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Capital Cost Evaluation for Optimum Process Design of Cryogenic Air Separation

Diploma Thesis
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London, SS 2012

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Nomenclature

POT	Payout time	[\$]
$\alpha_{i,n}$	volatility parameter of species i on tray n	[—]
\dot{e}_{ij}	Energy flow of to equipment i from energy carrier j	[kW]
\dot{m}_i	Mass flow of component i	$[\frac{kg}{s}]$
γ_i	liquid activity coefficient of species i	[—]
φ_i^0	reference vapour fugacity coefficient of species i	[—]
φ_i	vapour fugacity coefficient of species i	[—]
a	Annuity	[\$]
A_n	parameter in K_b model for tray n	[—]
B_n	parameter in K_b model for tray n	[K]
$b_{i,n}$	parameter for CMC equations	[—]
C_B^i	Reference cost of equipment i	[\$]
C_E^i	Cost of equipment i	[\$]
C_{EC}^i	Mass specific cost of energy carrier i	$[\frac{\$}{kW}]$
C_{RM}^i	Mass specific cost of raw material i	$[\frac{\$}{kg}]$
C_0	Initial value of an investment	[\$]
C_1	Reference equipment cost at time 1	[\$]
C_2	Reference equipment cost at time 2	[\$]
C_n	Final value of an investment	[\$]
C_P	Total process cost	[\$]

Nomenclature

C_P^0	Reference process cost	[\$]
C_{0e}	Present value of all expenses	[\$]
C_{0r}	Present value of all revenues	[\$]
C_{EC}	Total cost of energy	[\$]
C_{FILL}	Cost of raw materials to fill the process	[\$]
$C_{i,n}$	parameter for CMC equations	[—]
C_{RM}	Total cost of raw materials	[\$]
f_C^i	Design complexity correction to equipment cost	[—]
f_M^i	Material selection correction to equipment cost	[—]
f_P^i	Pressure correction to equipment cost	[—]
f_T^i	Temperature correction to equipment cost	[—]
f_i^L	liquid fugacity coefficient for species i	[—]
f_i^V	vapour fugacity coefficient for species i	[—]
F_j^L	Liquid feed to tray j	$[\frac{mol}{s}]$
F_j^V	Vapour feed to tray j	$[\frac{mol}{s}]$
$F_{p,i}$	liquid compressibility factor for species i	[—]
i	Interest rate	[%]
I_1	Cost index at time 1	[—]
I_2	Cost index at time 2	[—]
$K_{b,n}$	K_b parameter	[—]
$K_{i,n}$	equilibrium ration for species i on tray n	[—]
L_j	Liquid flow from tray j	$[\frac{mol}{s}]$
M^i	Equipment specific factor	[—]
N_E	Number of equipment pieces in the process	[—]

Nomenclature

N_{RM}	Number of raw materials	$[-]$
NPV	Net present value	$[\$]$
p^S	system pressure	$[Pa]$
p_i^S	vapour pressure of species i	$[Pa]$
q	Interest factor	$[-]$
Q^i	Specific quantity for equipment i	$[variable]$
Q_B^i	Equipment specific reference quantity	$[variable]$
Q_P	Process capacity	$[\frac{kg}{h}]$
Q_P^0	Reference process capacity	$[\frac{kg}{h}]$
R_n^L	liquid withdrawal parameter for stage n	$[-]$
R_n^V	vapour withdrawal parameter for stage n	$[-]$
S_b	base splitting factor	$[-]$
S_j^L	Liquid side flow from tray j	$[\frac{mol}{s}]$
S_j^V	Vapour side flow from tray j	$[\frac{mol}{s}]$
S_n	splitting factor for stage n	$[-]$
$S_{R,n}$	relative splitting factor for stage n	$[-]$
T	system temperature	$[K]$
t_{op}	Time of process operations	$[s]$
V_j	Vapour flow from tray j	$[\frac{mol}{s}]$
x	Degression coefficient	$[-]$
x_i	liquid mole fraction of species i	$[\frac{mol}{mol}]$
y_i	vapour mole fraction of species i	$[\frac{mol}{mol}]$

Abstract

here comes an abstract

1 Introduction

Air separation technology, or – more generally speaking – gas separation technology, lies at the heart of the modern process industry. Highly pure oxygen and nitrogen are used in many industrial applications. Modern power generation processes, such as the currently developed OXICOAL process, rely on incineration with pure oxygen to produce flue gases with very high carbon dioxide content for further storage. Nitrogen is essential to many widely used processes such as the production of ammonia in the Haber-Bosch synthesis, as fertilizer or in many organic reactions.

The paper following this introduction is structured as follows....

Figure 1.1: Demand for industrial gases. []

2 Air separation technology

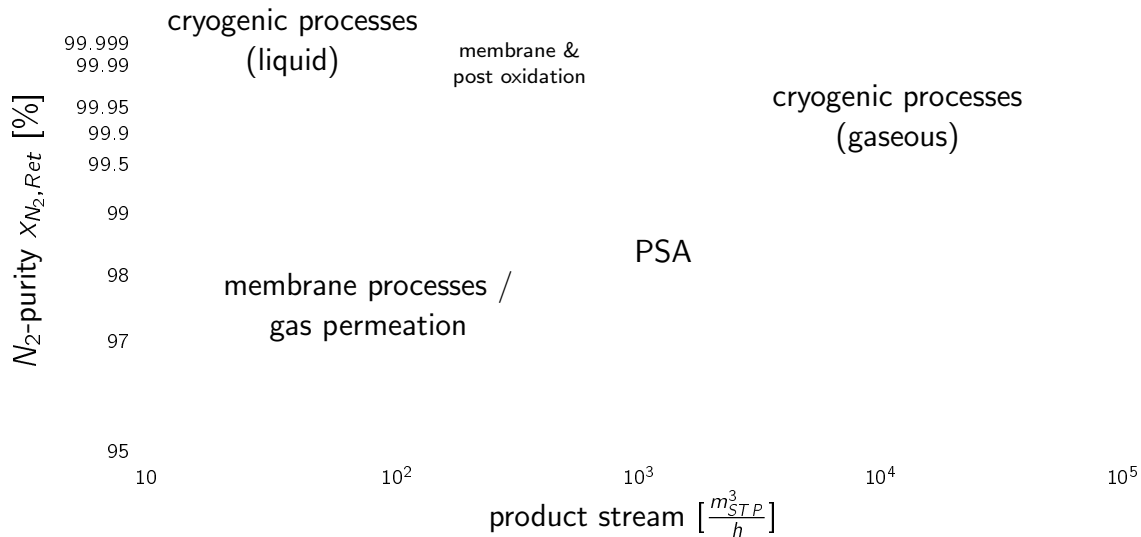


Figure 2.1: Comparison of Air Separation Technologies [8].

There are several ways besides cryogenic air separation that can be employed to separate gas mixtures. In this chapter different competing technologies and their main applications will be discussed. The predominately used technologies are cryogenic distillation, pressure swing adsorption (PSA) as well as gas permeation (GP). In the distillation process the gas is first liquefied. Separation is achieved by the different concentration differences in vapor and liquid phase. PSA relies on the different affinities of gaseous species to adsorb to certain materials in order to extract a component from a mixture. During gas permeation membranes are used. Each species migrates in different quantities through a given membrane depending on process parameters and membrane structure.

fig. 2.1 illustrates the most economically viable processes depending on product purity and product stream volume. It can be seen that alternative air separation processes cannot supply the high quality or quantity of the cryogenic process. Due to that cryogenic air separation is thought to be the main supplier of highly pure gases in industrial quantities for years to come [4]. The alternative processes however offer some very appealing characteristics, which make them the favorable choice when lower quantities of product or more moderate purity is required. The cryogenic process is always connected with a considerable energy consumption for the liquefaction and compression. Due to that smaller implementations of the process are very unlikely to yield economically sound solutions to a separation problem.

add citation



Figure 2.2: Schematic representation of the cryogenic air separation process.

2.1 Cryogenic air separation

Cryogenic Air Separation finds applications over a great variety of industries among others refining, petrochemicals, medical, food & beverages and environmental [10]. Furthermore prospective processes for power generation from fossil sources in form of the integrated gaseous combined cycle (IGCC) integrates the air separation process in order to enable more environmentally friendly power generation [6].

As can be seen in fig. 2.2 double effect heat integrated distillation column lies at the heart of the air liquefaction processes. It consists of a high pressure column (HPC) operating at 0.68 MPa and temperatures below 130 K as well as a low pressure column (LPC) which operates at around 0.13 MPa and comparable temperatures. In order to also attain highly pure argon as a product the process may also include a crude argon column (CAC) which works at slightly lower pressures than the LPC.

The plant air entering the process is initially purified, where carbon and nitrogen oxides as well as solid contaminants are removed, and then compressed to process conditions. The compressed air is then cooled against product streams namely liquefied nitrogen, oxygen and argon. The air stream is then divided into several sub-streams. One of those is fed into the HPC bottom, while another is expanded by means of a turbine and further cooled down through the Joule- Thompson effect. Aside from further cooling energy from the initial compression is thus partially recovered. This expanded air stream is then fed into the LPC. At the bottom of the LPC liquid as well as gaseous oxygen are

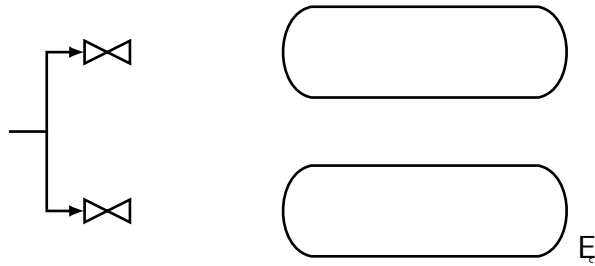


Figure 2.3: Schematic representation of the PSA process.

Figure 2.4: Schematic representation of the PSA process.

recovered as desired products. The bottom and top streams from the HPC are made up of an oxygen rich liquid as well as liquid nitrogen. The liquid nitrogen stream is led through a heat exchanger and fed as reflux into the top of the LPC. The bottom stream is, after heat integration, partially fed into the LPC as well as CAC. From the lower part of the LPC a side stream is drawn and led into the bottom of the CAC. At the same point the reflux from the CAC is fed back into the LPC [11].

2.2 Pressure swing adsorption

Pressure Swing Adsorption has been employed to separate gaseous mixtures for some time. During the 80's and 90's commercial applications for the production of oxygen or nitrogen have gained more and more attention. Especially the ability to construct very compact units the size of a briefcase, have led to the implementation of PSA processes for treatment of asthma patients or other medical appliances. But also larger scale plants have successfully been utilized, for example in the paper industry during the de-lignation of pulp. It remains true however, that for large scale industrial settings with high product quality demands, cryogenic separation remains the most viable alternative.

Separation is achieved during the PSA process by adsorption of one component in the mixture to a given bed. Once the bed is saturated with the adsorbing species, it has to be regenerated in order to continue production. The ability to adsorb a certain species is dependent on the system pressure. At higher pressures more gas can be adsorbed than at lower pressures. Thus by reducing the pressure in the reaction vessel, the Adsorbent can be regenerated.

In order to avoid non-continuous processes, two or more reaction vessels are employed. Therefore the saturated vessel can be regenerated, while the other one continues production. By alternating

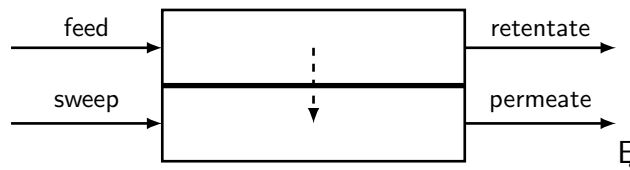


Figure 2.5: Membrane unit for gas permeation.

adsorption and regenerating in the different vessels continuous production can be achieved. A schematic for a simple two bed cycle is shown in fig. 2.4. Ambient air is first led through the first reaction vessel at the elevated pressure. Within the vessel nitrogen is adsorbed until saturation is reached. At that point the ambient air is led through the second vessel. A fraction of the product stream is fed into the first vessel and used as sweep for the regeneration of the adsorbent at lower pressure.

Depending on the size of the process two different pressure level are used. One cycle adsorbs the nitrogen at a pressure of approximately 7.5 bar while regeneration is done at ambient pressure. Within the alternative approach adsorption occurs under ambient condition, while for the regeneration step a vacuum pump reduces the vessel pressure. This process is called Vacuum Pressure Swing Adsorption (VPSA).

An important role when designing the product is the choice of the adsorbent. For almost all current applications of PSA aluminosilicates or zeolites have been designed, tailored to the specific separation task. Their main advantages include a high selectivity towards a specific gas to be adsorbed as well as a very homogenous distribution of diameters in the molecular sieve.

2.3 Gas permeation

find paper: DOI: 10.1002/cite.330480804

add reference: ISBN-10: 354034327X

The separation of mixed gases by membrane process is called gas permeation. Its main strength in comparison with alternative processes are the low energy consumption and the possibility to produce flexible mobile units. As mentioned before it is not however capable of producing high quantity highly pure product streams. As fig. 2.1 illustrates the main application for the gas permeation process are small to moderate product streams at intermediate purities.

fig. 2.5 shows the schematic for a single stage membrane unit. Within the feed stream the gaseous mixture is fed into the unit, which can quickly be implemented. Within the unit one or more species migrate favorably through the membrane. In this case mostly dense polymer membranes are employed used. There have been some impressive results with metallic membranes, but due to the very high material costs they have not been adapted by the industry. Furthermore, since gaseous phases often have rather small molecular species, porous membranes cannot achieve desired separation. The driving force the separation process is a difference in partial pressure or species activity across the membrane. According to the molecular structure of each species, the structure of the separating

membrane as well as the process parameters pressure and temperature, they permeate through the membrane in different quantities.

The process of permeation can be subdivided into three separate steps. Sorption at the membrane / feed interface, diffusion through the mostly dense polymer membrane and finally desorption at the permeate side of the membrane.

3 Process design under uncertainty

For many real life decisions uncertainty plays a major role. As one might react differently to various scenarios that might occur in the future. In terms of process design two types of uncertainties can be distinguished. *Internal* and *external* uncertainties., where the internal ones refer to transfer-coefficients, diffusivities, efficiencies and other process parameters that cannot be exactly predetermined or that might change over time. External uncertainties denote all aspects that are not directly part of the process such as future prices for raw materials, energy, or the marketed product. In addition feed composition, pressures or ambient conditions are likely to change during process operations. All these factors will have an impact on operations and profitability of a given process.

The aim of the process design is to ensure feasibility for all possible realizations of the uncertain parameters. The naive way to account for such uncertainties is to find an optimal solution for nominal values of the uncertain parameters and then employ heuristic over design in the hope of maintaining feasibility and remain close to an optimal solution. However in practice this strategy will almost always fail to deliver an nearly optimal design [5].

Therefore several approaches have been developed to incorporate an rational approach to include flexibility in the design process. Ideally the design optimization would simultaneously recognize *feasibility*, *controllability*, *reliability* and *safety* in an multi-objective optimization. Although all the aspects stem from similar principles they differ considerably in their manifestation. While feasibility describes the mere possibility to operate a process under the defined conditions, controllability denotes whether those conditions can be reached from an initial starting point and gives a measure for quality and stability of the process in connection with the dynamic response to process disturbances.

Reliability and safety are qualities of a process that describe the consequences of unit failure on the operations of the process or the severity of those consequences with regard to how harmful they might be for personnel, environment or wildlife.

While all these aspects should be considered during the design phase it is questionable how well they all can be incorporated into a single optimization scheme.

3.1 Earlier work

In its most general form the design problem for chemical processes can be written as:

$$\begin{aligned} &\underset{d,z}{\text{minimize}} && C(d, z, x, \theta) \\ &\text{subject to} && h(d, z, x, \theta) = 0 \\ &&& g(d, z, x, \theta) \leq 0 \end{aligned} \tag{P 1}$$

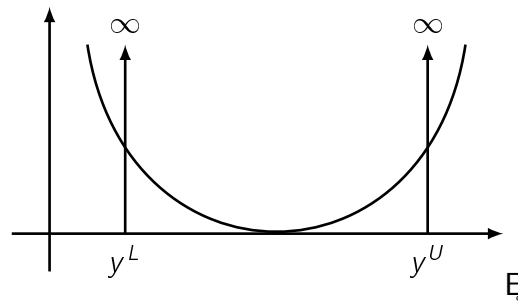


Figure 3.1: test. [2]

Where d , z are the vectors for design and control variables respectively. The vector x contains all states specified by the physical process model and θ is comprised of all parameters subject to uncertainty. The aim of the program is therefore to identify the optimal set of design variables d for which by manipulating the control variables z feasible operations can be ensured for all possible realizations of the uncertain parameters θ .

Much research has been done within the field of process design under uncertainty that meet the requirements of optimal process design to different degrees. Most frequently used was the stochastic approach. If the probability distribution functions of all uncertain values is available, different minimization schemes can be employed. Kittrel and Watson [] thought the optimal design to be the one which minimizes the expected value of cost. Wen and Chang [] proposed a *relative sensitivity* of the cost – defined as fractional change in the cost function from its nominal value – and minimized either the expected value or the maximum probable value of this fractional change. Other researcher included penalty functions to drive a solution away from constraint violations and then perform an unconstrained minimization or employ Monte Carlo simulation to find suitable over-design factors []

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All the aforementioned approaches do not account for a fact derived from the actual application of the problem. In chemical processes, once a certain design is determined by the design variables d , the control variables z can still be adjusted to meet feasible operations once the uncertain parameters are realized. It is therefore advantageous to include this basic difference between the design and control variables in the mathematical formulation of the program. Again several different approaches have been studied. A summary of some of those can be found in []

add ref: flexibility

As mentioned before the main aim in terms of an design engineer when considering uncertainty must be to ensure feasible operations of a process for all or the most likely realization of the uncertain parameters with the most attractive investment scheme.

4 Process economics

Aside from question whether a certain process is capable of producing products according to its specifications, it needs to be investigated if it does so in an economically viable manner. The modeling of process economics is a powerful tool to estimate project profitability. The evaluation of process economics has three major aims in the design phase.

- Compare design options with regard to profitability.
- Economically optimize a given design.
- Estimate project profitability

In any case the total cost of the project as well as the cash flow structure will have to be analyzed to supply an accurate estimate of the economic conditions. Furthermore an adequate measure to compare and analyze a project in economic terms needs to be employed.

The following sections will first describe how to estimate the total project cost in different stages of the design process. It is evident that, as the more information about a given process becomes available, the accuracy of any cost estimate will increase as well. During the design phase of a process roughly three different stages of cost estimation can be formulated.

- An estimate before designing the process yields an order of magnitude estimation for supporting market research efforts. Error $> 30\%$
- Estimate in the early design phase based on essential process equipment. Error $\pm 30\%$
- Estimate based on an advanced flowsheet and relevant process parameters. Error $\pm 20\%$

Once detail engineering commences, even more accurate calculations with errors reducing to $\pm 5\%$ can be undertaken^[7]. At that point a concrete process option will have to be chosen and the investment decision will already have to be made. All optimization measures within the scope of this thesis will have concluded at that time.

Within sec. 4.1 first we will take a look at how the total cost of a chemical process might be estimated at different design stages. Subsequently in sec. 4.2 the different ways of evaluating a certain investment options and estimating a projects profitability will be discussed.

4.1 Project cost

An important factor in every given project is the total cost. During the design of a chemical process many important aspects of the future cost structure are unknown, as the final design is in development.

In general the total cost of implementing and operating a production site can be broken down into several subcategories.

- Battery limit investment
- Utility investment
- Off-Site investment
- Engineering fees
- Working capital

4.1.1 Before process design

Before any details about the process to be implemented are known, an estimate can only give an order of magnitude towards cost to be expected. The cost of the new process C_P can be related to the cost of a reference process C_P^0 by

$$C_P = C_P^0 \cdot \left(\frac{Q_P}{Q_P^0} \right)^x. \quad (4.1)$$

The degression coefficient x needs to be correlated from historical data.

As the overall price structure will change over time, the reference price will not reflect the current market situation. In order to adjust for that shortcoming several price indices are published all over the world. Some of those tailor to special branches of the industry, others give a picture of the price-development in a economy as a whole. The price ration of the prices at different times will then be equal to the ration of the price indices at the respective times

$$\frac{C_1}{C_2} = \frac{I_1}{I_2}. \quad (4.2)$$

For each index an somewhat arbitrary reference year is chosen. Among the most common indices are the Marshall & Swift index, the Nellson-Farrar-Index or the Chemical Engineering index. Some exemplary values for these indices are given in tab. 4.1. As one can see the development within the process industry very well matches the development in the economy as a whole, which is why for this rough estimate general indices should suffice.

4.1.2 During process design

Once the future design has been broken down to fewer potential options and first process flowsheets are available a more elaborate approach becomes possible.

year	Marshall & Swift Installed Equipment Index 1926 \equiv 100		Nelson-Farrar Refinery Construction Index 1946 \equiv 100	Chemical Engineering Plant Cost Index 1957 \equiv 100
	all industries	process industry		
1975	444	452	576	182
1980	560	675	823	261
1985	790	813	1074	325
1990	915	935	1226	358
1995	1027	1037	1392	381
2000	1089	1103	1542	394
2001	1093	1107	1565	396

Table 4.1: Price indices and their development.

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Battery limit investment

The battery limit investment denotes all investments necessary to have all required equipment for process operations installed on-site. This includes structures necessary to house the process as well as delivery and installation of all individual assets. One major part of these cost will be the process equipment. As the exact manufacturers and models of the equipment will not be known in early design stages, an approach similar to the one in sec. 4.1.1 still needs to be employed. In contrast to before now the cost for individual pieces of process equipment will be considered separately. Each piece of equipment will have an specific feature that most influences its cost. For vessels and reactors this might be volume, while for heat exchangers the required heat exchange area is essential. The price for an piece of equipment i C_E^i can again be approximated by a simple power law

$$C_E^i = C_B^i \left(\frac{Q_E^i}{Q_B^i} \right)^{M^i} \quad (4.3)$$

A reference price C_B^i is multiplied by the determining quantity Q^i normalized to a reference state Q_B^i and raised to the power M^i specific to each piece of equipment. Reference prices and quantities for various installations can be obtained from literature.

add reference

If information on the process conditions are available, they also can be considered in price calculations. Aside from the mere size of the equipment the process conditions will also have an affect on the expected cost. The predominant factors to that respect are pressure, temperature and the question wether corrosive or reactive media, which will require more resistant materials, will be present. Furthermore if a more detailed choice of process equipment is known this is considered as well. For example an plate-fin heat exchanger might be more expensive than a tubular model with the same heat-exchange area. In order to account for all those effect a form factor f_F is applied to the equipment cost

$$C_E^i = C_B^i \left(\frac{Q_E^i}{Q_B^i} \right)^{M^i} f_F^i = C_B^i \left(\frac{Q_E^i}{Q_B^i} \right)^{M^i} \underbrace{(1 + f_C^i + f_M^i + f_P^i + f_T^i)}_{=f_F^i} \quad (4.4)$$

Where f_F denotes the form factor, f_C corrects for design complexity, f_M for material selection, f_P adjusts for extreme pressures and f_T for temperature.

As in the previous section all reference prices need to be corrected to compensate for the temporal price development, Here again the already discussed indices are used. Furthermore can regional changes in price structures be considered. Here again have correction factors to prices in an reference region in the world (e.g. USA) been published.

add ref.

In addition to the purchased cost, the costs for installing the process equipment have an significant effect on the total needed investment of the process. These installation costs include:

- Installations costs
- Piping ,valves and electrical wiring
- Control system
- Structures and foundations
- Insulation and fire proofing
- Labour fees

Those again can be expressed as correction factors to the equipment price. Depending on the status of the information available they can be expressed as one unified factor or broken down to each specific category. One however needs to bare in mind, that costs for piping and valves – pieces of equipment in direct contact with process media – will be affected by the process conditions in a similar way as the actual equipment, whereas the other categories are more likely to remain unchanged. Thus attention needs to be paid, in with fashion the factors will be applied.

A word should be said to the cost for the control system. Most obtainable data will most likely refer to a decentralized control system, as it has been in use for many years. With ever more powerful computers a centralized approach, namely model predictive control (MPC) is becoming more relevant. As the structure for such a control system may vary significantly from the common designs, the cost factors may as well.

Services

The utility investments and off-site investments are often referred to as services. Therein included are all measures necessary to supply the process with the media required for operations. This includes but is not limited to generation and distribution of energy, steam, process gases. The utility investments in this context refer to all investments within the greater production site but out of the battery limits of the process. Off-site investments contain everything not contained in the site such as roads, power cables, communication systems or waste disposal. All these costs are expressed as fractions of the equipment cost at moderate temperature and pressure. This means, when applying these fractions, the factors f_M , f_P and f_T should not be considered at this point.

Once again in early design stages one has to resort to factors derived for statistical data, to calculate the cost of raw materials, energy and support media such as lubricants, heat or catalysts. If more detailed information on process streams is available the approach should be refined.

The cost of raw materials C_{RM} can then be calculated if the streams of individual raw materials m_i as well as their specific cost are known.

$$C_{RM} = \left(\sum_i^{N_{RM}} \dot{m}_i \cdot C_{RM}^i \right) \cdot t_{op}. \quad (4.5)$$

Much in the same way the cost for energy can be calculated. This is once more done for each individual piece of equipment, rather than for the whole process as it has been done for the raw materials. Hence with the needed energy for equipment i with respect to energy carrier j e_{ij} along with the price for energy carrier j C_{EC}^j the total energy cost C_{EC} can be assessed.

$$C_{EC} = \left(\sum_i^{N_E} \sum_j^{N_{EC}} \dot{e}_{ij} \cdot C_{EC}^j \right) \cdot t_{op}. \quad (4.6)$$

Working capital

The working capital includes all investments necessary for process operations. This means raw materials, payroll, extended credit to customers and so on. In contrast to all other costs the working capital can partially be retrieved when the process stops operations. How different types of cash flows, extended or owed credit should be handled will be discussed in sec. 4.2. In addition to the cost of raw materials needed during process operations, which generate a product stream, raw materials are also needed to fill all vessels, reactors, columns and piping that make up the process. The cost of these needs to be considered as investment and not as operation cost, since more or less the same amount will remain bound until the process ceases operations and it can (partially) be retrieved.

$$C_{FILL} = \sum_i^{N_{RM}} V_i \cdot C_{RM}^i. \quad (4.7)$$

Total investment

When all contributions to the total investment are considered an estimate for the total price of the process can be calculated

$$C_P = \sum_i^{N_E} \left[C_B^i \left(\frac{Q_i}{Q_B^i} \right)^{M^i} \left(f_F \cdot f_{PIPE} + \sum_j f_j \right) \right] + C_{RM} + C_{EC} + C_{FILL} \quad (4.8)$$

It should be emphasized that in early design stages these calculations will at best yield an order of magnitude estimate for the expected cost of implementing a chemical process. Most literature sources give an accuracy of $\pm 30\%$ [7]. As the project progresses more and more information becomes available an a more accurate estimate can be prepared. Those often rely on actual proposals from prospective manufacturers and suppliers.

4.2 Investment criteria

The total cost of a project is a very important measure to decide whether to undergo a certain endeavor. However in a complex financial system it cannot be taken as the sole factor to compare investment alternatives. Different other indices are used to measure the attractiveness of an investment. One main distinction can be made between different measurements. Those that work with averaged cash flows and consider the project as a single time periods (sec. 4.2.1) and models that take into account cash flows made at different points in time – so called multi-period models (sec. 4.2.2).

4.2.1 Single period estimation methods

Among the most prominent single period methods are the payout time (POT) and the return of investment (ROI).

Payout time

Payout or amortization time is the time necessary to earn the total investment of the process. It is also often referred to as the break even point. A profitable venture will from that point on begin to make money. A shorter payback time is a measure for an more attractive investment.

$$POT = \frac{\text{capital expenditure}}{\text{incoming cash flow} / \text{period}} \quad (4.9)$$

Return of investment

The return of investment is defined as

$$ROI = \frac{\text{average return} / \text{period}}{\text{capital expenditure}} \cdot 100\%. \quad (4.10)$$

It denotes the equivalent to an interest rate if the earned interest is not reinvested such that the same investment is considered in every period. The average return is calculated from the expected returns over certain duration of time. The time considered might either be the total lifecycle of the process or the expected write-off time. As capital expenditure most likely the total investment will be used. However it might give a more precise picture if write-off or the time of individual payments is considered when evaluating the capital expenditure.

4.2.2 Multi period estimation methods

As discussed earlier, when using only averaged values and considering only one time period, a distorted picture of the financial situation will evolve. The source of the money to be invested plays a critical role in the evaluation process. Cash reserves, loans, preferred stock or other financial instruments are all viable sources of investment capital. Often a mixture of many different sources is used to allocate

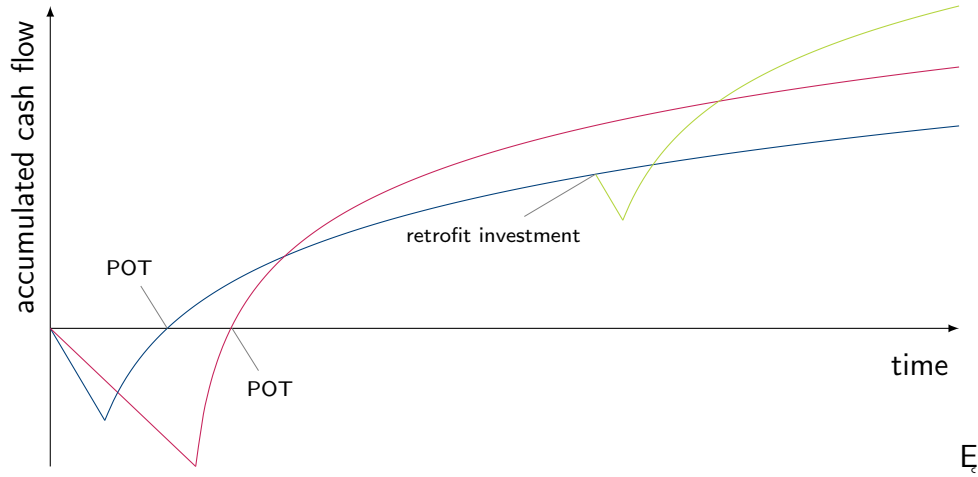


Figure 4.1: Accumulated cash flows over project life cycle.

all necessary funds. A generic structure of the cash-flows during the life-cycle of a given project is shown in fig. 4.1. When the project commences no revenue is generated and only investments are made. As process operations begin revenue is generated and the slope of the accumulated cash flow curve switches to an upward directions – assuming the project is profitable. As time progresses the produced product might reduce in value through competitors entering the market or other factors. When the curve intersects the abscissa the project investment is earned and the break point is reached. The two investment alternatives highlight that the amount of initial investment will affect the expected revenue. As more information is gathered during operations, opportunities may arise to optimize the process and leverage so far dormant potentials. These so called retrofit Investments would ideally lead to an improved cash flow structure as indicated by the green line.

add ref: (fig. 4.1) Script PE-VT

Before further investigating multi-period model some basic ideas about financial mathematics and the treatment of interest should be reviewed. When investing the capital C_0 at compounded interest for n years at a rate of i %, the compound amount will yield

$$C_n = C_0 \cdot q^n. \quad (4.11)$$

Where q denotes the interest factor

$$q = 1 + \frac{i}{100}. \quad (4.12)$$

On the other hand the current value of an investment that will yield C_n in n years can be calculated by

$$C_0 = C_n \cdot q^{-n} \quad (4.13)$$

The above considerations always assume a single payment at the beginning or end of the entire period. Annuities however are usually in several trances with regular payments to be made or received at predefined instances. Assuming those payments are of equal size a , the final value can be computed by

$$C_n = a \cdot q^\alpha \cdot \frac{q^n - 1}{q - 1}, \quad (4.14)$$

while the current value of an annuity yields

$$C_0 = a \cdot q^{\alpha-n} \cdot \frac{q^n - 1}{q - 1}, \quad (4.15)$$

The factor α in the previous equations denotes whether payments are made at the beginning of a period ($\alpha = 1$) or at the end ($\alpha = 0$)

With that multi-period model can be discussed. Here not only different alternatives can be compared, but also the profitability in comparison with investments in financial products can be assessed.

Net present value

The net present value (*NPV*) describes the amount of money to be invested if all cash flows – incoming and outgoing – are discounted to the project start ($t = 0$). The present value of all expenses is then

$$C_{0e} = e_0 + e_1 \cdot q^{-1} + \dots + e_n \cdot q^{-n} = \sum_i^n e_i \cdot q^{-i}. \quad (4.16)$$

Here it is given that all expenses are paid at the beginning of each period, as it is the most common case. If revenues r_i are realized then as well an equivalent formula would be attained. In most cases revenues will come in at the end of a period in which case the present value becomes

$$C_{0r} = r_0 \cdot q^{-1} + r_1 \cdot q^{-2} + \dots + r_n \cdot q^{-(n+1)} = \sum_i^n r_i \cdot q^{-(i+1)}. \quad (4.17)$$

The *NPV* of a given project is then derived from the present values of all expenses and revenues

$$NPV = C_{0r} - C_{0e}. \quad (4.18)$$

For any project to be considered as investment alternative the present value needs to be positive since otherwise the investment would yield losses.

Discounted cash flow rate of return

The formula for the discounted cash flow rate of return is very similar to the one for a net present value. The difference is, that rather than computing the net present value with given interest rates, the present value is set to zero and the resulting interest rate is then calculated. Other than with the previous methods no analytical solution can be presented but rather an iterative approach to find a solution to

$$0 = \sum_i^n (r_i - e_i) \cdot q^{-i}. \quad (4.19)$$

Here it was assumed that all payments – incoming and outgoing – are made at the beginning of a period. The only variable is the interest rate which is included in the interest factors q . This method gives the interest rate which would be necessary to earn all time dependent expenses within n years. In this case a higher *DCFRR* indicates a more attractive investment.

Annuity method

Within the annuity method two different annuities are calculated and then compared. First the annuity a of an investment of C_0 at market conditions is of interest.

$$a = C_0 \cdot \frac{q^{n-\alpha}(q-1)}{q^n - 1} \quad (4.20)$$

This annuity is the amount that could be paid out each period if C_0 is invested, compound interest is considered and all funds are used up at the end of n years.

This is then compared to the annuity of the considered project

$$a_P = \sum_i^n (r_i - e_i) \cdot q^{-i} \cdot \frac{q^{n-\alpha}(q-1)}{q^n - 1}. \quad (4.21)$$

Only if $a_P > a$ is the project more profitable than simply investing the required capital in an financial product.

Interest Rates

With all the presented models its was implicitly assumed that interest rates for debit and credit are equal. The reality however is much different. It will therefore be prudent to use different rates of interest for each case. The basic calculations however remain unchanged. Especially the interest rate that can be earned when investing a certain amount will need to be estimated. As certain products with a know *ROI* will not necessarily be the most attractive options on the capital market. Thus in many companies there is an internal value given for this interest rate, which is calculated from historical data.

5 Mathematical process model

5.1 Steady state model

5.1.1 Distillation column

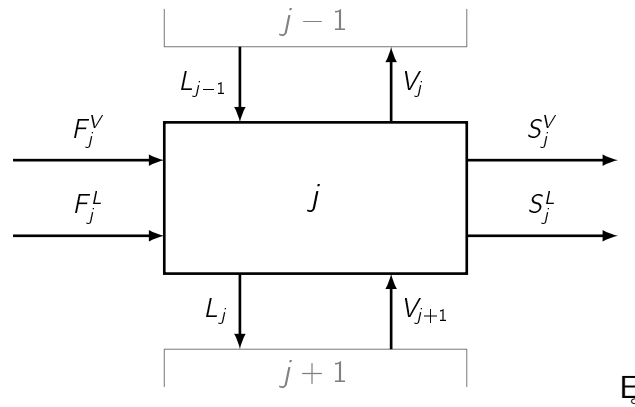


Figure 5.1: Distillation column tray model.

Mass balance

$$0 = F_j^V + F_j^L + V_{j+1} + L_{j-1} - V_j - S_j^V - L_j - S_j^L \quad (5.1)$$

Component balances

$$0 = V_{j+1}y_{i,j+1} + L_{j-1}x_{i,j-1} + F_j^V z_{i,j}^V + F_j^L z_{i,j}^L - (V_j + S_j^V) y_{i,j} - (L_j + S_j^L) x_{i,j} \quad (5.2)$$

Energy balance

$$0 = V_{j+1}H_{j+1}^V + L_{j-1}H_{j-1}^L + F_j^V H_j^{FV} + F_j^L H_j^{FL} - (V_j + S_j^V) H_j^V - (L_j + S_j^L) H_j^L \quad (5.3)$$

Vapour liquid equilibrium

$$y_{ij} = \gamma_{ij} \cdot K_{ij} \cdot x_{ij} \quad (5.4)$$

Multi stream heat exchanger

5.1.2 Compressor / expander

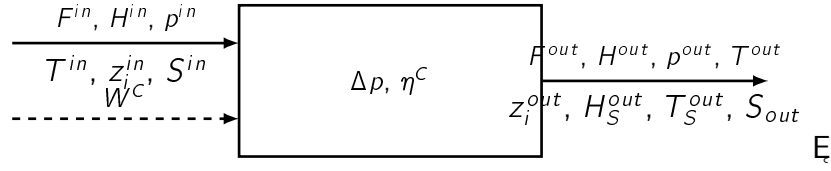


Figure 5.2: Compressor model.

Mass and component balances

$$0 = F^{in} - F^{out} \quad (5.5)$$

$$0 = z_i^{in} - z_i^{out} \quad (5.6)$$

Isentropic work

$$S^{in}(T^{in}, p^{in}, z_i^{in}) = S^{out}(T_S^{out}, p^{out}, z_i^{out}) \quad (5.7)$$

$$W_S = F^{in} \cdot H^{in}(T^{in}, p^{in}, z_i^{in}) - F^{out} \cdot H^{out}(T_S^{out}, p^{out}, z_i^{out}) \quad (5.8)$$

Compression work

$$W \cdot \eta^C = W_S \quad (5.9)$$

$$W_S = F^{in} \cdot H^{in}(T^{in}, p^{in}, z_i^{in}) - F^{out} \cdot H^{out}(T^{out}, p^{out}, z_i^{out}) \quad (5.10)$$

Pressure drop

$$p^{out} = p^{in} + \Delta p \quad (5.11)$$

5.1.3 Centrifugal pump

Cost estimation The cost for the pump excluding the motor can be approximated by

$$C_B = \exp [9.7171 - 0.6019 \ln[S] + 0.0519(\ln[S])^2] \quad 40 \leq S \leq 100000 \quad (5.12)$$

$$C_p = f_T f_M C_B. \quad (5.13)$$

The cost for the centrifugal pump is approximated by the value $S = Q \cdot \sqrt{H}$, where Q denotes the volume flow through the pump in gallons per minute [gpm] and H the pump head in [ft].

The costs given above is excluding the motor needed. It is then estimated separately. In this case the specific quantity is the power consumption P_C needed for the desired stream transport.

$$C_B = \exp \left[5.8259 + 0.13141 \ln[P_C] + 0.053255(\ln[P_C])^2 + 0.028628(\ln[P_C])^3 - 0.0035549(\ln[P_C])^4 \right] \quad (5.14)$$

add formulas for vapour fraction

check if . or , are used for decimals ...

Expander

Condenser

5.1.4 Reboiler

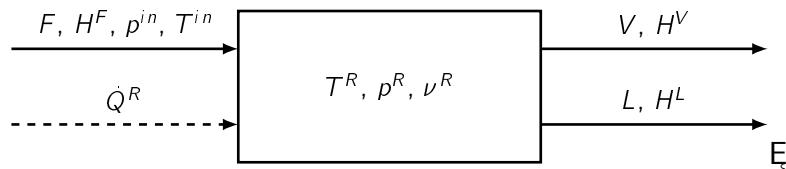


Figure 5.3: Reboiler model.

Mass balance

$$0 = F - V - L \quad (5.15)$$

Component balance

$$0 = Fz_j - Vy_j - Lx_j \quad (5.16)$$

Pressure drop

$$p^R = p^{in} + \Delta p \quad (5.17)$$

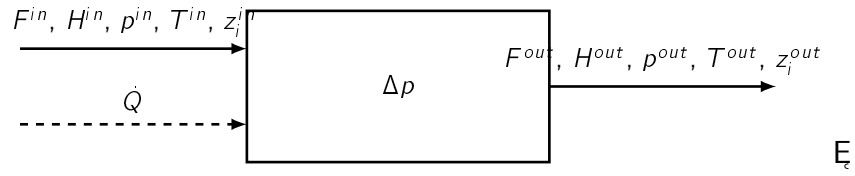


Figure 5.4: Heater model.

5.1.5 Heater

Mass and component balances

$$0 = F^{in} - F^{out} \quad (5.18)$$

$$0 = z_i^{in} - z_i^{out} \quad (5.19)$$

Pressure drop

$$p^R = p^{in} + \Delta p \quad (5.20)$$

add formulas for vapour fraction

Pump

Separator

Joule-Thompson valve

5.1.6 Splitter

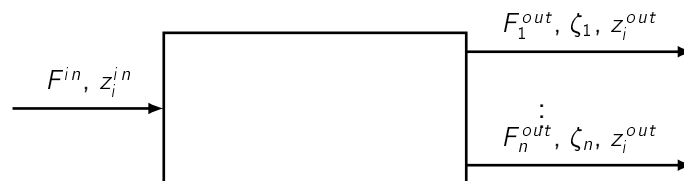


Figure 5.5: Splitter model

Mass and component balances

$$0 = F^{in} - \sum_i^N F^{in} \zeta_i \quad (5.21)$$

$$0 = z_i^{in} - z_i^{out} \quad (5.22)$$

Energy balance

$$0 = F^{in} H^{in}(T^{in}, p^{in}, z_i^{in}) - \sum_j^N F_j^{out} H^{out}(T^{out}, p^{out}, z_i^{out}) \quad (5.23)$$

Pressure drop

$$p^{out} = p^{in} + \Delta p \quad (5.24)$$

add formulas for vapour fraction

5.2 Economic models

As discussed earlier economic consideration play a major role in process design. In order to account for the process economics the cost of the process to be implemented needs to be estimated at the design level. However as limited information is available estimation methods have to be employed. In sec. 4 the general approach for cost estimation of process equipment was introduced, where a specific value such as heat-exchange area or vessel size is used to approximate equipment cost. However for more specific units extended models are available, where statistical data is employed to yield a more realistic fit to cost data. The cost functions and correction factors presented in this chapter are, if not stated otherwise, taken from [9]. Also unless otherwise stated the unit cost is given for the year 2006 ($CE = 500$).

5.2.1 Distillation column

Out of all the process equipment the distillation column probably is the most elaborate unit. It also poses the greatest challenges when it comes to finding an appropriate estimate for its cost. This is due to the fact that the column in itself is rather large and complex. To properly operate a column the vessel needs to have numerous valves, scaffolding and several manholes. Due to its size further factors come into play that need not to be considered for the other relatively small units. Those location dependent factors might include resilience towards earthquakes, the ability to withstand close winds or intensive ambient temperatures. However as the scope of this work explicitly focuses on early design stages those location specific influences will be disregarded to arrive at simpler models for cost estimation.

Vertical tower

The cost for the vessel C_V which is to be vertically erected vertically is dependent on the weight of the vessel W ([lbs]). This includes valves, manholes and other details directly

connected with the tower. However the cost for ladders, platforms and railings necessary to properly operate the column are calculated separately

$$C_p = f_M C_V + C_{PL}. \quad (5.25)$$

The correlated equation for the cost of the tower is given by

$$C_V = \exp \{ 7.2756 + 0.18255 \cdot \ln[W] + 0.02297 \cdot (\ln[W])^2 \}, \quad 9000 \leq W \leq 2.5 \cdot 10^6. \quad (5.26)$$

To the cost of the tower, the cost of the surrounding support structure is added. It is dependent on the inner diameter of the vessel (D_i) as well as the so called tangent to tangent length (L). This denotes the length of the tube that makes up the vessel excluding the spherical domes that close the column on each side. With that the additional cost is then computed by

$$C_{PL} = 300.9 \cdot (D_i)^{0.63316} \cdot (L)^{0.80161}. \quad (5.27)$$

Weight

As can be seen from the above correlations the weight of the column is a determining factor for the estimated and actual cost. Therefore some thought should be put into how this can be determined, when the final design is unknown. Again several correlations have been applied to real life units which yield satisfactory results. In general the weight of the empty vessel can be computed by determining the volume of the material and multiplying it with its density (ρ)

$$W = \pi(D_i + t_s)(L + 0.8 \cdot D_i)t_s \cdot \rho. \quad (5.28)$$

The term $0.8D_i$ is included to approximate the weight of the domes, whereas t_s is the shell thickness. To determine how thick the walls of the shell need to be the ASME pressure vessel code formula is often applied

$$t_s = \frac{P_d D_i}{2 S E - 1.2 P_d}. \quad (5.29)$$

Where the maximal allowable stress S , which the chosen material can withstand at process conditions is multiplied by the fractional weld efficiency E to regard the effects of the manufacturing process on the material strength. To ensure an error on the side of caution the design pressure P_d is calculated from the actual operating pressure P_o by means of

$$P_d = \exp \{ 0.60600 + 0.91615 \cdot (\ln[P_o]) + 0.0015655 \cdot (\ln[P_o])^2 \} \quad (5.30)$$

It is important to consider, that the maximum allowable stress especially needs to take into account the operating temperature of the distillation process, as it might have significant effects.

Furthermore the given formulas only apply to pressures above ambient conditions. Thus low pressure or vacuum distillation is not covered by the presented formulas.

number of stages	shaft rpm	case-split orientation	flow rate range ([gpm])	pump head range ([ft])	maximum power ([Hp])	type factor f_T
1	3600	VSC	50 - 900	50 - 400	75	1.00
1	1800	VSC	50 - 3500	50 - 200	200	1.50
1	3600	HSC	100 - 1500	100 - 450	150	1.70
1	1800	HSC	250 - 5000	50 - 500	250	2.00
2	3600	HSC	50 - 1100	300 - 1100	250	2.70
2+	3600	HSC	100 - 1500	650 - 3200	1450	8.90

Table 5.1: Pump type factors [9].

Column internals

While internal support structures are already considered by the equations given above, the internals responsible to ensure product separation are not. Those make up a very significant amount of the total column cost and are available .

5.2.2 Centrifugal pump

Pumps are among the most common units of process equipment. While there are several different kinds of punps that can be used, the crtrifugal pump is one of the most popular choices and denotes a very likely choice for the porcess conditions considered in this application. Hence other pump types will not be considered at this point.

Pump

In terms of operations pumps are best described by the volumetric flow transported Q as well as the pumph head H , the hight that needs to be overcome. Data taken from the company Mosanto was used to correlate the pump cost to a specific value

$$S = Q\sqrt{H}. \quad (5.31)$$

As a reference unit the base price C_B is estimated for a cast iron single-stage vertically split case at 3600 rpm

$$C_B = \exp \{ 9.7171 - 0.6019 \cdot \ln[S] + 0.0519(\ln[S])^2 \}, \quad 400 \leq S \leq 100000. \quad (5.32)$$

The most influential addition factors for the pump price are the material, which is accounted for in the material factor f_m , as well as the rotation, case split orientation (horizontal and vertical), the number of stages, covered flow rate range, pump head range and maximum motor power, which are all agglomerated in the type factor f_T . Values for these factors are given in tab. 5.1 and tab. 5.2.

material of construction	material factor
cast iron	1.00
ductile iron	1.15
cast steel	1.35
bronze	1.90
stainless teel	2.00
Hastelloy C	2.95
monel	3.30
nickel	3.50
titanium	9.70

Table 5.2: Pump material factors [9].

Electric motor

Separately from the pump itself the motor to drive the compression is considered. While the volumetric flow and the pump head certainly are valid choices to correlate motors for pumps especially, the power consumption is a more general specific value

$$P_C = \frac{P_T}{\eta_P \eta_M} = \frac{P_B}{\eta_M} \quad (5.33)$$

It can be calculated from the theoretic power of the pump P_T and the efficiencies η_P η_M . While an estimate for the expected power consumption might be already available at rather early design stages, the efficiencies will have to be correlated as well if resorting to average values is considered too coarse. Those correlations rely on the volumetric flow in gallons per minute ([gpm]) and the brake horse power $P_B = \frac{P_T}{\eta_P}$.

$$\eta_P = -0.316 + 0.24015 \cdot \ln[Q] - 0.01199 \cdot (\ln[Q])^2 \quad 50 \leq Q \leq 5000 \quad (5.34)$$

$$\eta_M = 0.80 + 0.0319 \cdot \ln[P_B] - 0.00182 \cdot (\ln[P_B])^2 \quad 1 \leq P_B \leq 1500 \quad (5.35)$$

After having calculated the power which the motor needs to supply its base cost of an open, drip-proof enclosed motor at 3600 rpm can be approximated by

$$C_B = \exp \left\{ 5.8259 + 0.13141 \cdot \ln[P_C] + 0.053255 \cdot (\ln[P_C])^2 + 0.028628 \cdot (\ln[P_C])^3 - 0.0035549 \cdot (\ln[P_C])^4 \right\} \quad 1 \leq P_C \leq 700 \quad (5.36)$$

To adjust the cost for different types of electric motors the type factors from tab. 5.3

5.2.3 Compressor

The cost of compressors is correlated with their respective power consumption measured in horsepower. Although not the most efficient type of compressor, centrifugal compressors are very popular in the process industry, as they are easily controlled and deliver a very steady flow. However as different types might be employed as well base cost correlations for centrifugal, reciprocation and screw compressors are given.

type motor enclosure	3600 rpm	1800 rpm
open, drip-proof enclosure, 1 to 700 Hp	1.0	0.9
totally enclosed, fan-cooled, 1 to 250 Hp	1.4	1.3
explosion-proof enclosure, 1 to 250 Hp	1.8	1.7

Table 5.3: Type factors for different motor types.

Centrifugal compressor

$$C_B = \exp \{7.5800 + 0.80 \cdot (\ln[P_C])\} \quad 200 \leq P_C \leq 30000 \quad (5.37)$$

Reciprocating compressor

$$C_B = \exp \{7.9661 + 0.80 \cdot (\ln[P_C])\} \quad 200 \leq P_C \leq 20000 \quad (5.38)$$

Screw compressor

$$C_B = \exp \{8.1238 + 0.7243 \cdot (\ln[P_C])\} \quad 200 \leq P_C \leq 750 \quad (5.39)$$

Again as with most other equipment types correction factors are used to adjust for different realization of this piece of equipment. Here type of motor as well as the construction material have the biggest effect on the unit price and are explicitly considered.

$$C_p = f_D f_M C_B \quad (5.40)$$

The alternatives to the electric motor ($f_D = 1.0$) are a steam turbine ($f_D = 1.15$) or a gas turbine ($f_D = 1.25$). It should however be noted that aside from being the cheapest choice, the electric motor is also the most efficient. Thus the turbines are mostly considered, when process steam or combustion gas is easily available, such that the drawbacks might be eliminated by not having to supply the electric energy for the electric motor. In terms of construction material all base costs are for cast iron or carbon steel. Some appliances may require more resistant and also more expensive materials such as stainless steel ($f_M = 2.5$) or a nickel alloy ($f_M = 5.0$).

5.2.4 Reboiler / condenser

Reboiler and condenser can be characterized as heat exchangers, and be handled in the same way, as the main difference is whether heat is transferred to or from the process stream. In that sense they must be distinguished when considering the operating cost, as the cost for hot or cold auxiliary streams might differ significantly. As customary for heat exchangers the specific quantity for cost correlations is the necessary heat exchange area A measured in ft^2 .

Again the construction material as well as the operating conditions have an effect on the final cost

$$C_p = f_P f_M C_B. \quad (5.41)$$

The correction for pressures f_P takes into account the operating pressure P_o and is computed by

$$f_P = 0.8510 + 0.1292P_o + 0.0198 * P_o^2. \quad (5.42)$$

The material correction factor f_M

$$f_M = \quad (5.43)$$

Shell and tube heat exchanger

$$C_B = \exp \{ 11.667 - 0.8709 \cdot (\ln[A]) + 0.09005 \cdot (\ln[A])^2 \} \quad (5.44)$$

Double pipe

$$C_B = \exp \{ 7.146 + 0.1600 \cdot (\ln[A]) \} \quad (5.45)$$

6 Mathematical considerations

6.1 Robust column model

The column model, although rather simple on first sight, form a highly non-linear and highly coupled set of equations, which need to be solved simultaneously. Due to that even advanced computers and solution algorithms often fail to find feasible steady-state solutions for this highly complex problem. For every solution approach good initial estimates are essential when it comes to finding a feasible solution. Those problems are amplified when non-ideal or very close boiling systems are encountered in the distillation column.

In order to address these problems Boston and Sullivan [3] developed an alternative model formulation alongside a solution algorithm that has been proven to very effectively and efficiently converge towards a feasible steady state solution. Furthermore they describe a scheme by which initial guesses for all relevant column variables can be derived.

This alternative formulation involves the introduction of several new variables in order to decouple the intrinsic interdependencies and facilitate the solution of the column model. While the general formulation of the distillation column has been presented in sec. 5.1.1 the alternative formulation will be given in the following sections. The alternative model formulation and solution algorithm Boston and Sullivan arrived at are described in the following sections. They are widely referred to as the "inside-out" – algorithm as will be adopted in this paper.

Vapour-liquid equilibrium (VLE)

In general the vapour-liquid equilibrium (VLE) between a liquid and a vapour phase can be described by [1]

$$x_i \underbrace{\gamma_i(\mathbf{x}, T, p^S) F_{P,i} \varphi_i^0(T, p_i^S(T)) p_i^S(T)}_{f_i^L} = y_i \underbrace{\varphi_i(\mathbf{y}, T, p^S) p^S}_{f_i^V} \quad i = 1, \dots, N_s \quad (6.1)$$

Here γ_i denotes the activity coefficient of species i in the liquid mixture, φ_i and φ_i^0 the vapour fugacity coefficient and the reference vapour fugacity coefficient at the species's vapour pressure respectively. They are computed from an applicable equation of state (EOS) such as the Soave-Redlich-Kwong (SRK) equation or the Peng-Robinson (PR) equation. For highly non-ideal systems often excess Gibbs energy models such as the Wilson or NRTL model are employed to compute the liquid activity coefficients. Considering, that the mentioned models in itself often form cubic or even more complex equation it becomes evident that finding a feasible solution for all involved

species simultaniouly form a major challange. One predominant obstacle is that almost all terms in are temperature dependent which introduces tremendous interdependencies between all equilibrium equations for all species N_s N on all stages in the distillation column.

To adress this problem the inside out algorithm includes the so called " K_b - model" which aims to separate the the temperature dependencies from the composition dependent terms.

eq. (6.1) can be rewritten in terms of a vapour-liquid equilibrium ratio K_i

$$y_{i,n} = \frac{f_{i,n}^L}{f_{i,n}^V} x_{i,n} = K_{i,n} x_{i,n} \quad i = 1, \dots, N_s. \quad (6.2)$$

In order to achieve the desired effect the equilibrium ratio was devided in an solely temperature dependent parameter K_b and the so called volatility parameter α_i defined by

$$K_{i,n} = K_{b,n} \alpha_{i,n}, \quad i = 1 \dots N_s. \quad (6.3)$$

This volatility parameter is mainly dependent on system composition and only mildly dependent on temperature. To ensure the for the K_b parameter to absorb the temperature effects is was required, that the modified bubble point equation (BP) with an temperature independent volatility parameter

$$\sum_{i,n} K_b \alpha_{i,n} x_{i,n} = 1, \quad i = 1 \dots N_s, \quad n = 1, \dots, N, \quad (6.4)$$

matches the temperature sensitivity of the original bubble point equation,

$$\sum_i K_{i,n} x_{i,n} = 1 \quad (6.5)$$

as closely as possible. This leads directly to [3]

$$\frac{\partial \log K_{b,n}}{\partial \frac{1}{T_n}} = \sum_i y_{i,n} \left(\frac{\partial \log K_{i,n}}{\partial \frac{1}{T_n}} \right)_{x,y} \quad i = 1 \dots N_s \quad (6.6)$$

It was then further assumed, that a simple model would suffice to capture the temperature dependence of K_b over a small temperature interval

$$\log K_{b,n} = A_n - \frac{B_n}{T_n}, \quad n = 1, \dots, N. \quad (6.7)$$

The value of B_n is determied by eq. (6.6) while A_n is initially set to

$$A_n = \sum_i y_i \log K_{i,n} + \frac{B_n}{T_n} \quad (6.8)$$

Component mass conservation (CMC)

In order to transform the component mass conservation equations eq. (5.2) into a system which would be more robust in terms of numerical solution algorithms, they were reformulated in terms of the liquid component flows ($\ell_{i,n}$) alone

$$f_{i,n} = -\ell_{i,n-1} + b_{i,n}\ell_{i,n} - c_{i,n}\ell_{i,n+1}, \quad i = 1, \dots, N_s, \quad n = 2, \dots, N-1. \quad (6.9)$$

Where the parameters $b_{i,n}$ and $c_{i,n}$ are expressed in terms of the newly introduced "S-parameters" or splitting factors and the "R-parameters" or withdrawl factors

$$b_{i,n} = R_{L,n} + R_{V,n} S_b S_{R,n} \alpha_{i,n} \quad i = 1, \dots, N_s, \quad n = 2, \dots, N-1, \quad (6.10)$$

$$c_{i,n} = S_b S_{R,n+1} \alpha_{i,n+1} \quad i = 1, \dots, N_s, \quad n = 2, \dots, N-1. \quad (6.11)$$

With the definitions for the newly introduced variables

$$R_n^L = 1 + \frac{S_n^L}{L_n}, \quad (6.12)$$

$$R_n^V = 1 + \frac{S_n^V}{V_n}, \quad (6.13)$$

$$S_n = \frac{K_{b,n} V_n}{L_n}, \quad (6.14)$$

$$S_{R,n} = \frac{S_n}{S_b}, \quad (6.15)$$

$$S_b = \sqrt[N]{\prod_n S_n}. \quad (6.16)$$

From the liquid streams the vapour and liquid compositions are calculated

$$x_{i,n} = \frac{\ell_{i,n}}{\sum_i \ell_{i,n}}, \quad (6.17)$$

$$y_{i,n} = \frac{\alpha_{i,n} \ell_{i,n}}{\sum_i \alpha_{i,n} \ell_{i,n}}. \quad (6.18)$$

Energy conservation (EC)

In order to simplify the energy conservation equations the total stream enthalpies were approximated by several new variables referred to as "energy parameters". Here separate models are employed for vapour and liquid enthalpies.

The total vapour enthalpy can be expressed as

$$H_n^V = \sum_i y_i H_{i,n}^0 + \Delta H_n^V(\mathbf{y}_n, p_n, T_n), \quad i = 1, \dots, N_s \quad (6.19)$$

where $H_{i,n}^0$ is the ideal gas enthalpy of species i on tray n and ΔH_n^V the pressure and composition correction, which can be expressed in terms of the vapour fugacity

$$\Delta H_n^V(\mathbf{y}_n, p_n, T_n) = R \sum_i y_i \left(\frac{\partial \log \varphi_{i,n}}{\partial \frac{1}{T}} \right)_{p, y_n} \quad (6.20)$$

To avoid the computationally expensive property calls the correction term was approximated by

$$\Delta H_n^V(\mathbf{y}_n, p_n, T_n) = \Phi_y + \Phi_T(T - T^*) \quad (6.21)$$

where

$$\Phi_y = \frac{\Delta H_n^V(\mathbf{y}_n^*, p_n, T_n) - \Delta H_n^V(\mathbf{y}_n^*, p_n, T_n^*)}{T - T^*} \quad (6.22)$$

$$\Phi_T = \Delta H_n^V(\mathbf{y}_n^*, p_n, T_n^*) + \Delta H_n^V(\mathbf{y}_n, p_n, T_n) - \Delta H_n^V(\mathbf{y}_n^*, p_n, T_n) \quad (6.23)$$

$$H_n = \Gamma \Theta + \Phi_y + \Phi_T (\Gamma - \Gamma^*) + \sum_i y_i H_{b,i}^0 \quad (6.24)$$

$$\Phi_i = \frac{H_i^0 - H_{b,i}^0}{T - T_b} \quad (6.25)$$

$$\Theta = \Theta_b \Theta_r \quad (6.26)$$

$$\Theta_r = \sum_i y_{r,i} \Phi_{r,i} \quad (6.27)$$

$$\Theta_b = \sum_i y_i \Phi_{b,i} \quad (6.28)$$

$$\Phi_{b,i} = \lim_{T \rightarrow T_b} \Phi_i \quad (6.29)$$

$$\Phi_{r,i} = \frac{\Phi_i}{\Phi_{b,i}} \quad (6.30)$$

$$y_{r,i} = \frac{y_i \Phi_{b,i}}{\sum_j y_j \Phi_{b,j}} \quad (6.31)$$

An equivalent approach is chosen to model the liquid enthalpy

$$H_n^L = h_i^0 + h_i^E \quad (6.32)$$

$$\phi_i = \frac{h_i^0 - h_{b,i}^0}{T - T_b} \quad (6.33)$$

$$\theta = \theta_b \theta_r \quad (6.34)$$

$$\theta_r = \sum_i x_{r,i} \phi_{r,i} \quad (6.35)$$

$$\theta_b = \sum_i x_i \phi_{b,i} \quad (6.36)$$

$$\phi_{b,i} = \lim_{T \rightarrow T_b} \phi_i \quad (6.37)$$

$$\phi_{r,i} = \frac{\phi_i}{\phi_{b,i}} \quad (6.38)$$

$$x_{r,i} = \frac{x_i \phi_{b,i}}{\sum_j x_j \phi_{b,j}} \quad (6.39)$$

With those the modified energy conservation equation is formulated

$$E_n - a_n S_n^L - a'_n (M_{T,n-1} + S_n^V) + a'_{n+1} M_{T,n} = -(a_{n-1} - a'_n) L_{n-1} + (a_n - a'_{n+1}) L_n \quad (6.40)$$

where

$$a_n = \Gamma_n \theta_n + h_n^E - \lambda_{b,n}^0 \quad (6.41)$$

$$a'_n = \Gamma_n \Theta_n + \Phi_{y,n} + \Phi_{T,n} (\Gamma_n - \Gamma_n^*) \quad (6.42)$$

7 Conclusion and further research

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