Distillation Absorption 2010
A.B. de Haan, H. Kooijman and A. Górak (Editors)

ESTABLISHING INTERNAL CONFIGURATION OF DIVIDING WALL COLUMN FOR SEPARATION OF A MULTICOMPONENT AROMATICS MIXTURE

Ivar J. Halvorsen[1], Igor Dejanović[2], Ljubica Matijašević[2], Žarko Olujić[3] and Sigurd Skogestad[4]
[1] SINTEF ICT, Applied Cybernetics, 7465 Trondheim, Norway, Email: ivar.j.halvorsen@sintef.no
[2] University of Zagreb, Department of Chemical Engineering and Technology, 10000 Zagreb, Croatia, Email: ideja@fkit.hr;
[3] TU Delft, Process & Energy Laboratory, 2628 CA Delft, the Netherlands, Email: z.olujic@tudelft.nl;
[4] Norwegian University of Science and Technology (NTNU), Department of Chemical engineering, 7491 Trondheim, Norway, Email:skoge@chemeng.ntnu.no;

Abstract
In this paper the so called V-min diagram method is used to evaluate potential for energy saving and to indicate most beneficial internal configuration for a single dividing column (DWC) considered as an alternative for conventional three columns configuration used in an aromatics processing plant for separation of a multicomponent feed into four specified product streams. A DWC employing multiple partition walls to separate central part of the column into three sections appeared to be a much more attractive option than its, more practical single partition wall counterpart.

Keywords: Distillation, Minimum Energy, Dividing Wall Columns,

1. Introduction

Petlyuk (1965)[1] showed the potential for energy savings with fully thermally coupled distillation arrangements. In the last decades, energy saving distillation configurations like the Dividing Wall Column (DWC) as introduced by Kaibel (1987)[2] has gained increased attention due to savings in both energy- and capital cost. Industrial usage is now increasing both in number and equipment size[3]. Most of the installed DWC are for three products, however, some four-product DWCs with a single partition wall[2] have also been built and installed[3]. To obtain the maximum of the potential savings in practical operation it is required that we know how to set the correct flows in each column section. Here we will apply the Vmin-diagram method introduced by Halvorsen and Skogestad (2003)[4-6] to find the overall energy requirement and the individual flow rates in each section of four-products dividing wall columns with a multi-component feed.

2. The Vmin diagram

The basis for the Vmin-diagram is a simple two-product distillation column at constant pressure with a given multicomponent feed (F). Then we have at steady state two degrees of freedom in operation. There are several choices, but we select to use the vapor flow rate above the feed (V/F) and the net flow of product to the top (D/F) per unit feed. For each given pair (D/F, V/F) all other properties are completely determined, such as all component recoveries and product compositions. The reflux (L=V-D) and bottom product (B=F-D) are related by simple mass balance. The thermal condition of feed is given by the parameter (q), which in the range between saturated vapor and saturated liquid ($0 < q < 1$) represents the liquid fraction of feed.

The Vmin-diagram in Figure 1 shows how the feed components for a ternary feed (ABC) are distributed to the top and bottom products in a simple two-product “infinite stage” distillation column as a function of the operating point (D/F,V/F). For values of V/F above the upper “mountain-like” boundary in the diagram ([0,0]-P_{AB}-P_{AC}-P_{BC}-[1,1-q]) the column is over-fractionated, that is, we are wasting energy. The values at the peaks are Vmin for sharp neighbor component splits. As V is reduced below the line for a given D, one more component will become distributed as we cross boundary lines. The knots are Vmin for splits where we specify sharp split between two key-components, while we allow intermediate components being distributed. To find the diagram for a multicomponent feed, we only need to solve for sharp split between each possible pair of key components. That is for n components ($n>1$), we can find the complete diagram by calculating 1+2+3…+n-1= n(n-1)/2 points. For the three-component example we only need three points: sharp A/B, sharp B/C and sharp A/C. A/C is here the so-called “preferred split”[7] where we obtain sharp split between the heavy and light keys while the intermediate distribute to both column ends. Note that we use capital letter A,B,C,... to tag feed components where A is the most volatile component. We also use the letter D and B for distillate and bottoms product flow rates in a column or net product flows in the two-product sub-columns inside the arrangements. The interpretation should be clear form the context.

The diagram may be obtained for real mixtures simply by simulating a binary column at each of these points with the given multicomponent feed. In practice we may specify small impurities of heavy key in the top and light in the bottom for each pair of keys. With a stage number of $N \approx 4N_{\min}$ we obtain reasonable values for the selected impurity level close to a result with infinite number of stages. For an ideal mixture with constant relative volatility, constant molar flows and infinite number of stages, all column properties can be calculated by the classical Underwood equations. Thus, all data in the Vmin-diagram can be calculated directly from the feed properties[4]. And we also find that boundaries are linear and that all the recoveries in a region are linear functions of the operating point (D,V). The calculations in this paper will be based on the ideal assumptions.

It is also important to note that the same feed distribution will occur for the same D,V also when we consider a full thermal coupling to a succeeding column[4].Then there is no single product stream and D is the net flow D=V-L. Thus the Vmin-diagram can also be applied for fully thermally coupled columns.

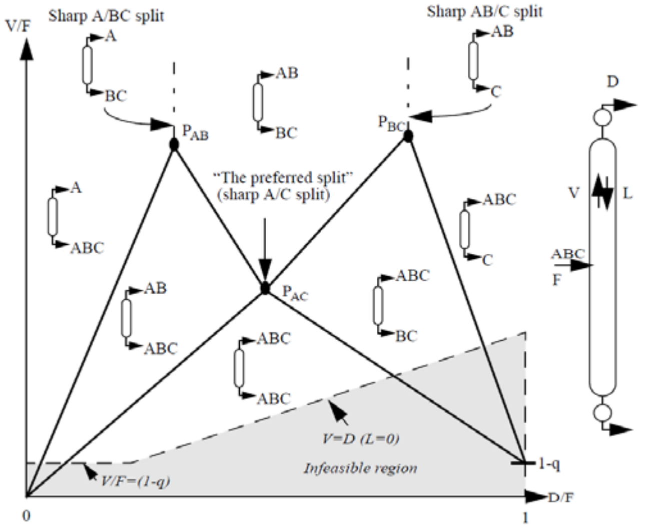


Figure 1. The Vmin-diagram for a ternary feed

Table 1. Feed composition and properties.

Tag	Component	Mole fraction	**K-value**	**In flow**
A	**N-Butane**	0.031	6.277	D
B	**Isopentane**	0.082	3.387	D
C	**N-Pentane**	0.058	2.833	D
D	**2-Methylpent.**	0.086	1.630	D
E	**N-Hexane**	0.046	1.326	D
F	**Benzene**	0.101	0.942	S1
G	**3-Methylhex.**	0.019	0.735	S1
H	**Toluene**	0.248	0.415	S2
I	**Ethylbenzene**	0.031	0.203	B
J	**M-Xylene**	0.037	0.189	B
K	**P-Xylene**	0.106	0.185	B
L	**O-Xylene**	0.048	0.164	B
M	**M-Ethyltoluene**	0.036	0.096	B
N	**1-3-5-Trimethylb**	0.059	0.084	B
O	**1-4-Diethylbenze**	0.011	0.048	B

3. The Vmin diagram applied to generalized extended Petlyuk arrangements

The real power of the Vmin-diagram is that it contains all necessary information to calculate the overall minimum energy requirement and all the internal flow rates for an optimally operated extended Petlyuk arrangement for an arbitrary multicomponent feed and any number of products. This is the main result by Halvorsen (2003)[5,6]. The overall minimum energy is simply given by the highest peak. This peak represents the most difficult product split in a two-product column. It may be a bit surprising that by supplying that vapor rate to an extended Petlyuk arrangement we get all the other products separated for "free". The key is that in an optimal operated Petlyuk arrangement, each sub-column in the structure must be operated at its local "preferred split". That is, at minimum energy for separation of the light and heavy keys for that column while the intermediates distribute to both ends. We would generally anticipate that we would need to calculate the minimum energy for each succeeding column by a new column computation, but Halvorsen[5] showed that the properties determining minimum energy in each sub-column can be found from the previous column, and at optimal operation in the sequence, all the information can be obtained from the Vmin-diagram which is based on feed data only. It is also shown[6] that an optimally operated generalized Petlyuk arrangement results in the lowest overall vapor flow requirement for any distillation configuration when we consider constant pressure and no external heat integration.

The Vmin diagram is not just a graphic tool. Under the assumptions of constant relative volatility and constant molar flows it is also followed by a set of analytical functions that can be used to obtain exact values for recoveries and flows for any operating point and feasible combination of two specifications.

For example: Two components recoveries, one recovery and one flow, two compositions and of course one vapor and one distillate flow rate. By calculating the flow requirements for each sub-column and inspecting the mass balances at each junction, we can find all the internal streams in the extended 4-product Petlyuk arrangement shown in Figure 2. However, it is much easier to show the relationship graphically in the Vmin-diagram. Each sections vapor flow and net top product flow can be found directly as a difference between the peaks and knots in the Vmin diagram. We show this for a 4-component feed in Figure 2 (Superscripts denote sub-columns, and the subscripts T and B denote the top or bottom section in that sub-column). The liquid flow rates and bottom net flows are uniquely determined from simple mass balances.

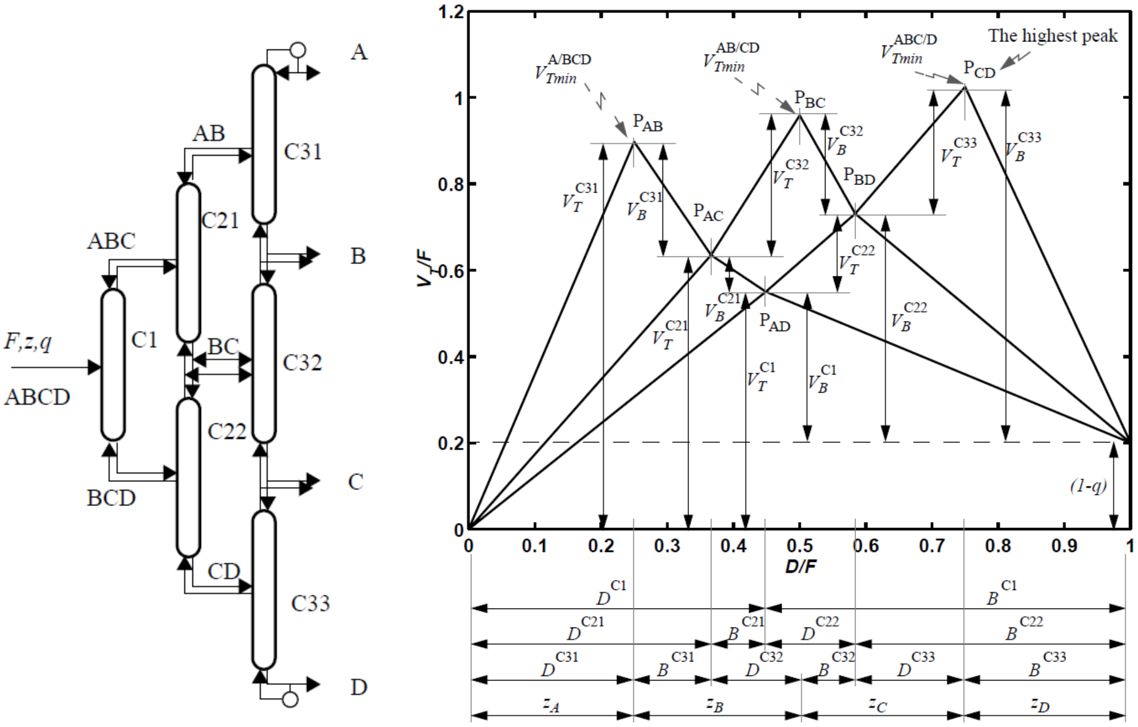


Figure 2. The extended 4-product Petlyuk arrangement and a Vmin diagram for a 4-component feed ABCD with indication of how to calculate the individual vapour rates in all sub-columns.

Note that when the peaks are of different height we might apply heat exchange at each side-stream stage and condense or vaporize an amount of vapor/liquid representing the difference in height of the peaks. However, in industrial applications with DWC columns this is not common practice. The vapor flow corresponding to the highest peak is normally supplied in the reboiler and passes through the whole column and the splits representing the other peaks will then be done with higher vapor rate than actually required. This actually gives us a certain slack in the operation since each sub-column does not have to be operated exactly at its local preferred split. We only have to make sure that we operate in a way that does not increase the minimum vapor for the most difficult split (the highest peak). We will not go into the details here, but this is the reason for the flat optimality region[8] that enables a DWC to operate optimally and handle feed property variations even with a fixed vapor split. However, the optimality region is still limited and suboptimal operation is characterized with higher energy consumption for a given product specification, or that the column is unable to produce the required product purities for the given heat supply.

4. Assessment of a 15-component hydrocarbon feed

The composition of the feed considered in this study is given in Table 1. The vapor liquid equilibrium data is obtained by Chemcad™ simulation[9]. There are of course several options for grouping components into products, but we here choose to look closer at the case when we want to get 4 products, with component grouping given in the right hand column. We see that the key components for the three splits Distillate/Side 1, Side 1/Side 2 and Side 2/Bottoms are E/F (n-hexane/benzene), G/H (3-methylhexane/toluene) and H/I (toluene/ethyl benzene), respectively. For every feasible combination (D,V) in a binary column, a certain product distribution will result. For V at or above the solid line the solution is simple and we obtain sharp split and only one component may be distributed to both ends, given directly by the actual D-setting. The D/F value for the peaks is found directly from the feed composition (*z*) since they represent the sharp component splits.

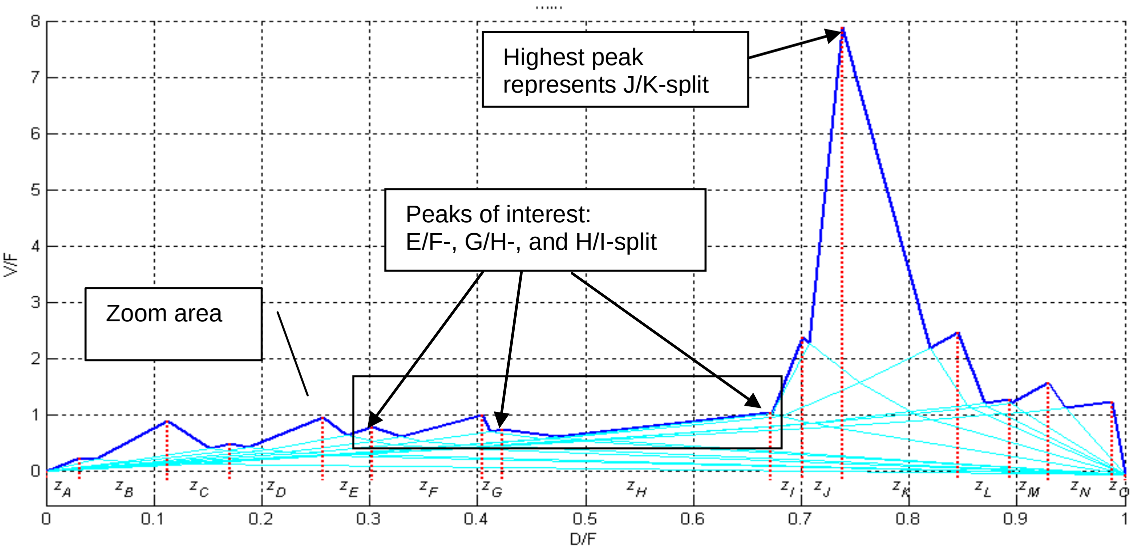


Figure 3. The full Vmin-diagram for the 15-component feed

The detailed Vmin-diagram in Figure 3 shows that the most difficult split, represented by the highest peak, is the J/K (m-xylene/p-xylene), but this separation is not required in this case. The diagram shows that for separating the light adjacent components from n-butane to ethylbenzene (A-I), the required boilup to feed ratio (V/F) is less than one. The splits between the heavier components are more difficult, but according to the specified four-product grouping in Table 1 we lump ethyl-benzene (I) and heavier into the bottoms.

5. Fully extended four-products Petlyuk arrangement

In Figure 4 we zoom in on the marked box in Figure 3 to se the detailed energy flow requirements for the selected product groups. The easy separation between the light key in the bottom product (I:ethylbenzene), and the heavy key in the top product (E:n-hexane) will determine the preferred split for the case, and thereby set the minimum vapor requirements for the prefractionator (Column C1). The overall vapor flow requirement for a full Petlyuk arrangement is determined by the most difficult product split which in our case is H/I (toluene/ethylbenzene).

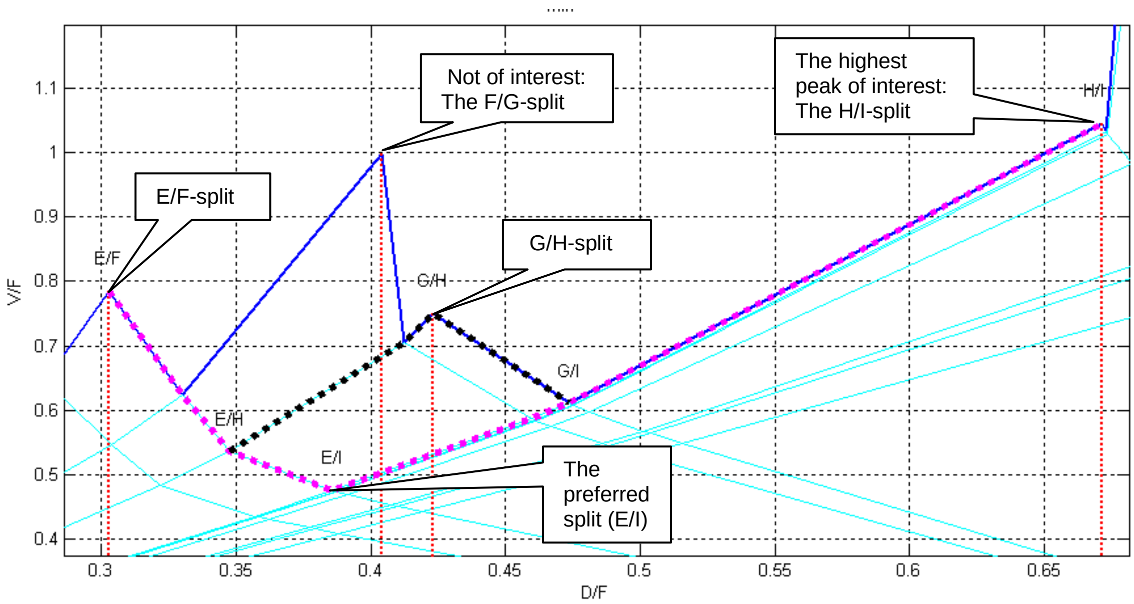


Figure 4. Zooming in on the Vmin diagram. The relevant distribution boundaries between the four selected products component groups are indicated by the dotted lines.

We subtract (1-q)F which is negative since we have slightly subcooled liquid (thermal condition of the feed: q=1.0641) to find that the required boilup is Vmin/F=1.11. All relevant data obtained from the Vmin diagram are given in Table 2. Then we can use the relations shown in Figure 2 to find all flows in each sub-column. The flow rates in Table 2 refer to a two-product column as in Figure 1.

Table 2. Flow rates from the Vmin diagram for the key product splits.

Splits\Flows/F	**D**	**V**	**L**	**B**	**Vb**	**Lb**
E/F (Distillate/Side 1)	0.303	0.785	0.482	0.697	0.849	1.550
E/H (Distillate/Side 2)	0.347	0.536	0.188	0.653	0.600	1.250
E/I (Distillate/Bottoms)	0.386	0.475	0.089	0.614	0.539	1.150
G/H (Side 1/Side 2)	0.423	0.751	0.328	0.577	0.815	1.390
G/I (Side 1/Bottoms)	0.474	0.610	0.137	0.526	0.674	1.200
H/I (Side 2/Bottoms)	0.671	**1.050**	0.374	0.329	**1.110**	1.440

Note that the columns D,V are taken directly from the diagram. L=V-D, Lb=L+qF, Vb=V-(1-q)F, B=F-D.

The different peak heights indicate that the Top/S1-split and the S1/S2-split can be obtained by a lower vapor rate than the S2/Bottom-split (highest peak). There are several alternatives to use this property, one is that we may take out the entire S2 as vapor, and obtain available heat at the boiling point of S2, in stead of condensing everything at the top. Another possibility is that we may use relatively less stages in C32 and C31 since they will be operated with a higher Vreal/Vmin ratio than the other sections when we let all the boilup go all the way through to the top.

We should also look closer at the feed junction to C32. From the diagram data we find that ideally we should have a combined vapor and liquid feed given by the flow rates in C21 and C22 where the vapor feed is 0.074 ($V_{G/I}$-$V_{E/H}$) and liquid feed is 0.053 ($L_{E/H}$-$L_{I/G}$) giving a total of 0.127 into C32. In a DWC it might be more practical to take out only liquid from the junction of C21 and C22. This can be done easily, and we just increase the vapor and liquid in C21 correspondingly. This will lead to a slightly less efficient operation in C32 and C31, but since we have a quite large margin due to the different height of peaks, this should be feasible in our case without having to increase the overall boilup.

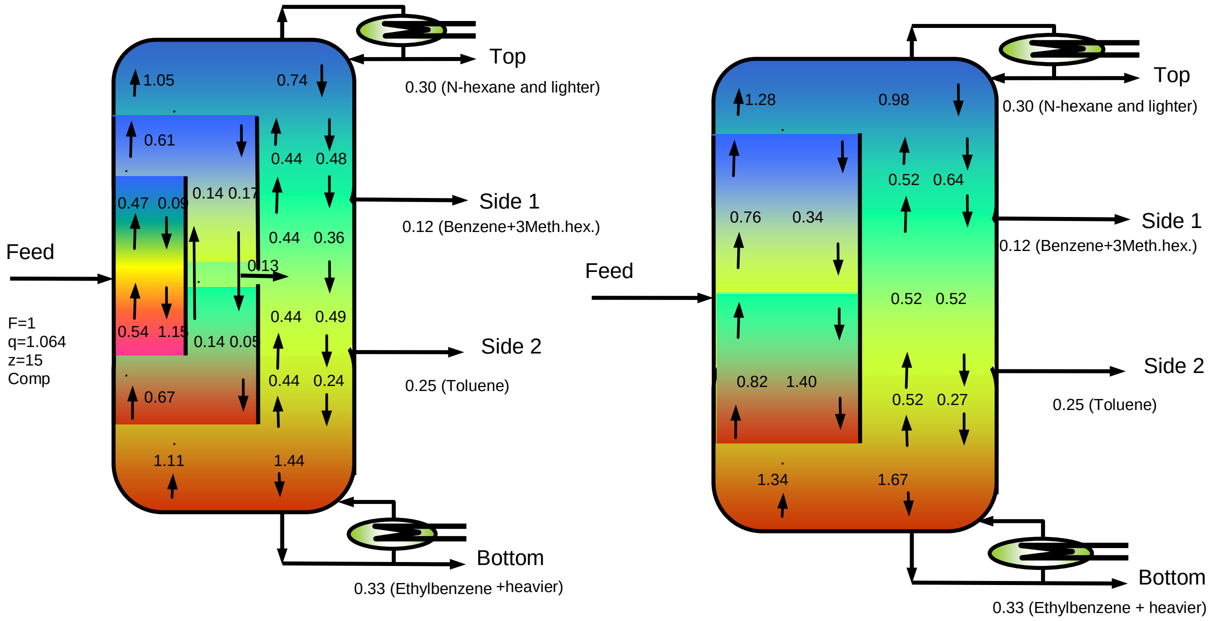
The adjusted internal streams, when we have liquid side-streams and only a liquid connection into the feed junction of C32, are indicated in Figure 5a. This configuration with three partition walls creating three parallel column sections is thermodynamically equivalent to the extended Petlyuk arrangement in Figure 2. The relatively high peak in Figure 4 at V/F=1, D/F=0.405 representing the sharp split F/G (benzene/3-methylhexane) does not have any importance for our original case since we group these two components together in Side-stream 1.

6. Four-product Kaibel column with a single partition wall

We may also consider the 4-product Kaibel column with a single partition. This column is simpler in construction and operation, but requires higher vapor rate (more energy) than the full Petlyuk arrangement. The calculation procedure is first to determine the G/H split in the prefractionator. This is obtained directly from the Vmin-diagram as V1/F=0.75 and D1/F=0.423 which correspond to the sum of mole fractions of the light component A to G in the feed. Then we may find the requirement for the Top/S1 split based on that the net feed flow is given by D1, and that the equivalent liquid fraction is 1-V1/D1. And similarly for the S2/Bottom split. For the given feed, the resulting minimum boilup for the Kaibel column is found as V/F=1.34. The distribution of flows in each section of the single partition DWC is shown in Figure 5b. A detailed analytical procedure is given by Halvorsen (2006)[10].

7. Comparing with the conventional direct split and sloppy split sequences

Minimum vapor for three succeeding columns in a direct split configuration can be found as follows:
C1: Split: ABCDE/FGHIJKLNO, V_{Tmin} = 0.7849 (The peak E/F in the diagram, add (1-q)F to get boilup)
C2: Split: FG/HIJKLMNO, V_{Tmin} = 0.5213 (New calculation with bottom of C1 as feed, q=1)
C3: Split: H/IJKLMNO, V_{Tmin} = 0.6442 (New calculation with bottom of C2 as feed, q=1)
Total boilup requirement: V_{Bmin}=(0.7849+0.061)+0.5213+0.6442= 2.01 per unit feed to the first column.
The conventional sloppy split with three conventional columns where C1 first separates A-G/H-O and then two succeeding columns are feed with the saturated liquid products of C1 and separate A-E/FG and H/I-O, respectively, the sum of total minimum boilup in all three is found as V_{Bmin}/F=2.21. The relative saving by going from the single partition Kaibel column to the full Petlyuk column is 21 %. As shown elsewhere[9], estimated energy savings related to sloppy split resemble those obtained by rigorous simulation.



a) Full Petlyuk arrangement DWC

b) The Kaibel-column

Figure 5. Flow distribution in four product dividing wall columns.

Energy requirements of two conventional and two feasible DWC configurations are compared in the following table:

	Reboiler vapor flow per unit feed V_{Bmin}/F	**Energy savings related to direct split**	**Energy savings related to sloppy split**
Full Petlyuk configuration	1.11	45.0 %	49.7 %
Kaibel column	1.34	33.3 %	39.1 %
Direct split sequence	2.01	Reference	8.7 %
Sloppy split sequence	2.21	-9.5 %	Reference

8. Conclusion

We have shown that the Vmin-diagram is an excellent tool for assessing the energy requirements for multicomponent zeotropic mixtures, and to find flows and distribution in a complex column arrangement. The graphical tool provides direct insight in the optimal separations behavior in fully thermally coupled arrangements. The numerical results can be used to initialize simulations for doing detailed designs for real separations[9]. This confirms that a rather simplistic but fundamentally sound analytical method can be used with confidence for screening the energy saving potential associated with separation of multicomponent mixtures and in conjunction with common engineering sense can help identify in a fast way fully thermally coupled column arrangements suitable to be implemented as a DWC for obtaining four (best solution in present case), five or even more products.

References

1. F. Petlyuk, V. Platonov, D.M. Slavinskii, *Int. Chem. Eng*. 5 (1965) 555-561.
2. G. Kaibel, Distillation Columns with Vertical Partitions, *Chem. Eng. Technol*. 10 (1987) 92-98.
3. Ž. Olujić, J. M., A. Shilkin, G. Schuch and B. Kaibel, *Chem. Eng. Process*. 48 (2009)1089-1104.
4. I.J. Halvorsen and S. Skogestad*, Ind. Eng. Chem. Res*. 42 (2003) 594-604.
5. I.J. Halvorsen and S. Skogestad, *Ind. Eng. Chem. Res*. 42 (2003) 610-615.
6. I.J. Halvorsen and S. Skogestad, *Ind. Eng. Chem*. Res. 42 (2003) 616-629.
7. J.G. Stichlmair, *Distillation and Rectification*, Ullmann's Encyclopedia of Industrial Chemistry, 5th ed.VCH Verlag, 1988
8. I.J.Halvorsen and S. Skogestad, *J. Proc. Control* 9 (1999) 407-424.
9. I. Dejanović, L. Matijašević, Ž. Olujić, I.J.Halvorsen, S. Skogestad, H. Jansen and B. Kaibel, *Distillation Absorption 2010*, Eindhoven, NL. Editors: A. de Haan, H. Koijmaan, A. Górak.
10. I.J. Halvorsen and S. Skogestad, AIChE Annual Meeting, Nov. 12-17, 2006, San Francisco (paper 216d).