber: Fig. 3), which represents the existing solution heat during absorption can be taken out from the GCC of Fig. 2 and a graphical individual taken in the new GCC without solution heat. The graphical profile of the existing solution heat stream represents possible modification of the absorption column. The existing absorption column can be operated at higher pressure and, therefore, the absorption efficiency and solution heat were higher. The gas emissions of important components can be lower from the absorption (gas out in Figure 1). The stream of solution heat in the modified absorber will increase the temperature profile from 66 ^{o}C to about 90 ^{o}C (stream: modification of absorber). The most important aim is that the heat flow of the solution heat can approach the hot utility flow rate (Q_{HU}). The fraction of the maximum possible integration during the process (f_{MPI}) can be focused to 1 – to maximal heat efficiency (eq. 5). Different process design modifications depend on different case studies.

The new modification stream, after the rising the pressure to higher bars, can be put in GCC, which include the all energy streams and the new design is more efficiently (Fig. 4). The fraction of the maximum possible integration in the process (f_{MPI}) was 1, because the hot utility flow rate (Q_{HU}) was zero (see equation 5).

4 Conclusion

The method of absorber modification during the processes can reduce energy usage, emissions of important components, and enhance product production. This method of absorber modification is based on the use of the solution heat. It is composed from these two steps:

- First step - Analysing the existing heat integration during the process
- Second step - Modification of absorption column, by usefully using solution heat during the process.

This analysis of solution heat in the absorber requires profitable integration during the process, and energy efficiency. The technique is based on the pinch-analysis method by using a grand-composite curve. Pinch analysis does not guarantee a global optimum solution, but it quickly proposes good ideas for heat integration during the process.

The use of solution heat during absorption can be useful during the process, for example, heat integration with distillation, and an improved distillation column, so steam is unnecessary for heating the reboiler.

The most important aim of this method is approached by maximal heat efficiency. Hot utility can be saved by using this method of absorber modification.

The modified silver formaldehyde process can increase additional production by 5 % and save heat utility.

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