Abstract
In this paper exergy analysis is applied to select the most efficient rectification structures for separation of quaternary hydrocarbon mixtures. The basis and usage of exergy analysis is shown, as well as the benefits of its application. Exergy loss and thermodynamic efficiency is calculated from basic equations of thermodynamics. The ranking, even based on exergy analysis, highly depends on the product purification prescription. Finally it is shown that heat integration of distillation columns is exergetically beneficial in a wide product purity range.

Keywords
exergy · distillation · quaternary mixture · thermodynamic efficiency

1 Introduction
Distillation is one of the oldest separation methods, but it is still the most widely applied technique. As the majority of crude oil undergoes at least once this procedure it is clearly visible that extremely large material quantities are still separated by this method, that can only be measured in billion tons a year. Importance of distillation is not going to decline while crude oil and hydrocarbons are used. Apart from crude distillation and hydrocarbon separation many other uses are known, such as processing wastewater [16, 25].

However, distillation has a great drawback, namely its high energy consumption. As most of the energy consumption is still covered by fossil energy sources, consuming energy also means emission of $\text{CO}_2$ into the atmosphere. This is considered to cause greenhouse effect and, at elevated concentrations, global warming. Energy prices are constantly rising, especially the price of crude oil [19], making energetic efficiency more and more important and it gives an economic direction of the research and development.

Many papers today still investigate different aspects of distillation. Most of the recent papers are related to three main topics: controllability, energetic improvements and complex design. Controllability of systems is important in order to avoid systems sensitive to disturbances [6, 8–10, 18, 26–28]. Such sensitive systems would not produce constant quality which is disadvantageous from an economic point of view; moreover, inappropriate product quality requires additional separational work, thus more energy. Other works are investigating different new improvements on thermally coupled distillation systems [7, 11, 12, 14, 15, 18, 27, 29]. These topics all show the importance and actuality of saving energy, especially in such energy consuming processes like distillation. It is important both from economical and environmental viewpoints, as these are closely related. Complex design is also a famous subject of investigation nowadays. These papers discuss the integrated technological, economical or environmental design together [11, 28, 29]. Kencse and Mizsey [14] presented a simpler way to aggregate these aspects with the desirability func-
tion. This paper is showing the usefulness of exergy analysis through ranking of commonly used distillation systems that may be included in the selection of distillation structures and complex design methodologies.

2 Energy and efficiency

Processes have been optimised for energy consumption for decades, but usually the value of the energy is not considered. The difference originates from the conversion of one type of energy into the other. The conversion is usually not possible without losses or not possible at all. Electricity can be converted almost lossless into heat, but heat cannot be converted into electricity without losing a great portion of it.

Regarding only thermal energy it can be declared that the same amount of heat can be more valuable if it is available on higher temperatures. With higher temperature heat can be utilised in more applications where it is possible to use it. In many cases, despite the large heat content, lower temperature heat can only be utilised in a few applications, due to the fact that heat can only be transferred to lower temperatures. So it can be concluded that the availability temperature of the energy is strongly associated with its value of utilisation.

Exergy, however, makes a difference between more and less valuable energies. In the calculation of exergy not only the first but the second law of thermodynamics is also taken into account. By definition, exergy is the maximal possible useful work during a process that brings the system into thermodynamic equilibrium with a heat reservoir. The heat reservoir usually is the environment. Exergy can also be expressed like in Eq. (1), where Q is the heat, T is the temperature of the heat and index 0 denotes the properties taken at the temperature of the heat reservoir. It can be seen that the Carnot efficiency is taken into account, not just the heat. Another form of exergy is Eq. (2), where H is the enthalpy, S is the entropy and T is the temperature.

\[
Ex = Q \times (1 - \frac{T}{T_0}) \quad (1)
\]

\[
Ex = (H - H_0) - T_0 \times (S - S_0) \quad (2)
\]

We can summarize the advantage of using exergy analysis: it takes irreversibilities into consideration and expresses that heat and work are not equivalents, and also shows that heat degrades from higher temperatures to lower temperatures. A simple enthalpy balance fails to indicate these differences between different forms of energy.

Published works either discuss the development of exergy analysis methods and expressive parameters to quantify exergy loss and thermodynamic efficiency of distillation columns [1][2][3][17][30] or use the basic equations of thermodynamics related to exergy to make the calculations to obtain thermodynamic efficiency of distillation systems [13][4][23][24]. Exergy analysis can be applied for the examination of complex distillation plants also to locate process sections where exergy losses are high and improvements are possible [21][24].

3 Exergy and distillation

The second law of thermodynamics also states that the entropy in a closed system can only increase. In the distillation process the heat is passed through the reboiler, then the column where it makes useful work, and finally it is gained back in the condenser at a lower temperature than it was introduced to the reboiler. The degradation of thermal energy makes it possible to lower the entropy of the material, that is, the separation of a liquid mixture. The low efficiency of distillation is a result of the difference between the lost energy and the useful work of the separation.

As the exergy loss and thermodynamic efficiency can be calculated described in the following [22]: first we need to calculate the irreversible entropy change (Eq. (3)). Knowing the entropy loss and the temperature of the heat reservoir it is possible to calculate the exergy loss (Eq. (4)). The work of separation is also needed, that is, the difference of the exergy flowing in and flowing out (Eq. (5)). Finally the efficiency is calculated by dividing the useful work by the energy we cannot recover, i.e., the useful work plus the exergy loss (Eq. (6)).

\[
\Delta S_{irr} = \sum_{out} (n \times S + \frac{Q_{cond}}{T_{cond}}) + \sum_{in} (n \times S + \frac{Q_{reb}}{T_{reb}}) \quad (3)
\]

\[
Ex_{loss} = T_0 \times \Delta S_{irr} \quad (4)
\]

\[
W_{sep} = \sum_{out} (n \times Ex) + \sum_{in} (n \times Ex) \quad (5)
\]

\[
\eta = \frac{W_{sep}}{W_{sep} + Ex_{loss}} \quad (6)
\]

The ideal distillation column would be the reversible distillation column (Fig[1] introduced by Fonyó [3][4]. It is reversible, because no irreversible change occurs in it, thus there is no entropy loss. To achieve this, equilibrium is needed in every point of the column. Regarding this condition, an infinite number of plates would be necessary as well as negligible pressure drop. Heat transfer should be distributed along the height of the column at each tray, and as a consequence its number is also infinite. Below the feed heat inputs and above the feed heat outputs are applied. This implies that the material flow also changes along the height, resulting in an unusual column shape.

The very strict criteria of the reversible column make it a theoretical, infeasible solution. However many of its features can be implemented during design of distillation columns. Thermally coupled distillation systems with side-stripper, side-rectifier or heat integration are steps towards the improvement of energetic efficiency. By allowing heat transfer on lower temperatures than the reboiler and partly substituting high temperature heat with less valuable, lower temperature heat, less exergy is consumed. Multiple feed inlets and multiple side-draws are also desirable. Internal heat transfer and even distribution of heat inputs and outputs is also required to build a thermodynamically efficient column. Optimisation of feed stages and feed thermal state is also necessary. In certain cases of single columns heat pumps can also be applied.
4 Case study

To determine the influence of design alternatives on the thermodynamic efficiencies of distillation, different distillation schemes are studied completing the same separation task. Simulations of the separation of a quaternary mixture are made and the exergy loss and efficiency of five distillation structures are examined. Due to the importance of distillation in hydrocarbon processing industry a quaternary hydrocarbon mixture is chosen, that are close to ideality. This mixture is an equimolar mixture of n-pentane, n-hexane, n-heptane and n-octane. We examine two cases of product purity:

- sloppy separation with lower purities,
- sharp separation with relatively high purities.

Purities in products can be seen in Table 1.

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Lightest frac.</th>
<th>Middle frac. 1</th>
<th>Middle frac. 2</th>
<th>Heaviest frac.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n-pentane</td>
<td>n-hexane</td>
<td>n-heptane</td>
<td>n-octane</td>
</tr>
<tr>
<td>Sloppy</td>
<td>0.82</td>
<td>0.68</td>
<td>0.64</td>
<td>0.76</td>
</tr>
<tr>
<td>Sharp</td>
<td>0.96</td>
<td>0.93</td>
<td>0.90</td>
<td>0.94</td>
</tr>
</tbody>
</table>

The base case of distillation structures is the conventional direct sequence (DS, Fig.2). A backwards heat integrated alternative of the direct sequence is also included in the structures (DQB, Fig.3). This configuration may look odd, but such solution exists in the separation industries. Forward integration proved to be uneconomical according to previous study by Emtir et al. [2], therefore it is not investigated. Another version of the direct sequence (Fig.2) is also examined: the pressures in Col. 2 and Col. 3 are higher, because backwards heat integration needs elevated pressures in order to be able to achieve higher temperature to be able to realise the necessary heat transfer between the source and sink columns. The parameters are identical to those of the DQB structure (Fig.3). Apart from the conventional direct sequence structures column with side products are also examined. One is a single column with four products (SC, Fig.4).

For the simulations the Aspen Plus software is used. The chosen thermodynamic property is Peng-Robinson.

5 Results

The efficiency of the different systems in the case of sharp separation can be seen in Fig.6. The most efficient alternative is the DQB system, which proves, that heat integration clearly has energetic and exergetic advantages. However, for the column match the source column pressure needs to be increased in order to increase the operational temperature. This could result that the source column is shifted from its optimal operational point and that could mean exergy loss. We can see this difference in the case of the DS and DS-HP structures. This shows the thermodynamic efficiency loss if the pressure of the columns is increased from the optimum. If there is nothing else to integrate, DQB configuration is the most efficient, moreover, requires the least energy. What we also need to note, is the low efficiency of

![Fig. 1. Reversible distillation column](image1)

![Fig. 2. Conventional direct sequence (DS, DS-HP)](image2)

![Fig. 3. Direct sequence with backwards heat integration (DQB)](image3)

![Fig. 4. Single column with side products (SC)](image4)
the single column with vapour feed (SC-OHV). The reason for this performance is that the whole feed stream needs to be heated to a temperature higher than in other cases. Higher source temperature is more valuable in terms of exergy, and this configuration even consumes more of this more valuable energy.

In the case of the sloppy separation the results are shown in Fig. 7. Single column with side products (SC) performs better than DQB and has a higher efficiency. The reason for the better efficiency of the SC system is the difference in reflux ratios. For sloppy separation lower reflux ratio is required where SC benefits from the vertical integration of columns and shows higher efficiency than DQB.

In the case of sharp separation reflux ratio of the single column must be raised more than that of the direct sequence, which means more additional energy for the same separation work. This explains the lower efficiency of the SC separation scheme.

6 Conclusion
Exergy analysis proves to be a useful tool in designing distillation systems. It is clear that heat integration helps to achieve higher thermal efficiencies regardless of circumstances. Columns with an overheated vapour feed, e.g., with the application of a furnace, have very low efficiencies due to the unnecessary usage of high temperature thermal energy. The conventional direct sequence scheme can be a good choice too, if the heat from condensers can be utilised in other processes. This way it is possible to avoid exergy loss which occurs when pressures are raised for heat integration of distillation columns.

For sloppy separation tasks single column with side products (SC) proves to be the most efficient. The backwards heat integrated direct sequence (DQB) system has good efficiencies in all cases and can be recommended for any applications. Good performance of the DQB structure is in correspondence with many previous studies [2][13][14][20]. DQB is a simple, reliable structure with good properties, its usage is recommended, especially for retrofitting, where the application of newer, complicated structures would be impossible.

References
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