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Chapter 3

SIMULATION OF THE SEPARATION OF INDUSTRIALLY IMPORTANT HYDROCARBON MIXTURES BY DIFFERENT DISTILLATION TECHNIQUES USING MATHEMATICA[®]

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ABSTRACT

In this chapter the simulation of several case studies for the separation by distillation of various industrially relevant hydrocarbon mixtures are worked out. Different techniques used to separate the complex mixtures are illustrated: classical column train and enhanced distillation (extractive and reactive).

This chapter is aimed primarily at chemical engineering students. But the information presented might be also useful for postgraduate and PhD students as well as professional engineers.

An important objective of this chapter is to show how these rather complex separations can be handled with great pedagogical benefits using the computer algebra Mathematica[®], a general purpose solver, not chemical engineering specific. Simulation results are compared to those obtained using the flow-sheeting software Aspen-HYSYS[®].

Five case studies are worked out: the separation of natural gas liquids (NGL), the fractionation of a C₄ cut to separate 1,3-butadiene with furfural as entrainer, the production of MTBE from *i*-butene and methanol, the reverse process: production of *i*-butene and methanol by the decomposition of methyl *tert*-butyl ether (MTBE), and the equilibrium-limited metathesis of cis-2-pentene to cis-2-butene and cis-2-hexene.

For every case complete information is given such that it can be easily reproduced with the process simulator and/or alternatively worked out using the relevant Mathematica[®] programs available at <http://demonstrations.wolfram.com>.

Keywords: Enhanced distillation, NGL train, Extractive distillation, Reactive distillation, Numerical simulations, Mathematica[®], Aspen HYSYS[®]

INTRODUCTION

Distillation is a reliable separation technique, and remains often the most efficient fractionation method. The ubiquity of the distillation installations in the gas, oil and petrochemical industry makes it indeed be considered as the “workhorse” separation process in this field.

In this chapter, the fractionation by different distillation techniques of various industrially relevant hydrocarbon mixtures is investigated. Mathematical modeling and numerical simulation are our exploration tools. The objective is to illustrate different distillation techniques used to separate complex mixtures: classical column train, and enhanced distillation (extractive and reactive).

Five case studies illustrating different separation distillation techniques are worked out.

The first case study deals with the separation of natural gas liquids (NGLs), a mixture of light hydrocarbons (ethane, propane, butane, pentane, hexane and heptanes). The raw NGLs mixture is separated using a sequence of distillation columns in which the desired hydrocarbons are gradually isolated.

The second case study is the extraction of 1,3-butadiene from a C₄-cut using extractive distillation with furfural as entrainer.

The remaining three cases are dedicated to the simulation of reactive distillation columns for:

- The production of methyl *tert*-butyl ether (MTBE) from *i*-butene and methanol,
- The production of *i*-butene by the reverse process of decomposition of MTBE,
- The equilibrium-limited metathesis of cis-2-pentene to cis-2-butene and cis-2-hexene.

The various case studies are *first* worked out using the well-known flow-sheeting software Aspen-HYSYS[®]. It is an important objective of this chapter however to show how these rather complex separations can also be handled with great pedagogical benefits using the more accessible computer algebra Mathematica[®], a general purpose solver, not chemical engineering specific.

This approach is particularly suitable for undergraduate students, as at this level of chemical engineering formation, the synthetic pedagogical approach is more effective and can be very rewarding. The student builds all from starch and has to elaborate by himself a model for the process under investigation. During this step of model development, one learns a lot about equations of state, departure functions, activity models, MESH equations...

By integrating the basic mathematical functions with the powerful and easy-to-use programming language Mathematica[®], it is possible to handle processes that would be extremely tedious to encode in traditional programming environments. Using this powerful tool let the student concentrate on the very process he/she is investigating and enhances dramatically the overall understanding of his/her project. As illustrated in this chapter various

process alternatives can easily be probed (integration of the pressure drop in the stages, taking account of the non ideal efficiency of the plates, trying different solvents, etc.).

NATURAL GAS LIQUIDS, NGL, TRAIN

In a natural gas processing plant, the raw gas is pre-treated to remove liquid water and condensate, on one side, and the accompanying impurities that may interfere with the following separation processes and/or are undesirable in the final products, on the other side. Important steps in this pre-treatment are acid gas and sulfur compounds removal (CO_2 , H_2S , mercaptans, etc.), dehydration and eventually mercury removal and finally nitrogen rejection if the N_2 content of the gas is high. In the next separation unit, the Demethanizer, the dry sweet gas is cooled to separate the sales gas—containing mainly methane and less than 0.1 mol% pentane and heavier hydrocarbons—from the rest, raw Natural Gas Liquids. NGL is a mixture of ethane and heavier hydrocarbons (propane, butane, pentane, hexane and heptane) and constitutes an important feedstock for petrochemical plants and facilities (steam crackers) producing olefins and aromatics. As the components of the NGL often have higher sales value compared to the gas itself [1] they are separated using a train of distillation columns in which the various hydrocarbons are boiled off one by one [2, 3, 4]. The fractionation columns are called: Deethanizer, Depropanizer, and Debutanizer (Figure 1).

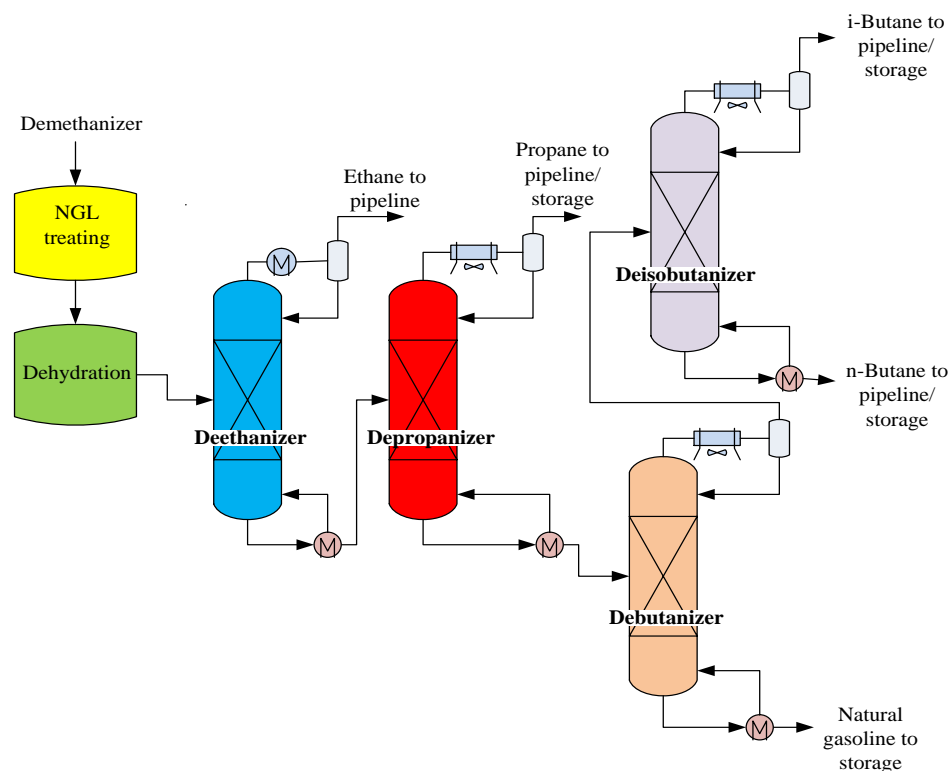


Figure 1. NGL separation train.

This first case study deals with the simulation of an NGL train. Raw NGL is to be separated in almost pure ethane, *i*-butane, *n*-butane, and a mixture composed of propane and the rest of the dissolved ethane. The bottom product of the last fractionation unit is natural gasoline.

As numerical example we consider a feed with a flow rate of 100 kmole/hr and a typical composition as given in Table 1 where C_7^+ is a pseudo-component that lumps together all components heavier than *n*-hexane. The four distillation columns (Deethanizer, Depropanizer, Debutanizer and Deisobutanizer) are operating at decreasing pressures: 26 bars, 17 bars, 10 bars and 7 bars, respectively. This pressure selection ensures, first, the separation of almost all components heavier than ethane in the Deethanizer at temperatures near 0°C, and allows, second, the usage of water as cooling medium in the condensers of the remaining units.

Table 1. Feed composition to the NGL train

Component	Mole Fraction
Methane	0.005
Ethane	0.370
Propane	0.260
<i>i</i> -butane	0.072
<i>n</i> -butane	0.148
<i>n</i> -pentane	0.085
<i>n</i> -hexane	0.040
C_7^+	0.020

Aspen HYSYS® Simulations

It is relatively straightforward to perform a simulation of the NGL train using Aspen HYSYS®. First, the components are chosen from the software's databank and the thermodynamic model for the prediction of the properties and the calculation of the vapor liquid equilibria—in the present case the Peng-Robinson equation of state (PR EoS, Appendix A). Then, the distillation columns for the Deethanizer, Depropanizer, Debutanizer and Deisobutanizer are added to the Process Flow Diagram (PFD, Figure 2). For the Deethanizer column, when the feed stream specifications are entered and the required column settings are selected properly, the column simulation can be performed and results are obtained. Next, in order to decrease the high pressure of the bottom stream of the Deethanizer (i.e., 26 bars), which serves as feed stream to the next column (i.e., the Depropanizer) operating at 17 bars, an expansion valve is incorporated in the PFD. Similarly, simulations can be performed for the Depropanizer and later for the rest of the distillation train (i.e., the Debutanizer and the Deisobutanizer). All distillation columns considered below have 40 equilibrium stages and in all four cases, the feed is entering at stage 20 counting from the top. The idea, behind the choice of these configurations, is to provide enough trays to separate ethane/propane in the Deethanizer, propane/*i*-butane in the Depropanizer, butanes/higher hydrocarbons in the Debutanizer and *i*-butane/*n*-butane in the Deisobutanizer. Furthermore, while a partial condenser is associated to the Deethanizer, a total condenser and a partial reboiler are considered in all other cases.

Results of the simulations are given in Table 2 with the composition of all material streams. We note in particular that the distillate of the Deethanizer is constituted of ethane (98.5 mol%) and methane (1.5 mol%). The top stream of the Depropanizer is composed of propane (85 mol%) with dissolved ethane (13.35 mol%) and a low fraction of *i*-butane (1.33 mol%). The streams exiting the last fractionation unit, the Deisobutanizer, are almost pure products: *i*-butane (99 mol%) in the distillate and *n*-butane (99 mol%) in the bottoms.

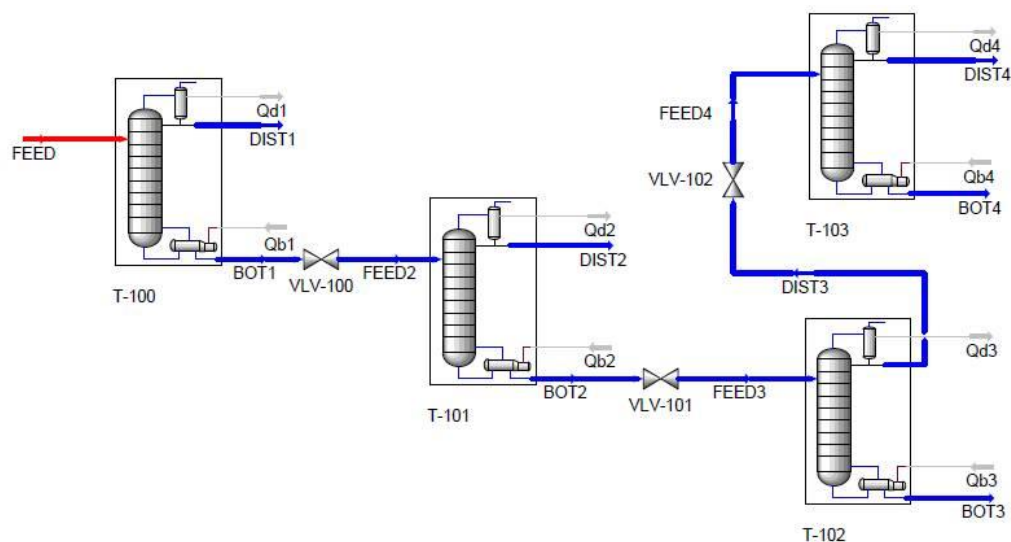


Figure 2. HYSYS[®] PFD of the NGL separation train.

Table 2. Results of the Aspen HYSYS[®] simulations

	DIST1	BOT1	DIST2	BOT2	DIST3	BOT3	DIST4	BOT4
Methane	0.0150	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Ethane	0.9850	0.0626	0.1365	0.0000	0.0000	0.0000	0.0000	0.0000
Propane	0.0000	0.3900	0.8500	0.0000	0.0000	0.0000	0.0001	0.0000
<i>i</i> -Butane	0.0000	0.1080	0.0133	0.1882	0.3149	0.0000	0.9899	0.0100
<i>n</i> -Butane	0.0000	0.2220	0.0002	0.4099	0.6851	0.0010	0.0100	0.9900
<i>n</i> -Pentane	0.0000	0.1275	0.0000	0.2355	0.0000	0.5856	0.0000	0.0000
<i>n</i> -Hexane	0.0000	0.0600	0.0000	0.1108	0.0000	0.2756	0.0000	0.0000
C ₇ ⁺	0.0000	0.0300	0.0000	0.0554	0.0000	0.1378	0.0000	0.0000

Mathematica[®] Simulations

In the four sections below, we present simulation results using Mathematica[®] for the same case study.

For both methods (i.e., calculations with Mathematica[®] and Aspen HYSYS[®]) and for all four separation units of the NGL train, the Peng-Robinson EoS has been used. MESH equations (Appendix B) for each one of the four separation units result in a set of 800

nonlinear algebraic equations, which are readily solved using Mathematica[®] in less than five minutes with an Intel[®] Core[™] 2 Duo CPU T9600 2.80 GHz RAM 4 GB.

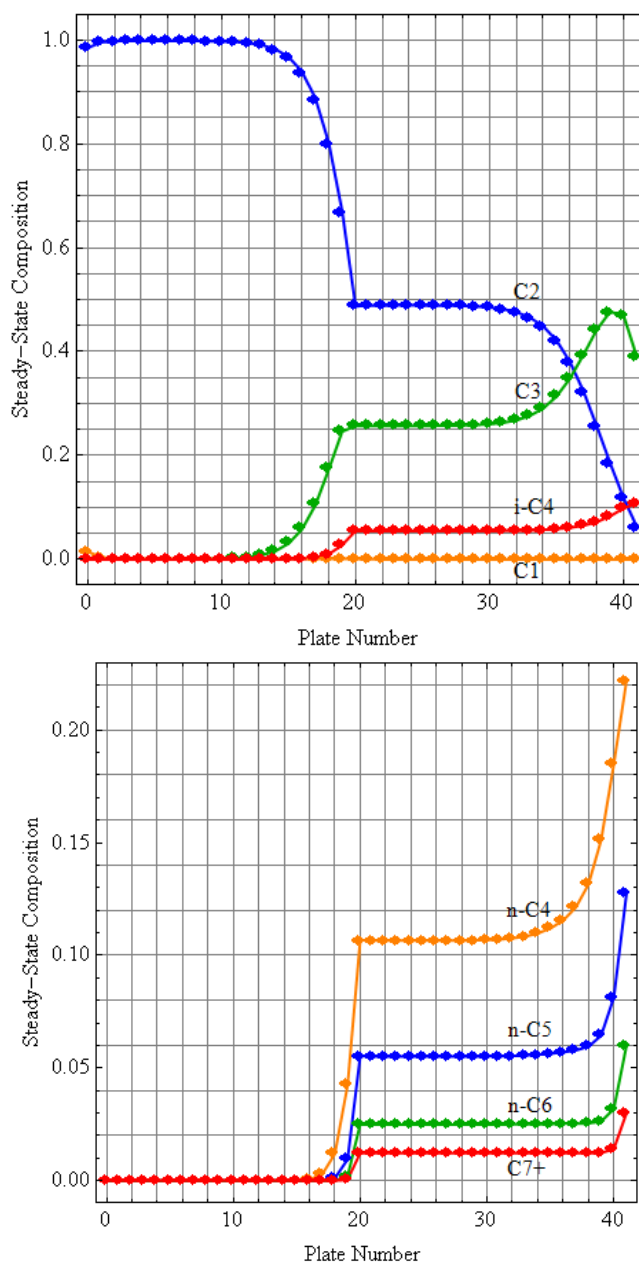


Figure 3. Steady-state composition profiles in the Deethanizer. (Continuous lines: Mathematica[®]; markers: Aspen HYSYS[®]).

Deethanizer

In this column ethane is separated out as overhead product. The reflux ratio and the mole % of ethane in the distillate have been set equal to 3 and 98.5, respectively.

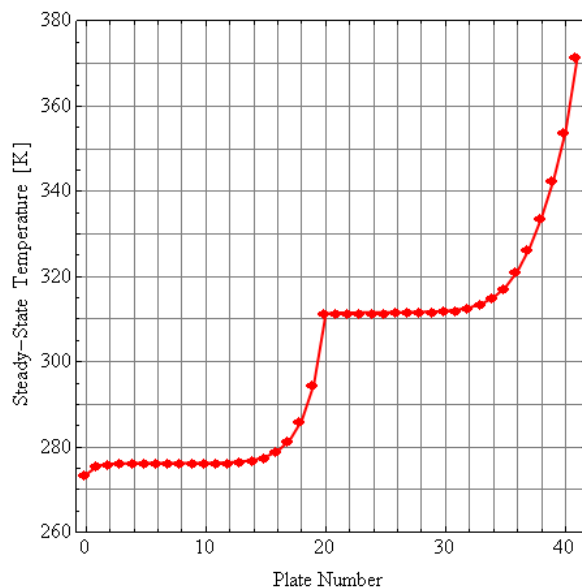


Figure 4. Steady-state temperature profile for the Deethanizer. (Continuous lines: Mathematica[®] and markers: Aspen HYSYS[®]).

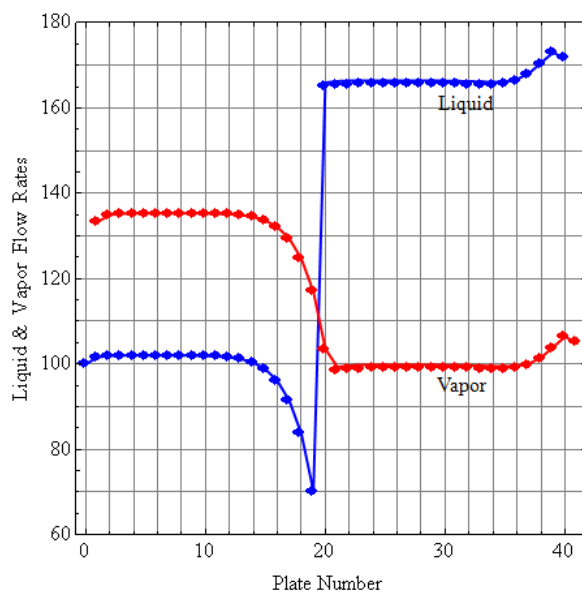


Figure 5. Steady-state liquid and vapor flow rate profiles for the Deethanizer. (Continuous lines: Mathematica[®] and markers: Aspen HYSYS[®]).

Figures 3-5 show the steady-state composition and temperature profiles as well as the liquid and vapor flow rates in the column. The distillate product has a flow rate of 33.33 kmole/hr and contains: 1.5 mol% methane and 98.5 mol% ethane. The bottom product from Deethanizer enters into the next column (i.e., the Depropanizer) with a flow rate equal to 66.66 kmole/hr and the following composition: 6.25 mol% ethane, 39.0 mol% propane, 10.8 mol% *i*-butane, 22.2 mol% *n*-butane, 12.75 mol% *n*-pentane, 6.0 mol% *n*-hexane and 3 mol% C_7^+ . The cooling and heating duties of the condenser and reboiler are $1.167 \cdot 10^6$ and $1.542 \cdot 10^6$ kJ/hr, respectively.

We note from Figures 3-5 also that the results of our Mathematica[®] simulations (continuous lines) match perfectly the results obtained with Aspen HYSYS[®] (markers). This is true for the composition profiles of all of the constituents in the column (Figure 3) as well as for the temperature evolution (Figure 4) and the total molar flow rates of vapor and liquid (Figure 5).

Depropanizer

The bottom stream of the Deethanizer serves as feed stream to the Depropanizer. The overhead product of this column is propane rich and is condensed in the condenser. The reflux ratio and the mol% of propane in the distillate have been set equal to 5 and 85.0, respectively. Figure 6 shows the steady-state composition profile of this distillation column. The distillate stream has a flow rate equal to 30.58 kmole/hr and contains: 13.64 mol% ethane, 85 mol% propane and 1.33 mol% *i*-butane. The bottom stream has a flow rate equal to 36.07 kmole/hr and is composed of 18.82 mol% *i*-butane, 41 mol% *n*-butane, 23.55 mol% *n*-pentane, 11.08 mol% *n*-hexane and 5.55 mol% C_7^+ . The cooling and heating duties of the condenser and reboiler are $2.429 \cdot 10^6$ and $2.348 \cdot 10^6$ kJ/hr, respectively. Again, perfect agreement was obtained with Aspen HYSYS[®], just as in the case of the Deethanizer. For simplicity, only compositions profiles comparison (continuous lines for Mathematica[®] and markers for HYSYS results) are shown in Figure 6.

Debutanizer

The stream exiting the Depropanizer reboiler serves as feed stream, after reduction of its pressure, to the Debutanizer. The reflux ratio and the mol% of *n*-butane in the residue have been set to 5 and 0.1, respectively. In Figure 7 the steady-state composition profiles of all constituents inside this distillation column are represented. *i*-butane and *n*-butane are separated out as overhead product. The distillate stream has a flow rate equal to 21.56 kmole/hr and contains a butane mixture with 31.48 mol% *i*-butane and 68.51 mol% *n*-butane. The bottom stream with a flow rate of 36.07 kmole/hr is composed of 58.56 mol% *n*-pentane, 27.55 mol% *n*-hexane and 13.87 mol% C_7^+ . The cooling and heating duties of the condenser and reboiler are found to be $2.200 \cdot 10^6$ and $2.070 \cdot 10^6$ kJ/hr, respectively. Once more, perfect agreement was obtained with Aspen HYSYS[®] results.

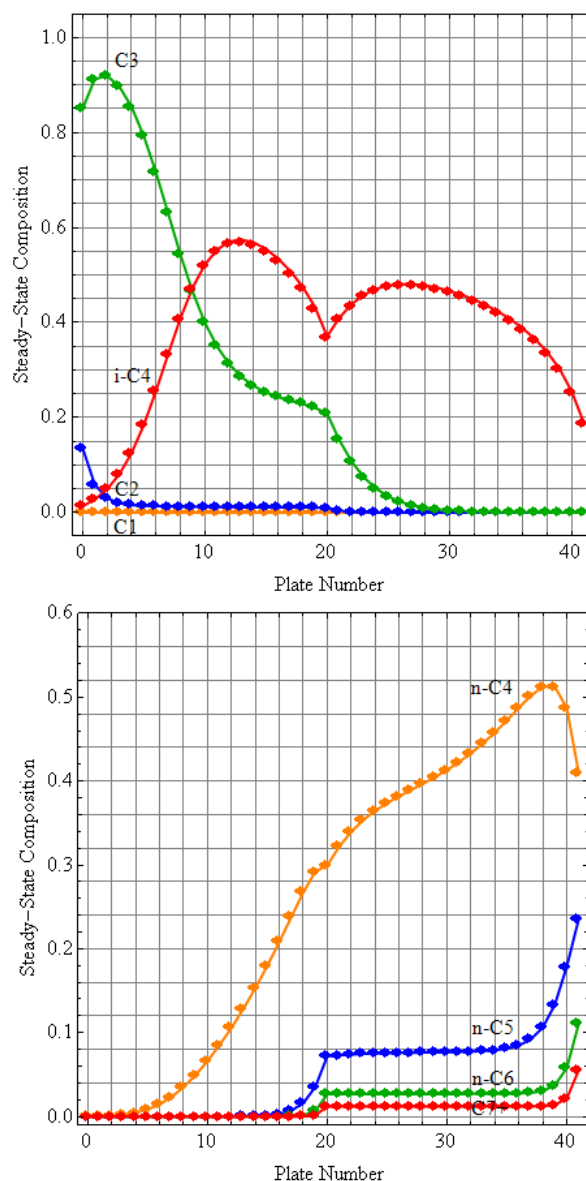


Figure 6. Steady-state composition profiles for the Depropanizer. (Continuous lines: Mathematica© and markers: Aspen HYSYS®).

Deisobutanizer

The liquid butanes mixture coming from the condenser of the preceding column will be separated now in its constituents *n*-butane and *i*-butane in the last distillate column of the NGL train, the Deisobutanizer. Figure 8 shows the composition evolution of *i*-butane and *n*-butane in the column. The distillate stream (flow rate: 6.70 kmole/hr) is composed of 98.98 mol% *i*-butane and 1.01 mol% *n*-butane and the bottom stream (14.86 kmole/hr), 1 mol% *i*-butane and 98.99 mol% *n*-butane. The cooling and heating duties of the condenser and

reboiler are: $3.560 \cdot 10^6$ and $3.461 \cdot 10^6$ kJ/hr, respectively. We note again the almost perfect concordance between Aspen HYSYS[®] and Mathematica[®] simulation results.

For pedagogical purposes only, two more simulations are realized to illustrate the use of Mathematica[®] as tool for chemical engineering modeling and calculations.

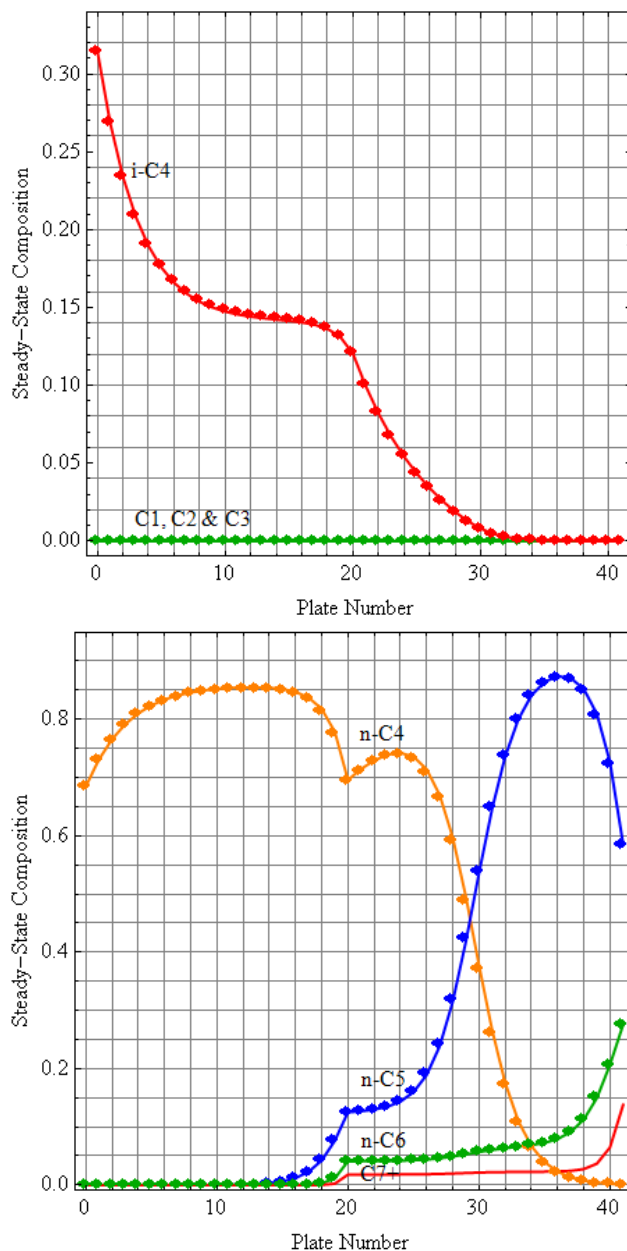


Figure 7. Steady-state composition profiles for the Debutanizer. (Continuous lines: Mathematica[®] and markers: Aspen HYSYS[®]).

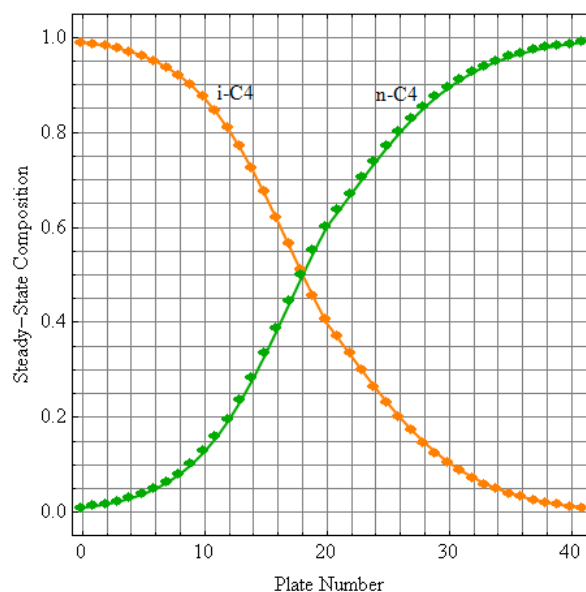


Figure 8. Steady-state composition profiles in the Deisobutanizer. (Continuous lines: Mathematica[®] and markers: Aspen HYSYS[®]).

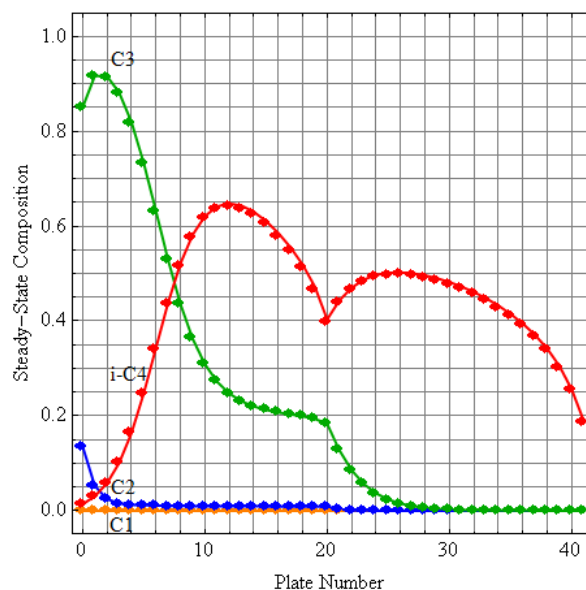


Figure 9. Steady-state composition profiles in the Depropanizer: case with pressure drop. (Continuous lines: Mathematica[®] and markers: Aspen HYSYS[®]).

Depropanizer with Pressure-Drop

For this case, we return to the Depropanizer but consider now the pressure drop in the column that was neglected previously. We set a Δp of 10 kPa for each stage and 20 kPa for condenser and reboiler. The reflux ratio and the mol% of propane in the distillate are set to 5

and 85.0, respectively, the same as before. Figure 9 shows the steady-state composition profiles of the lighter constituents in the distillation column (i.e., the Depropanizer), and Figure 10 the pressure evolution. No effect of the pressure drop on the distillate (13.61 mol% ethane, 85 mol% propane, and 1.37 mol% *i*-butane) and bottoms composition (18.79 mol% *i*-butane, 41.01 mol% *n*-butane, 23.56 mol% *n*-pentane, 11.08 mol% *n*-hexane and 5.56 mol% C_7^*) is observed. But we do now note an impact of the cooling and heating duties of the condenser and reboiler: $2.665 \cdot 10^6$ and $2.533 \cdot 10^6$ kJ/hr, respectively. More heat is supplied to the reboiler and more heat is rejected in the condenser, and hence more energy is consumed for the same separation by dissipative effects.

We notice once more the complete agreement with Aspen HYSYS® simulation results.

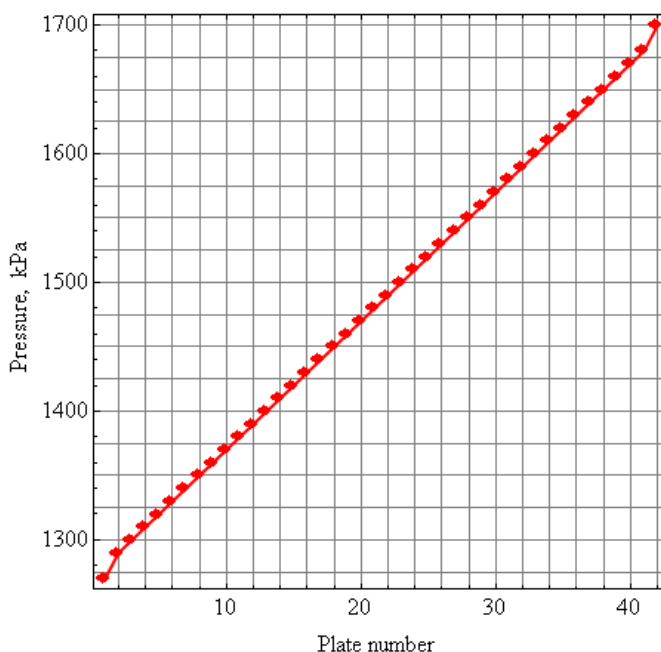


Figure 10. Pressure profile in the Depropanizer: case with pressure drop. (Continuous lines: Mathematica® and markers: Aspen HYSYS®).

Deisobutanizer with 75 % Liquid Murphree Efficiency

Real column plates rarely have the same performances as theoretical stages. Very often equilibrium is not reached and the separation is less efficient. To characterize real plate performances in comparison to theoretical separation under the same conditions, the Murphree efficiency is introduced [5]. It can be defined for the gas and for the liquid phase and for every tray in the column. To simplify the design and calculation of columns however, a mean Murphree efficiency is used for each phase.

We reconsider now the Deisobutanizer and assume a mean liquid Murphree efficiency of 75 % for otherwise similar operating conditions. In particular, the reflux and reboil ratios are set to 10 and 4.

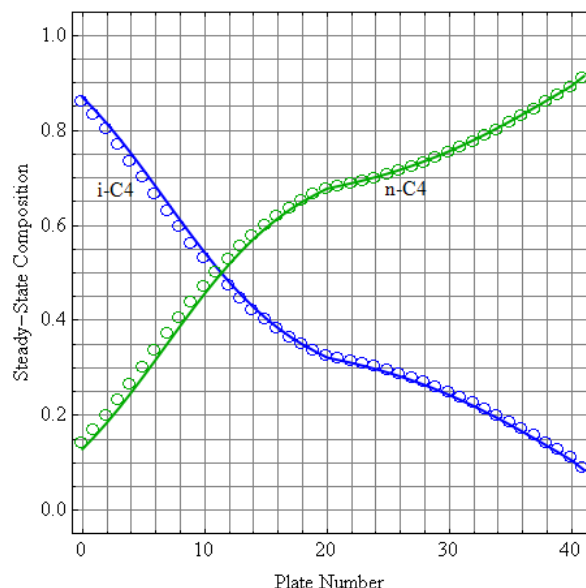


Figure 11. Steady-state composition profiles in the Deisobutanizer for 75% Murphree efficiency. (Continuous lines: Mathematica[®] and markers: Aspen HYSYS[®]).

The effect of the separation process is rather important: a lower distillate stream flow rate is produced (6.291 kmole/hr) and the desired purity of the products are not reached: 87.02 mol% for *i*-butane and 91.46 mol% for *n*-butane. The cooling and heating duties of the condenser and reboiler are now $1.290 \cdot 10^6$ and $1.190 \cdot 10^6$ kJ/hr, respectively.

We observe again a complete concordance with Aspen HYSYS[®] results (Figure 11).

EXTRACTIVE DISTILLATION

Extractive distillation is a ubiquitous technique used for the separation of close-boiling mixtures as well as non-ideal binary mixtures presenting either a minimum-boiling or a maximum-boiling azeotrope [6]. Total annualized cost (TAC) calculations show that this method is more economical than heterogeneous azeotropic distillation [7]. In addition, this technique applies even if the azeotrope is not pressure-sensitive.

For low relative volatility separations a large number of stages and a high reflux ratio are necessary. Energy savings become then an important issue. Some solvents, called entrainer in the context of extractive distillation, alter selectively the relative volatility of one component when added to the mixture. This species is dissolved in the entrainer and exit the column as the bottom liquid mixture because the entrainer is normally the highest boiling product. This separation scheme necessitates generally two columns, one for extraction and one for solvent recovery (Figure 12).

In most industrialized countries, butadiene, an important monomer used in the production of synthetic rubber, is produced as a byproduct of ethylene and other olefin production processes by steam cracking [8]. If mixed with steam and subjected to pyrolysis, aliphatic hydrocarbons give up hydrogen to yield mixtures of unsaturated hydrocarbons, including butadiene. The quantity of butadiene produced depends on the nature of the aliphatic

hydrocarbons fed to the steam cracker. Ethane cracking produces mainly ethylene. Heavier feeds favor the formation of higher molecular weight olefins, butadiene, and aromatic products. Butadiene is typically isolated from the other C_4 compounds produced by steam cracking using extractive distillation [8]. A polar aprotic entrainer such as acetonitrile, *n*-methyl pyrrolidone (NMP) or furfural is generally used as extractive solvent. This latter is then stripped from 1,3-butadiene by distillation.

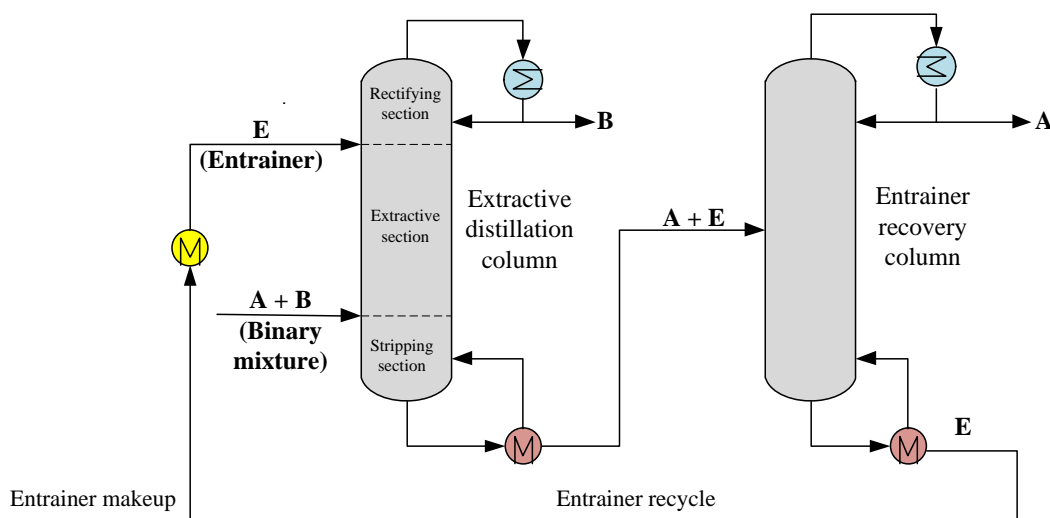


Figure 12. Set-up of the extractive distillation and regeneration columns.

As example of extractive distillation we consider a mixture composed of four close-boiling C_4 hydrocarbons: *n*-butane (normal boiling temperature: 272.7 K), *i*-butane (261.4 K), *i*-butene (266.2 K) and 1,3-butadiene (268.7 K) [9]. The objective is to separate 1,3-butadiene. The selected entrainer for our case study is furfural. As shown in Table 3, the relative volatilities of *n*-butane, *i*-butene and *i*-butane relative to 1,3-butadiene are close to unity and become larger if furfural is added to the mixture. One peculiar phenomenon is the fact that *n*-butane becomes more volatile than 1,3-butadiene in the presence of this solvent. Thus, the entrainer makes the separation of this close-boiling C_4 mixture possible simply by modifying the volatilities. It was shown that this effect can be further improved (i.e., much different from unity) if a small percentage of water is added to furfural [10].

Table 3. Relative volatilities of *n*-butane, *i*-butene and *i*-butane with respect to 1,3-butadiene at 448.15 kPa and 54.5 °C in the original mixture and after addition of furfural

	Original Mixture	Furfural Added
<i>n</i> -butane	0.8714	1.0777
<i>i</i> -butene	1.0449	1.2049
<i>i</i> -butane	1.1706	1.6066

We now study several aspects related to this separation method by performing simulations using Mathematica[®], and Aspen HYSYS[®] for comparison purposes. The Soave Redlich-Kwong EoS (Appendix A) will be used and in both simulations. The solvent regeneration column is also included in the simulations in order to show that the entrainer recovery is possible.

Extractive Distillation Column

We consider an extractive distillation column with 50 equilibrium stages, a partial reboiler and a total condenser and operating at 300 kPa. This column has an upper feed composed of pure furfural (i.e., the entrainer) with a flow rate equal to 55 kmole/hr. It is introduced at 20 °C at stage 3 counting from the top. The extractive column has also a lower feed composed of 5 mol% *n*-butane, 15 mol% *i*-butene, 20 mol% *i*-butane and 60 mol% 1,3-butadiene. The lower feed enters at stage 40 counting from the top at the same temperature of 20 °C with a flow rate of 10 kmole/hr. In the simulations, the mol% of 1,3-butadiene in the distillate and of *i*-butene in the residue are set equal to 3 and 0.4, respectively.

The mathematical model of the separation sequence consists of MESH set of 678 nonlinear algebraic equations, which are solved in less than 33 seconds using Mathematica[®].

Figures 13 and 14 show the steady state composition and temperature profiles in the extractive distillation column. It is clear from Figure 13 that furfural is an appropriate entrainer for the extraction of 1,3-butadiene. The distillate is composed of *n*-butane, *i*-butene and *i*-butane with a small fraction of 1,3-butadiene (i.e., 3 mol%). The bottom stream has a flow rate equal to 61.55 kmole/hr and is composed of mainly 1,3-butadiene and furfural (89.35 mol-% and 9.57 mol%, respectively). A non-negligible amount of *n*-butane (i.e., 0.65 mole %) is found in the bottom stream since the relative volatility of *n*-butane relative to 1,3-butadiene is very close to unity (1.077, Table 3). The heat and cooling duties of the reboiler and condenser are found equal to $1.509 \cdot 10^6$ kJ/hr and $0.786 \cdot 10^6$ kJ/hr, respectively.

Here also we notice the rather good agreement between the simulation results of Aspen HYSYS[®] (see Figure 15 for the extractive/recovery distillation set-up) and Mathematica[®].

Solvent Recovery Column

This column serves to recover the main product 1,3-butadiene and regenerate the solvent for recycling. The separation is realized in a 20 stages distillation column operating at 200 kPa and equipped with a partial reboiler and a total condenser. It is supplied with the bottoms of the extractive distillation column as feed that is introduced at stage 10 counting from the top. The reflux and reboil ratios are set to 5 and 0.777, respectively. Furfural is obtained as a bottom product and 1,3-butadiene as overhead stream.

The mathematical model of the recovery column is constituted of 288 nonlinear MESH equations system which is readily solved with Mathematica[®].

Figure 16 gives the steady-state composition profile for the different constituents. The distillate stream has a flow rate equal to 6.55 kmole/hr and is composed of 90.01 mol% 1,3-butadiene. The bottom stream is pure furfural and with a flow rate of 55 kmole/hr. A minor make-up solvent stream (flow rate: 0.001 kmole/hr) is necessary to compensate for

evaporation. The condenser and reboiler duties are evaluated to $0.863 \cdot 10^6$ and $1.813 \cdot 10^6$ kJ/hr, respectively.

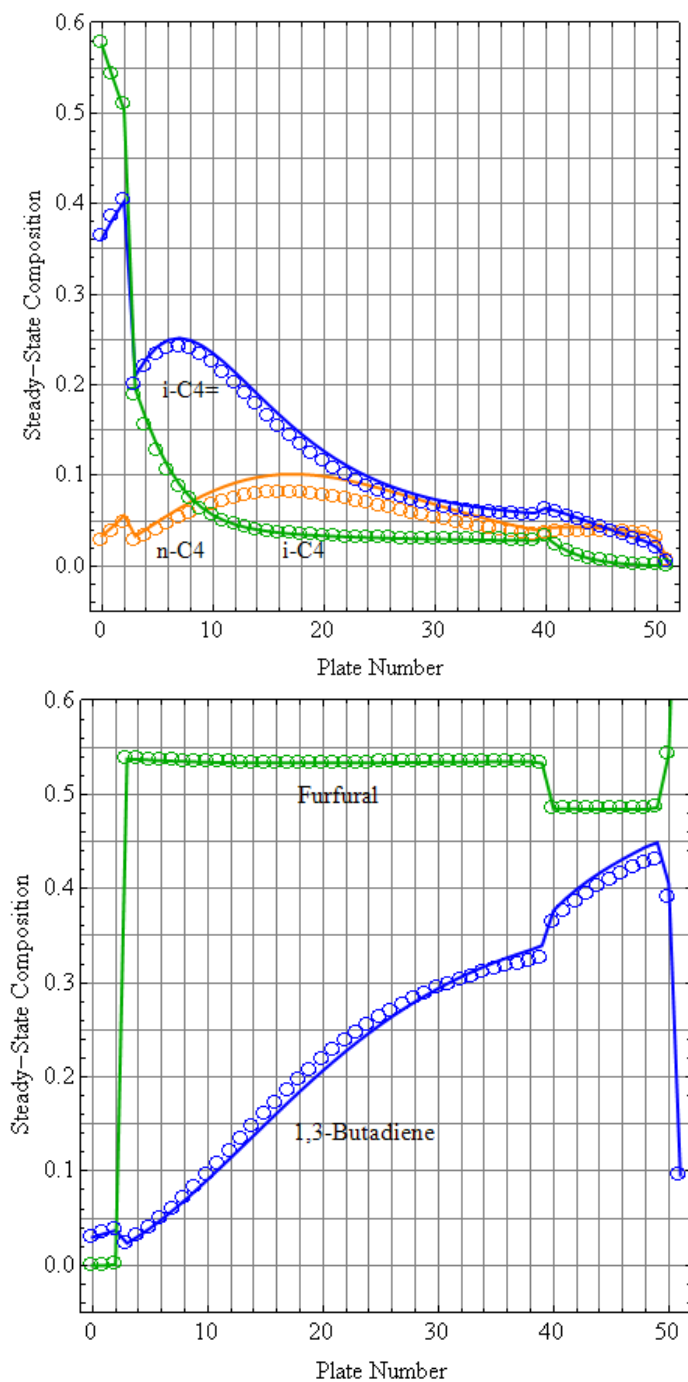


Figure 13. Steady-state composition profiles in the extractive distillation column. (Continuous lines: Mathematica[®] and markers: Aspen HYSYS[®]).

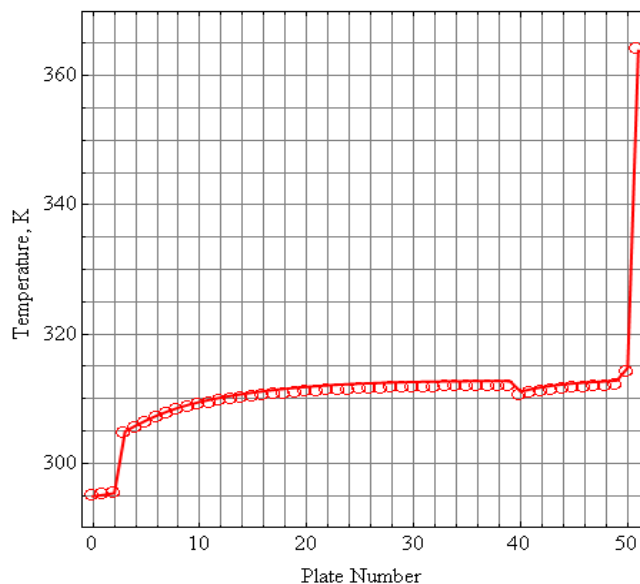


Figure 14. Temperature profile in the extractive distillation column. (Continuous lines: Mathematica[®] and markers: Aspen HYSYS[®]).

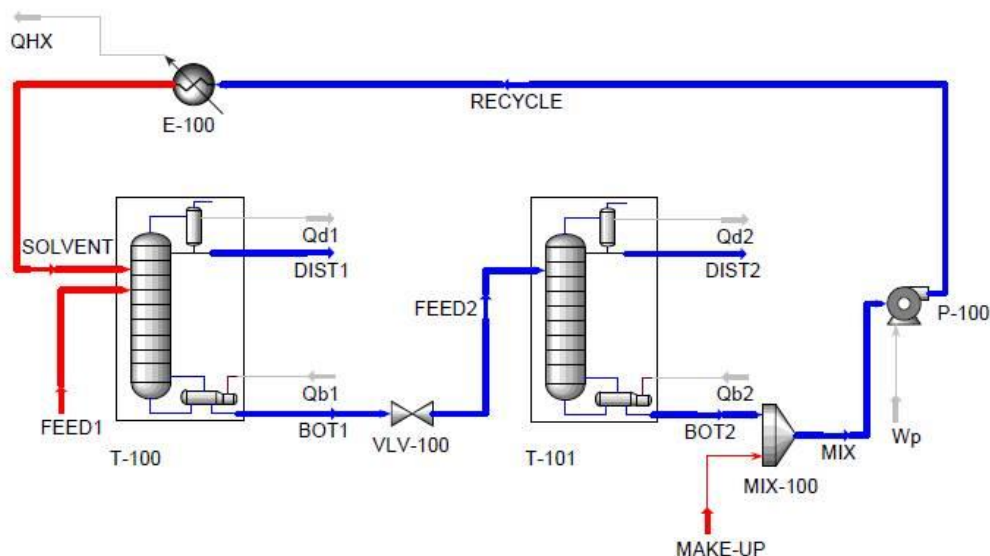


Figure 15. Aspen HYSYS[®] PDF for 1,3-butadiene furfural extraction.

REACTIVE DISTILLATION

In production processes involving chemical transformations, reaction and separation are usually handled in distinct devices. A simpler design integrating reaction and separation by distillation or distillation/liquid extraction in the same unit is in many instances possible and

realized in one piece of equipment, a reactive distillation setup. The first applications of this technology were the alkylation of aromatics [11, 12, 13].

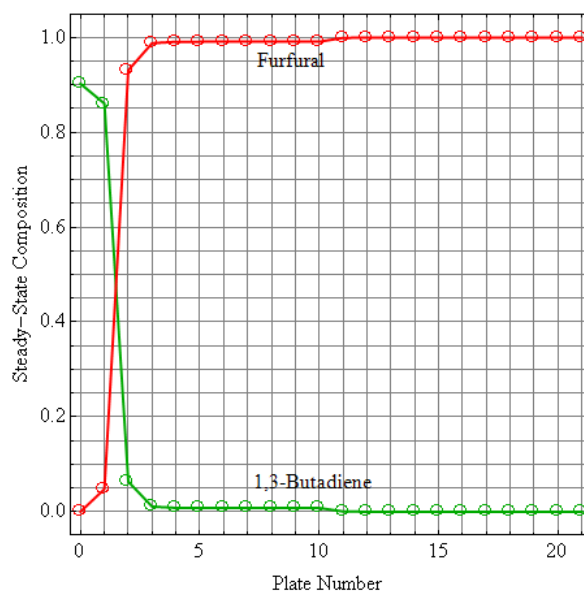


Figure 16. Steady-state liquid and vapor profiles in the extractive distillation column. (Continuous lines: Mathematica[®] and markers: Aspen HYSYS[®]).

With the continuous removal of reaction products, reactive distillation, when possible, offers the advantages of higher yields, energy savings and reduced capital costs [14].

The standard configuration of a reactive distillation column includes a rectification section, a reaction section and a stripping section. A set of reactive trays or reactive packing is used as reaction section.

Three applications of this innovative technology will be handled in the following.

Production of MTBE in a Reactive Distillation Column

Methyl-*t*-butyl ether, MTBE, is used as gasoline additive to increase its octane rating. It also allows the use of smaller amounts of lead alkyl compounds as anti-knock agents. It is further found that with this additive, the emission of carbon monoxide and nitrous oxides on combustion of gasoline is largely reduced [15]. The production reaction of methyl-*t*-butyl ether from *i*-butene and methanol takes place in the liquid phase in the presence of acidic ion-exchange resin as catalyst in a fixed bed reactor [16]. A simplified flow sheet of the process is represented in Figure 17.

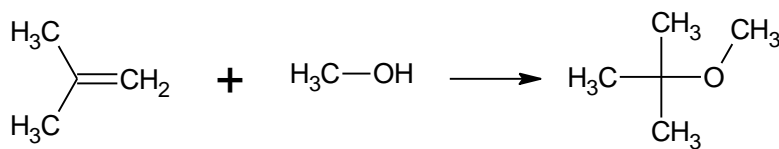


Figure 17. (Continued).

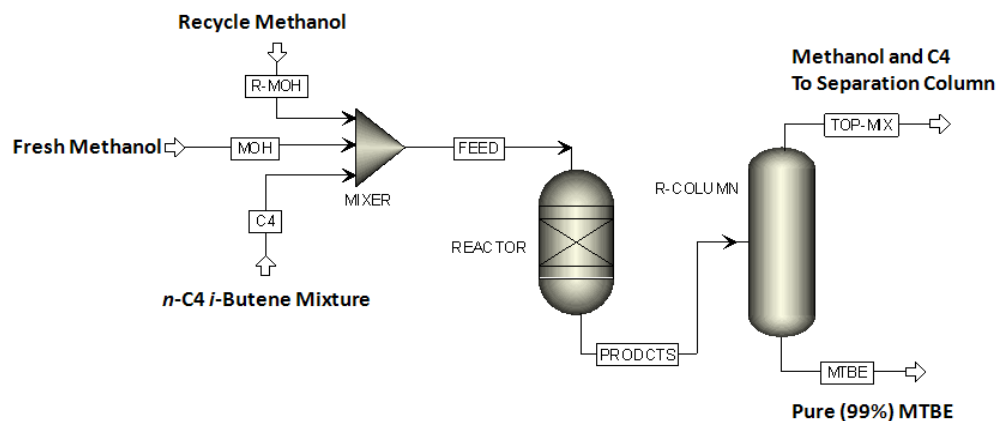


Figure 17. Schematics of the MTBE production process.

This case study deals with the simulation of the catalytic synthesis of methyl *tert*-butyl ether using reactive distillation. The objective is to achieve a high purity product, 99 % or better.

As a numerical example [17] we consider a reactive distillation column with 16 stages, a partial reboiler (stage 17) and a total condenser (stage 0). The reactive section where the synthesis reaction is taking place ranges from stage 3 to 9. The feed is a liquid mixture of 66.67% mole of *n*-butane as inert solvent and 33.33% mole of *i*-butene on one side, and pure methanol on the other side. It is introduced at stage 9. The operation pressure is set to 11.2 bars.

For the determination of the thermodynamic properties of the fluids and the calculation of the liquid-vapor equilibria the Wilson model [9, 18, 19, 20, 21] is used for the liquid phase and the Peng-Robinson equation of state (Appendix A) for the vapor phase.

The details of the Mathematica[®] model of the process can be found in reference [22]. We just emphasize here some results of this interactive program. As expected, no MTBE is formed for very low Damköhler numbers (molar hold-up near zero) and the only species exiting the column are the reactants *n*-butane, *i*-butene, and methanol.

At moderate Damköhler numbers, low conversions are achieved.

Finally, at high Damköhler numbers, almost pure MTBE (99% purity) is obtained as a bottom product and a mixture mainly composed of *n*-butane (88 mol%) as distillate (Figure 18). This composition is close to the binary nonreactive azeotrope mixture of methanol and *n*-butane.

As an exercise, the reader can run the Mathematica program to examine the effect of the molar hold up on the performances of the reactive distillation column.

Figure 19 presents a simplified flow sheet of the production of MTBE in a reactive distillation column as simulated with Aspen HYSYS[®] with similar operating conditions. As can be noted by comparing Figures 18 and 19, the simulation results obtained using Mathematica are in good concordance with those of Aspen HYSYS[®]. In particular, the bottom product meets the purity requirement imposed.

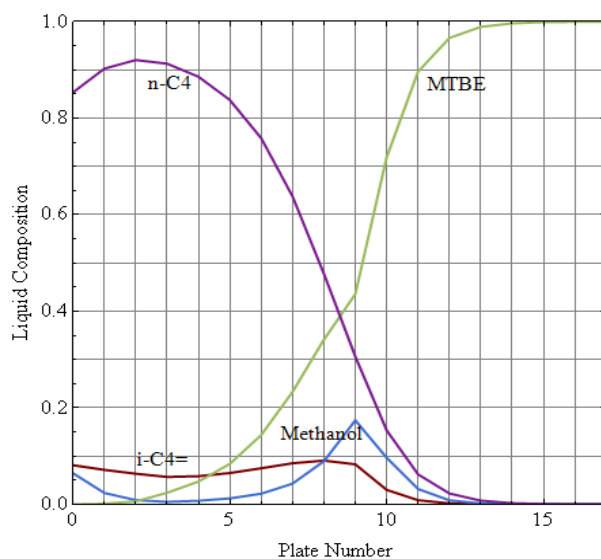


Figure 18. Profile of the compositions in the MTBE synthesis column.

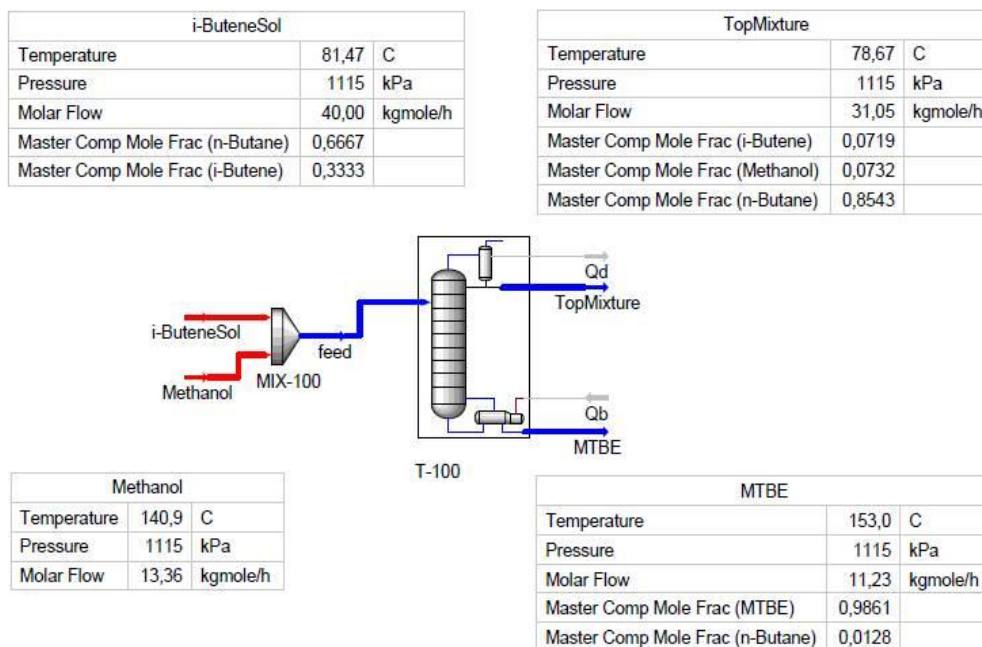


Figure 19. Aspen HYSYS® PDF of the reactive distillation column for the production of MTBE.

Decomposition of MTBE in a Reactive Distillation Column

Besides its major application as gasoline additive, MTBE offers also a method of selectively removing *i*-butene from a C_4 -mixture. Its subsequent decomposition by cracking yields highly pure *i*-butene and methanol [16, 23].

In the present case study we simulate a reactive distillation column that produces *i*-butene and methanol from the decomposition of methyl *tert*-butyl ether (MTBE), the reverse reaction of that of the preceding case.

The reaction is taking place in the liquid phase in the presence of acid catalyst. Distilling the decomposition products under reflux yields an overhead fraction composed mainly of *i*-butene and bottoms effluent containing almost pure methanol.

The sieve tray column has 16 stages, a partial reboiler, and a total condenser. The column is fed with pure MTBE at stage 8. The reactive stages range from 6 to 11.

An asymmetric thermodynamic approach (ϕ - γ) is used to predict the properties of the fluid mixture and the calculation of the liquid-vapor equilibria: Wilson model for the liquid phase and ideal gas law for the vapor phase. The operation pressure is set to 11.2 bars. The details of the kinetics of this equilibrium limited reaction can be found in references [24, 25].

The Mathematica[®] interactive simulation model of this reactive distillation column can be found in reference [25]. Figures 20 and 21 are generated with this program. The reader is encouraged to run the program in order to study the effect of the operating conditions on the purity of the distillate.

For low Damköhler numbers (low molar holdup), the conversion is low. Figure 20 shows the composition profiles vs. stage number for the case of a molar holdup of 20 kmol. As can be noted unconverted MBTE is found in the bottoms mixed with the product methanol.

At high Damköhler numbers, we get almost pure methanol as bottoms and pure *i*-butene in the distillate (Figure 21). As Figure 22 depicts, similar results are obtained using Aspen HYSYS[®].

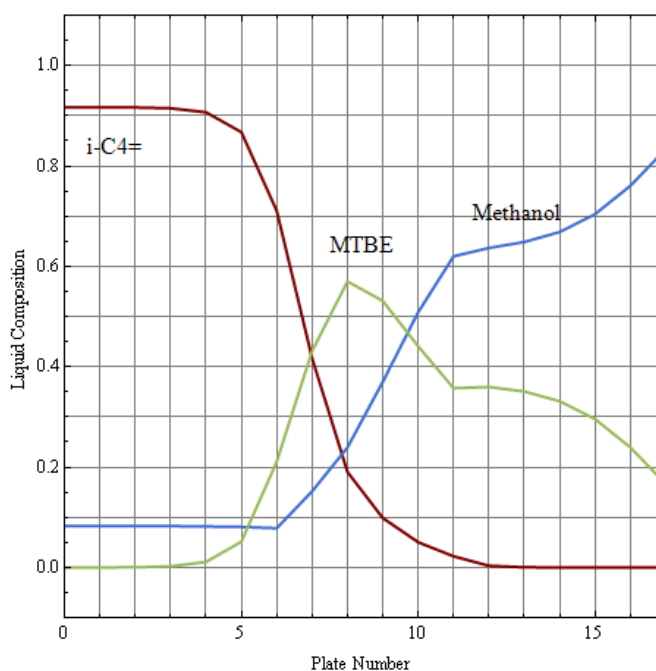


Figure 20. MTBE decomposition: Profiles of the compositions in the column in the case of a molar holdup of 20 kmol.

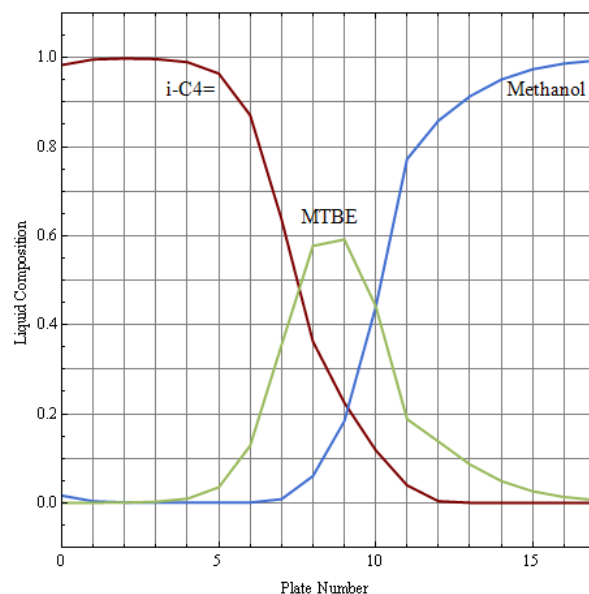


Figure 21. MTBE decomposition: Compositions in the for a molar holdup of 500 kmol.

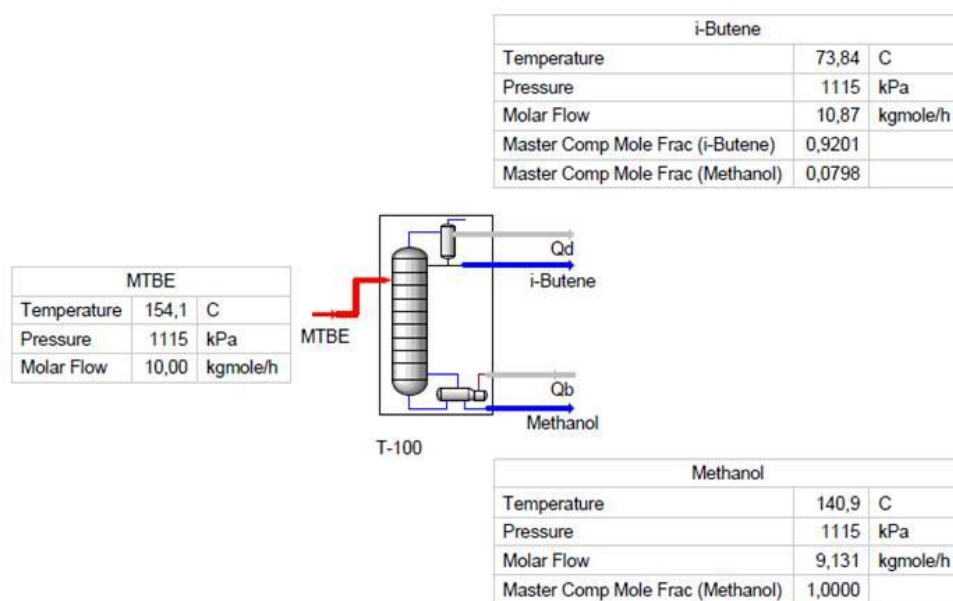
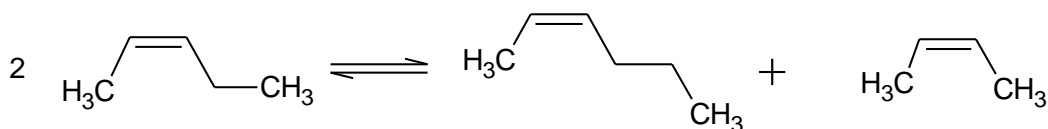


Figure 22. Aspen HYSYS[®] model of the reactive distillation column for the decomposition of MTBE (Reflux ratio: 7.5; Boilup ratio: 8.25).

Metathesis of cis-2-pentene in a Reactive Distillation Column

We consider at last case the disproportionation reaction, known also as a metathesis, of cis-2-pentene to cis-2-hexene and cis-2-butene.



In order to simplify the notations, we designate by C, B and A respectively the components cis-2-pentene, cis-2-hexene and cis-2-butene.

The ternary mixture is subject to an equilibrium-limited chemical reaction with reaction rate [26, 27]

$$r = 0.5k \left[x_C^2 - \frac{x_A x_B}{K_{eq}} \right]$$

where K_{eq} is the temperature dependant equilibrium constant, and

$$k = 3553.6 \exp \left[-\frac{6000}{RT} \right]$$

the reaction rate constant, with $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$.

The pure reactant C (cis-2-pentene) is fed to a reactive distillation column operating at a pressure of 3 atmospheres with 13 plates; the feed stage location is stage 5, the reactive stages go from stages 2 to 7. The feed flow rate is set to 100kmol/hr.

The following simulations are made with the simplifying assumption of constant molar overflow (CMO) and by neglecting heat effects [6, 27, 28].

The Mathematica[®] interactive simulation model of this reactive distillation column can be found in reference [28]. Figures 23, 24 and 25 illustrate some results of the calculations, namely:

- the composition profile vs. plate number for the three components of the ternary system (A in red, B in blue, C in green and the reactive zone in light blue) (Figure 23),
- the temperature profile in the column (Figure 24), and
- the ternary diagram with the composition (mole fraction) of B vs. the composition of A. The feed composition is shown by a dot and the reactive stages 2 to 7 are displayed (Fig. 25).

It is worth noting that for high hold-up values (i.e., large Damköhler numbers) one recovers the equilibrium case shown by the green solid curve in the ternary diagram.

We note again the good concordance between the simulations results of the Mathematica program with those obtained with the Aspen HYSYS[®] software (Figure 26).

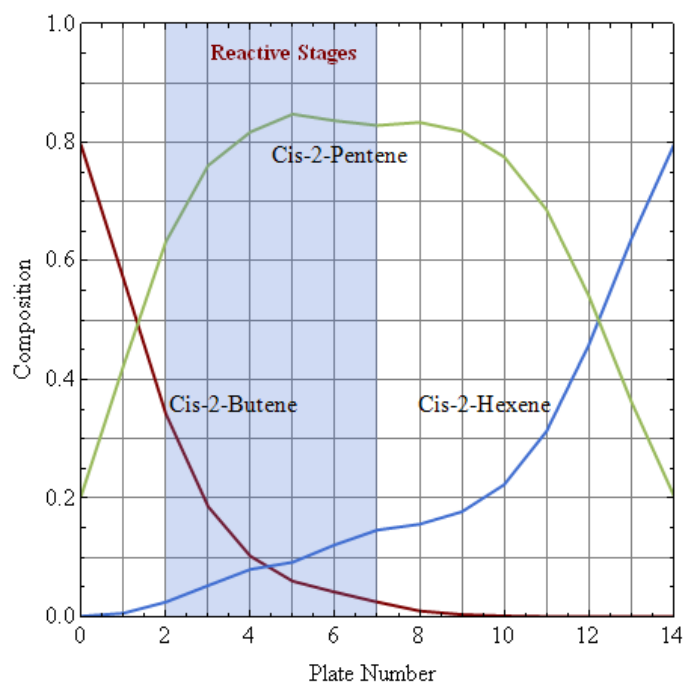


Figure 23. Compositions in the metathesis column (Reflux ratio: 14; Molar holdup: 500 kmol).

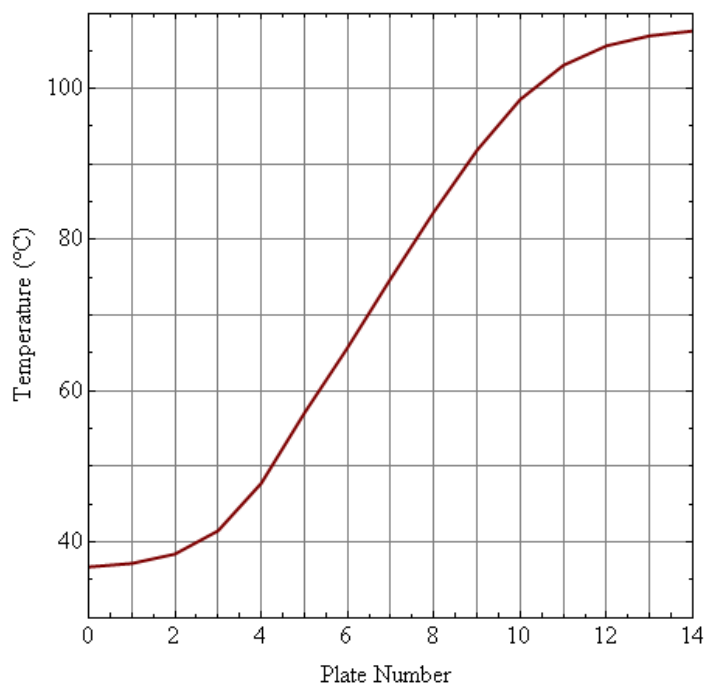


Figure 24. Profile of temperature in the metathesis column (Reflux ratio: 14; Molar holdup: 500 kmol).

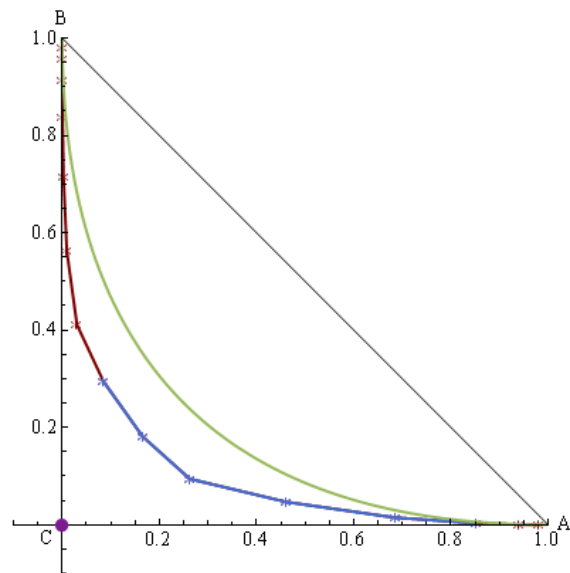


Figure 25. Ternary diagram (Equilibrium curve in green) (Reflux ratio: 6.5; Molar holdup: 450 kmol).

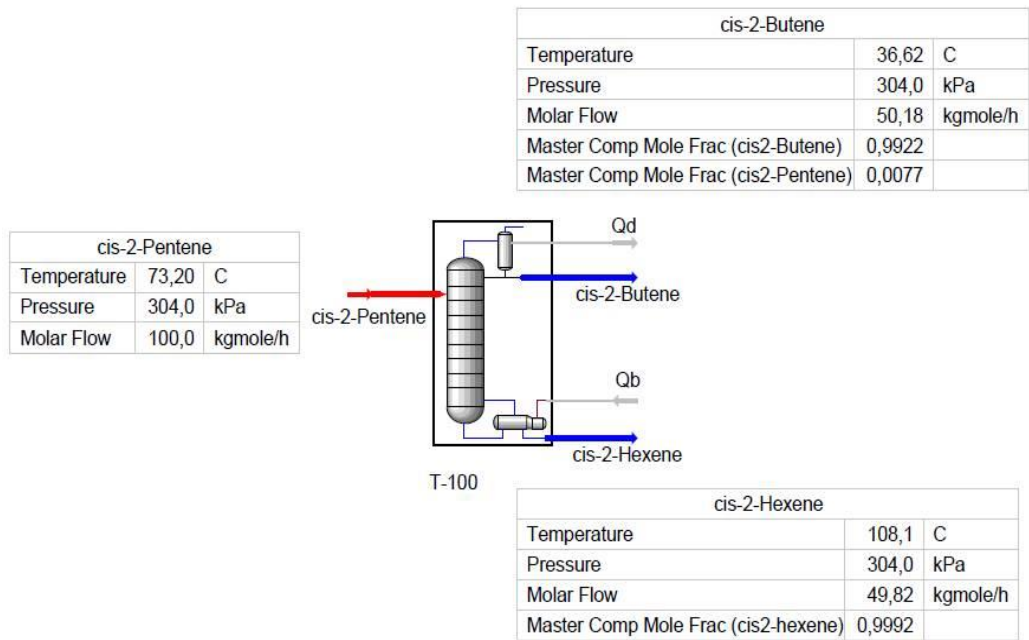


Figure 26. Aspen HYSYS® model of the reactive distillation column for the cis-2-pentene metathesis with operating conditions and product properties.

EXPLORING FURTHER PEDAGOGICAL PROBLEMS USING MATHEMATICA[®]

In all the distillation simulations presented for the different case studies, no optimizations have been attempted. Indeed, the number of trays, the feed tray locations as well as the reflux and reboil ratios could be varied easily in order to come-up with more economical designs. For this purpose, TAC calculations [29] could be performed. In addition, column diameters could be determined based on the classical procedure by Fair [30, 31]. In principle, it would also be possible with the help of Mathematica[®] to perform even dynamic simulations for these distillation columns [32] and then to devise appropriate control schemes [33].

For the case of extractive distillation, solvents other than furfural could be used. For example, NMP is known to be a very good candidate for the purification of C₄ mixtures containing 1,3-butadiene. Such calculations would require: (1) a good activity coefficient prediction model such as the UNIQUAC model [9, 19, 20, 34] to allow for non-ideal behavior in the liquid phase and (2) an EoS such as the SRK or PR EoS to predict the gas-phase fugacity coefficients since the column operates at relatively high pressures.

CONCLUSION

In this chapter five industrially relevant fractionation processes by different distillation techniques are simulated: the separation of natural gas liquids (NGLs) in a distillation train, the extractive distillation of 1,3-butadiene from a C₄ cut with furfural as the entrainer, the production of MTBE from *i*-butene and methanol in a reactive distillation column, the reverse process of production of *i*-butene by the decomposition of methyl *tert*-butyl ether, and the metathesis of cis-2-pentene to cis-2-butene and cis-2-hexene.

Routinely these processes are treated readily using a flow sheeting software like Aspen-HYSYS[®], similarly to what is done here for comparison purposes. The objective of this chapter was to show how these complex processes can also be handled with more pedagogical benefits using the computer algebra Mathematica[®]. In all investigated cases, the comparison between the two approaches of simulations shows very good agreement.

The Mathematica[®] interactive simulation models developed for the different case studies are available at <http://demonstrations.wolfram.com>.

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APPENDIX A: CUBIC EQUATIONS OF STATE

Cubic equation of states are pressure explicit equation in temperature and volume that, when expanded, would contain the volume raised to the third power. They are often used in the oil and gas and petrochemical industries to describe the behavior of the fluid mixtures. They allow the prediction of several important aspects of chemical engineering thermodynamics such as vapor-liquid equilibrium data, liquid-phase and vapor-phase compressibility factors, enthalpies of gases and liquids, etc. Simulations of the distillation of several industrially relevant hydrocarbon mixtures commonly build on equations of states such as the SRK and PR EoS.

van der Waals Equation of State

This well-known equation from which the other cubic EoS are derived, writes

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (\text{A-1})$$

where a and b are fluid specific constants that can be evaluated from the critical constants (pressure, P_c and temperature, T_c) of the substance [9],

$$a = \frac{27}{64} \frac{R^2 T_c^2}{P_c} \quad b = \frac{R T_c}{8 P_c} \quad (\text{A-2})$$

Redlich-Kwong Equation of State

This modification of the van der Waals EoS predicts better the vapor-liquid equilibrium of pure fluids. It writes

$$P = \frac{RT}{V-b} - \frac{a}{\sqrt{T} V(V+b)} \quad (\text{A-3})$$

The fluid specific constants a and b are now expressed as [9, 19]

$$a = 0.42748 \frac{R^2 T_c^{2.5}}{P_c} \quad b = 0.08664 \frac{R T_c}{P_c} \quad (\text{A-4})$$

Peng-Robinson Equation of State

This equation, as well as the Soave-Redlich-Kwong equation, is often used to describe the volumetric behavior of fluid mixtures in the oil and gas industry and to deduce the relevant thermodynamic properties as illustrated in the case of the SRK EoS. The expression of the pressure is now [9, 19, 34, 35]

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \quad (\text{A-5})$$

where the constants a and b are given as follows [9, 19]:

$$a = 0.45724 \frac{(RT_c)^2}{P_c} \left(1 + m(1 - \sqrt{T_r})\right)^2 \quad (\text{A-6})$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (\text{A-7})$$

$$T_r = \frac{T}{T_c} \quad (\text{A-8})$$

$$m = 0.37464 + 1.5422\omega - 0.26992\omega^2 \quad (\text{A-9})$$

ω is the Pitzer acentric factor, also a fluid specific constant [9].

Soave-Redlich-Kwong Equation of State

For a pure component, the SRK EoS [9, 19, 36, 37] is given by,

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \quad (\text{A-10})$$

where the constant a is set as a function of the temperature

$$a = 0.42748 \frac{(RT_c)^2}{P_c} \left(1 + m(1 - \sqrt{T_r})\right)^2 \quad (\text{A-11})$$

$$b = 0.08664 \frac{RT_c}{P_c} \quad (\text{A-12})$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \quad (\text{A-13})$$

The cubic character of these EoS can be best seen when the equation is written in terms of the compressibility factor, Z ($Z = PV/RT$). For the SRK EoS we get an equation in the form

$$Z^3 - \alpha Z^2 + \beta Z - \gamma = 0 \quad (\text{A-14})$$

For a fluid mixture with C components, this equation writes

$$Z^3 - Z^2 + Z(A - B - B) - AB = 0 \quad (\text{A-15})$$

where A and B are deduced from the individual component constants [19]

$$A = \sum_{i=1}^C \sum_{j=1}^C y_i y_j A_{ij} \quad \text{or} \quad \sum_{i=1}^C \sum_{j=1}^C x_i x_j A_{ij} \quad (\text{A-16})$$

$$A_{ij} = \sqrt{A_i A_j} (1 - k_{ij}) \quad (\text{A-17})$$

$$B = \sum_{i=1}^C y_i B_i \quad \text{or} \quad \sum_{i=1}^C x_i B_i \quad (\text{A-18})$$

$$A_i = 0.42747 a_i \frac{P_{r_i}}{T_{r_i}^2} \quad \text{and} \quad B_i = 0.08664 \frac{P_{r_i}}{T_{r_i}} \quad (\text{A-19})$$

The reduced pressure and temperature for each component are given by $P_r = P/P_c$ and $T_r = T/T_c$ and the parameter a_i for the pure component i is given by the equation (A-11).

For the Mathematica[®] simulations, the values of the binary interaction parameters (i.e., k_{ij}) are all taken from the Aspen HYSYS[®] data bank.

The equilibrium constants are obtained using the $(\phi-\phi)$ method as follows [19],

$$K_i = \frac{\phi_{l_i}}{\phi_{v_i}} \quad \text{for } i = 1 \text{ to } C \quad (\text{A-20})$$

where the vapor fugacity coefficient is given by

$$\phi_{v_i} = \exp \left(\left(Z_{v_i} - 1 \right) \frac{B_i}{B} - \ln(Z_{v_i} - B) - \frac{A}{B} \left(\frac{2 A_i^{0.5}}{A^{0.5}} - \frac{B_i}{B} \right) \ln \left(\frac{Z_{v_i} + B}{Z_{v_i}} \right) \right) \quad (\text{A-21})$$

A similar expression is obtained for the liquid phase fugacity coefficient, ϕ_{l_i} , by replacing the gas-phase compressibility factor, with its liquid-phase counterpart, Z_{l_i} .

The liquid and vapor mole fractions are related by

$$y_i = K_i x_i \quad \text{with } i = 1 \text{ to } C \quad (\text{A-22})$$

In addition, the departure function from ideality for the enthalpy is given by [19],

$$H^D = RT(Z-1) + \frac{1}{B \frac{RT}{P}} \text{Log} \left(\frac{Z+B}{Z} \right) \left[T \frac{d}{dT} \left(A \frac{(RT)^2}{P} \right) - A \frac{(RT)^2}{P} \right] \quad (\text{A-23})$$

Similar equations are available for the PR EoS [19, 38],

APPENDIX B

MASS AND ENTHALPY BALANCE (MESH) EQUATIONS

F , L , and V are the molar flow rates of the feed stream, the liquid and the vapor (kmol/hr), respectively. x designates the mole fraction in the liquid phase, and y , in the vapor phase.

- Feed tray ($k = f$) balances

$$F + L_{f-1} + V_{f+1} - L_f - V_f = 0 \quad (\text{B-1})$$

$$F z_{f,i} + L_{f-1} x_{f-1,i} + V_{f+1} y_{f+1,i} - L_f x_{f,i} - V_f y_{f,i} = 0 \quad (i = 1, 2, \dots, C) \quad (\text{B-2})$$

$$F h_F + L_{f-1} h_{f-1} + V_{f+1} H_{f+1} - L_f h_f - V_f H_f = 0 \quad (\text{B-3})$$

- MESH equations for the k th tray ($k \neq f$ and $1 \leq k \leq N$)

$$L_{k-1} + V_{k+1} - L_k - V_k = 0 \quad (\text{B-4})$$

$$L_{k-1} x_{k-1,i} + V_{k+1} y_{k+1,i} - L_k x_{k,i} - V_k y_{k,i} = 0 \quad (i = 1, 2, \dots, C) \quad (\text{B-5})$$

$$L_{k-1} h_{k-1} + V_{k+1} H_{k+1} - L_k h_k - V_k H_k = 0 \quad (i = 1, 2, \dots, C) \quad (\text{B-6})$$

- Reflux drum ($k = 0$) balances

$$V_1 - (L_0 + D) = 0 \quad (\text{B-7})$$

$$V_1 y_{1,i} - (L_0 + D) x_{D,i} = 0 \quad (i = 1, 2, \dots, C) \quad (\text{B-8})$$

$$V_1 H_1 - (L_0 + D) h_0 - \dot{Q}_C = 0 \quad (i = 1, 2, \dots, C) \quad (\text{B-9})$$

- Reboiler ($k = N+1$) balances

$$L_N - B - V_{N+1} = 0 \quad (\text{B-10})$$

$$L_N x_{N,i} - B x_{N+1,i} - V_{N+1} y_{N+1,i} = 0 \quad (i = 1, 2, \dots, C) \quad (\text{B-11})$$

$$L_N h_N - B h_{N+1} - V_{N+1} H_{N+1} + \dot{Q}_B = 0 \quad (i = 1, 2, \dots, C) \quad (\text{B-12})$$