Assessment of Dividing Wall Column separations - Revisit to the Vmin-diagram

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Abstract.

The Dividing Wall Column (DWC) accommodates fully thermally coupled distillation sections for high purity separation of three or more products in a single unit. Compared to conventional distillation sequences, there are significant potentials for savings in energy, capital cost, and space. The technology has been in industrial use from before 1990 with large number of reported applications. However, even in recent literature, difficulties in design and operation are still listed as obstacles. Thus, there is a need for easily available assessment tools and methods such that the environmentally sustainable DWC technology will be applied wherever applicable. The Vmin-diagram and related methodology and knowledge is one such tool. In this paper we briefly explain the concept and on how the Vmin-diagram can be used to assess separation tasks and also to suggest simplifications to the internal configuration of a distillation system for a certain separation task or similar classes. The original papers presenting the Vmin-diagram made use of simplifying assumptions like constant molar flows, constant relative volatilities, and infinite number of stages. This opened for refined use of the Underwood equations to deduce the exact analytical expressions that can explain the complex column behavior and the minimum energy operating conditions. This may mislead some readers to get the impression that the concept is only valid for these kinds of ideal assumptions. But this is not so. The key properties that determine minimum energy and product distribution are valid also for real mixtures. In this paper it will be focused on how the Vmin-diagram concept can be used to assess separations that are candidates for 3- or 4 product DWC and show examples on how it can be used in the case of latter to arrive at some simplified and more practical structures for industrial implementation.

Keywords, Dividing Wall Column, Multicomponent distillation, Minimum Energy, Vmin-diagram

Introduction

The fully thermally coupled Dividing Wall Column (DWC) for multicomponent distillation has been in industrial use since around 1985, based on the work by Kaibel 1987 [1]. There are patents from as early as 1946 and some fundamental papers by Petlyuk 1965 [2]. The main benefits are lower energy consumption and in addition, lower capital cost (due to smaller internal flow rates), when comparing to conventional sequences for multicomponent separations. A comprehensive DWC technology overview was presented by Dejanović et.al 2010 [3]. Still, even in recent publications, uncertainties in design and operation are listed as key obstacles for more widespread use. It is now time to go to the next step – to lower the threshold for industrial applications. The design and operation of a DWC is not that complicated, but it must be done right to avoid running into the known pitfalls.

The Vmin-diagram for assessing minimum energy requirements and internal flow rate distribution in DWC or the equivalent Petlyuk arrangements was first presented at the AIChE Annual meeting in Dallas 1999, for ternary feeds. The result was extended to arbitrary number of components and products in the thesis by Halvorsen in 2001 [4]. The main chapters on the Vmin diagram were published as a series of three papers in 2003 [5]. The notation "Vmin" denotes minimum vapor flow rate with infinite number of stages with some given separation specification. The method has been picked up by some researchers in the field, but understanding this simple approach is beneficial to everybody. The Vmin-diagram has potential for very straightforward assessment of separation characteristics and direct solutions for internal flow rate requirements in Dividing Wall Columns. It should be utilized to better understand how to do design and operation for a particular separation task and resulting column arrangement. The original Vmin-diagram is developed based on the classical Underwood equations [6] and ideal mixtures. The concepts can be carried over and be applied to real zeotropic mixtures in available modern process simulators. The key is to know the characteristic of the optimal operation from the Vmin-diagram, and then it is very straightforward to initialize and apply that in a rigorous simulation, and to define suitable targets for the column arrangement. The information in the diagram can also be used to assess possible simplifications and flexibility of complex DWC configurations without sacrificing energy consumption. This may have great impact on the practical column design and on operability.

Vmin-diagram – minimum vapor and distribution regions in a binary column

Consider a ternary zeotropic feed with the components ABC. A typical Vmin-diagram for such a feed is shown in Figure 1. There will not be any detailed equations in this manuscript. Please see the referenced papers for that. But as the internal structure can become somewhat complicated, a convention for denoting internal column sections, components and streams is listed with this figure.

In essence, this diagram tells how the feed components will be distributed to the top and bottom product in a single binary distillation column at constant pressure and with infinite number of stages as a function of the vapor rate (V) and then distillate rate (D). The operating point is uniquely determined by two degrees of freedom, here selected as vapor rate (V) above the feed stage and the distillate rate (D), both normalized to a unit feed (F). Note that many other combinations of two independent degrees of freedom are available to be specified, but any alternative pair is uniquely related to the selected (D/F, V/F).

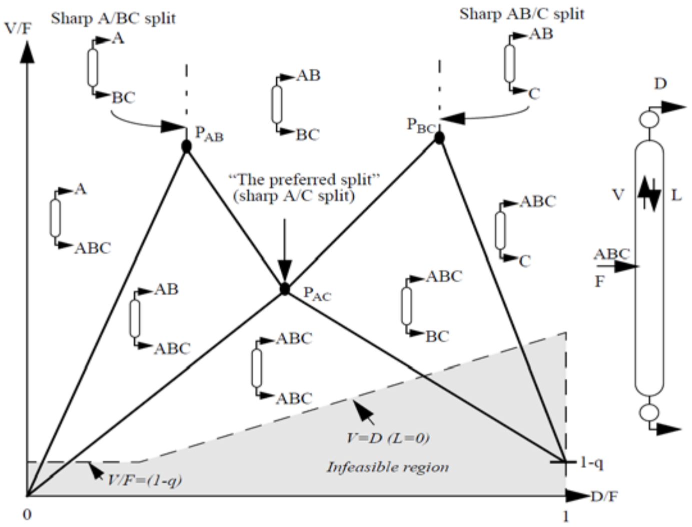

Figure 1 Vmin-diagram for a ternary feed

Notation in Figures:

Components: A,B,C,… sorted in order of volatility and A is the most volatile component. A,B,C,.. can also represent aggregate product streams for complex feeds

Internal binary sub-columns are numbered: C<column><row>. These may also be used as subscripts
F: Feed, D: Distillate, B: Bottom, L: Liquid , V: Vapor ,
Sx : Sidestream product no x.
(Component B or stream B will be given by the context)
Subscript T for top section, subscript B for bottom section.

R_i,(B|T) : recovery of comp. i in the feed at top|bottom
z: Feed composition (molar fractions), x: composition (at some location), q: Feed liquid fraction.

A peak in Vmin-diagram is denoted P (component group/component group) where "/" denotes "sharp split".
Material balance: D=V-L

There are three main characteristic points in this ternary diagram: P_{AB} that represents minimum vapor rate (Vmin) for sharp separation of A from B (or A/BC). P_{BC} that represents Vmin for sharp separation of B from C (or AB/C). and finally, P_{AC} (or AB/BC) that is called the "preferred split", and that point gives the minimum vapor rate for separating A from C while B is distributing to both products. There are the two more trivial points, the origin, and the point where V/F=(1-q) at D/F=1. By drawing lines between these points, the illustrated regions represent a certain component distribution where the column icons indicate the expected components present in top and bottom products, and the lines represents distribution boundaries where one component is at the boundary of becoming distributed to both products if the vapor rate is slightly reduced or being removed from a product when increased.

So far, we only consider a binary column. The diagram can be calculated very quickly by available code if the ideal conditions are assumed. It is also easy to do this by a small number of simulations if a rigorous simulator is available. A procedure can be outlined as: 1) Configure a standard binary column, make a quick assessment of stage numbers and use for example about four times the minimum for the most difficult of the separations. 2) Perform a simulation at the three points: P_{AB}, P_{BC} and P_{AC}. Find the three points by specifying a small impurity of A in bottom and B in top for point P_{AB}, specify a small impurity of C in top and B in bottom for P_{BC}, and finally find P_{AC} by specifying a small impurity of A in the bottom and C in the top. Make a note of the Vapor rate just above the feed stage for use in the diagram. You may also do a quick sensitivity check on the stage numbers ensure that adding more stage numbers do not lead to significant reduction in vapor rate. This will confirm that in practice the simulations are done with close to "infinite stage numbers".

The Vmin-diagram is not limited to ternary feeds. For any number of components in the feed there are still only two degrees of freedom in operation (for a binary column at constant pressure and infinite number of stages). Thus, the distribution of components to the two product streams can still be visualized in the two-dimensional Vmin-diagram as shown for a 5-component feed in Figure 2a. The thick lines indicate the distribution boundary with a recovery of one or zero. Any operating point can be selected as a point in this diagram by specification of the pair V/F, D/F.

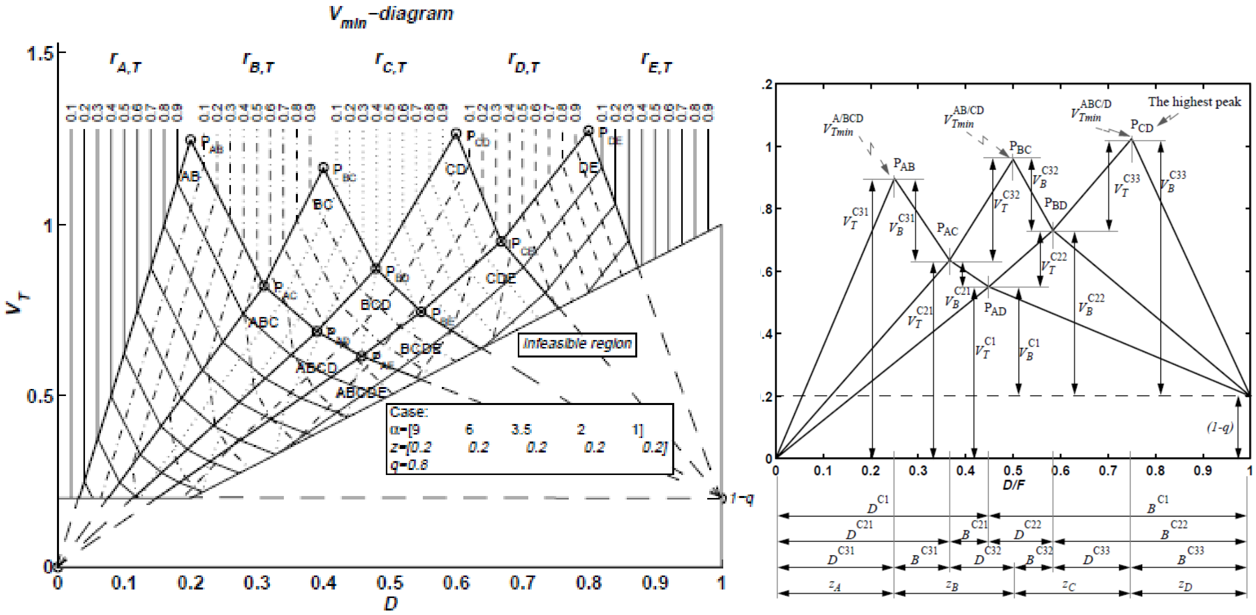

Figure 2a) Vmin-diagram for a 5-component feed ABCDE. The contours for each component recovery in the top are included. b) How the Vmin-diagram can be used to get internal flow rates in a 4-product Petlyuk arrangement (right)

The illustration shows that for example the minimum vapor rate for point P_{AD} is when all of A is recovered in the top ($r_{A,T}$=1), and none of D is recovered in the top ($r_{D,T}$=0), while the intermediate B and C are distributed to both products. The heavy E-product is heavier that D, so all of that will also appear in the bottom. It is also straightforward to see that even if there are five components, it is not possible to specify more than two independent properties at a time. For example, for the above case, the point P_{AD} may alternatively be specified $r_{B,T}$=0.66 and $r_{C,T}$=0.3 approximately. The illustrated infeasible region is simply when the distillate flow rate is larger than the vapor rate, and consequently (L=V-D), the reflux would be negative.

Observe that for any operating point with constant D/F and the vapor V/F is above the upper distribution boundary lines, the recoveries in the products become constant, and only one component is distributing as D is between two of the peaks. Thus, for any solution here V > Vmin and energy is wasted. Below the upper boundary line, any operating points is a minimum energy solution, but now related to a pair of recovery specifications for each point. Any adjustment in the operating point leads to a change in the distribution. This is by the way the background for denoting it the "Vmin-diagram". It easily shows all possible Vmin-solutions.

The presented diagram is for the ideal assumption, and for that case, all these contours become straight line segments in this view. It is also possible to find these relations by rigorous simulations from the procedure indicated above. Note than that for a finite stage number, a recovery value at exactly one or zero is not feasible, so as with composition specifications, use e.g., 0.99 or 0.01 to mimic close to sharp split recoveries in rigorous simulations.

So far, the above presentation shows that the Vmin-diagram can be used to visualize a complete characterization of a multicomponent feed for zeotropic mixtures. The next section will take this to the so-called "thermally coupled" columns like the DWC. The term "thermally coupled" may be somewhat confusing since there is no thermal heat transfer device, but instead there is a direct coupling of vapor and liquid streams between the sections. One background for the term is that the supplied heat in the reboiler is used for more than one product split, so from that view the term thermal coupling makes sense: The heat is used at several places, so the streams "couples" the heat.

Vmin-diagram for assessing operations in thermally coupled ternary arrangements

Analytic expressions for estimation of minimum reflux ratio of binary columns for separation of ideal multicomponent mixtures have been introduced long ago by Underwood [6]. A minimum energy solution for a ternary mixture in a Petlyuk arrangement was presented by Fidkowski 1986 [7]. During development of the Vmin-diagram this was extended to any number of components, any feed liquid split and any number of products in an extended Petlyuk arrangement. The product streams may either be a single component or an aggregate of adjacent components in terms of their relative volatility to the least volatile key component.

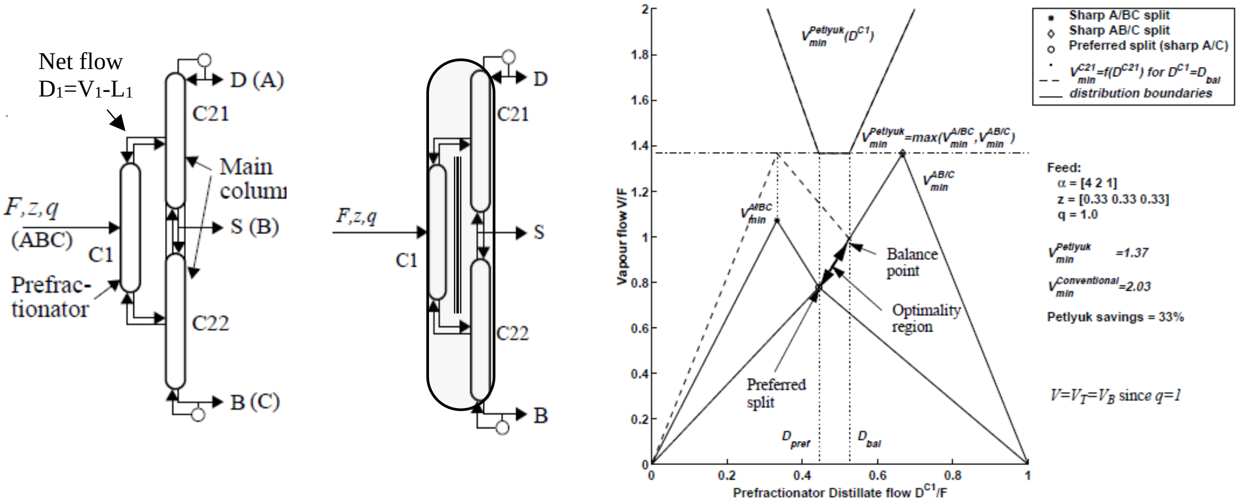

Figure 3. Petlyuk arrangement (left), As DWC-column (middle), Vmin-diagram, giving Vmin for the DWC arrangement (right)

To obtain the minimum energy for a Petlyuk arrangement e.g., as shown in Figure 3 is vital that the internal sub-columns are properly operated. A solution that always will give minimum overall energy consumption is to operate each individual sub-column at its local preferred split. In a Petlyuk arrangement (or in its equivalent DWC), the Vmin-diagram only characterize the feed by how the feed will become distributed based on its operating point given by the local V and D in sub-column C1. So really, a new analysis should be carried out for the succeeding columns C21 and C22. Fortunately, it turns out that if every sub-column is operated at its "local" preferred split, the Vmin-diagram for the succeeding columns can be shown to overlap the original diagram. So, all answers can be found in the first diagram anyway [4,5].

The key result is then that the highest peak of the Vmin-diagram for sets the minimum requirement for the whole complex extended Petlyuk arrangement. This implies in other words that the most demanding of the product/component separations performed one by one in a binary column is really the overall requirement for the whole arrangement. Or it may be formulated: When applying a properly operated DWC, we only need to supply the minimum vapor requirement for the most difficult split, and the other splits simultaneously come for free. When peaks in the Vmin-diagram are of different height this opens for flexibility in operation. In Figure 3 some of the vapor from the reboiler also goes through column C21. From the Vmin-diagram, the peak that is related to the A/B split (left) is below the actual flow given by the demand for the B/C split (right) and the C21 sub-column gets more vapor than required. The load in C21 can then be increased by moving the operating point from the preferred split along the V-shape to the right up to the indicated balance point. Then, the Vmin-diagram for C21 does not overlap any more (since C1 is not operated exactly at its preferred split) and the peak related to the A/B split in C21 is lifted (dashed lines). This can be done until the lifted left (A/B) peak hits the level of the right peak (B/C), and in this range the requirement for B/C split is "balanced" with the lifted A/B peak. This gives a range of operation of the pre-fractionator denoted the "flat optimality region" since the reboiler duty there is constant. The existence of this type of region is very important for the flexibility of operation of the DWC. The optimum is not reached just only at a single point, but in a region, and the extent of this region depends on the difference between the two peaks A/B, B/C.

Vapor splits – optimal values and need for on-line adjustment

The vapor split is defined as the ratio of the vapor rate to the pre-fractionator (C1) divided by the vapor rate supplied from the reboiler. A somewhat robust value is the vapor split that represents an operating point for C1 in the middle of the flat region, as indicated by where the arrow for the optimality region points in the V-shape in the figure. This region is why a DWC can operate optimally with a constant vapor split for some variations in feed conditions, because there will be a certain range of feed variations where the same constant vapor split will still be within the optimality region for each feed condition. The liquid split, however, is normally needed to be adjustable on-line to maintain correct pre-fractionator separation for any expected changes in feed conditions.

Note, if that constant vapor split is set outside the optimality region for the actual feed conditions, the consequence is a rapidly increased reboiler demand (as indicated by the function "$V_{min,Petlyuk}$" above the diagram in Figure 3), or what is the most common: The DWC will become unable to produce pure products, for the side-stream in particular, even at the maximum available reboiler duty.

In most industrial applications, the vapor split is not adjustable in operation and is determined by the vapor flow resistance on each side of the dividing wall. The split is not arbitrary, and it is important to do a proper simulation study to find a suitable design value and implement it by the design of the cross-section area and the pressure drop characteristics of the internals on each side of the dividing wall that will give the desired split in practice.

Using feed liquid fraction for optimal vapor split adjustment

If the optimality region is tight, there may be a need for active vapor split adjustment to maintain optimality on expected feed condition variations. The industry has been reluctant due to uncertainty of the complexity/reliability of internal devices. Some analysis has been done by simulations and pilot-labs and some industrial devices have been proposed. We will not dive into this subject here, but the need for active vapor split adjustment should always be properly checked.

But we will point at a very simple external method: Namely to adjust the feed liquid fraction. This can be done by controlling the feed temperature and this option is available upstream to the feed in many plants. Adjusting the feed temperature does not have so much direct impact on the vapor split itself. But more importantly, it has impact on the optimality region itself, that is, the minimum and maximum vapor split that limits the optimality region. So, if adding (or removing) more heat at the feed brings the actual constant vapor split from being outside to inside the optimality region, that impact will be very positive. A rule of thumb in distillation is to apply most heat in the reboiler, but this will not apply if adjusting the feed temperature brings operation from outside to inside the optimality region.

Four and more products

The savings potential when going to four and more products are even larger than for the ternary DWC. But the internal complexity too. A fully thermally coupled arrangement for separation into four products is shown in Figure 4a. Note the indicated heat exchangers at the side-stream product locations. This would allow "fitting" the operation to every peak as indicated by the streams in Figure 2b. Such exchangers are not normally used in a DWC. The reboiler must produce vapor related to the highest peak anyway. As for the ternary DWC this gives flexibility, but not only for a vapor split range. It is also possible to modify the arrangement to obtain a less energy efficient part, but more operable. In Dejanović et. al 2013 [8], a 15-component aromatic feed and its separation into four products was studied. Its Vmin-diagram is easily calculated for all 15 components as shown in Figure 4b. These are to be separated into four products, and in Figure 4c, the resulting Vmin-diagram for the aggregated four products are shown. Note here that the heavy C/D split dominates and sets the overall reboiler demand. However, there are several options of possible simplifications of the arrangement where the overall minimum reboiler demand is maintained. One possibility is to change the pre-fractionator to separate ABC/CD in stead of the preferred split ABC/BCD. Then sub-column C22 becomes superfluous and can be removed, and with that an internal wall in a DWC. This removes one internal DWC vapor split. Then the peak related to sub-column C21 and 31 are lifted (dashed) but still below the peak arising from the demand for the C/D split. Thus, the reboiler duty is maintained. Another modification is to introduce side rectifier in the top. Side rectifiers are less energy efficient than full Petlyuk arrangements but offer somewhat easier operation and possibility to impact the internal vapor split. The dash-dot peak indicates now higher overall demand for this case. But if the side-steam purity is relaxed, it is still a feasible modification without need for adding more reboiler duty. (In the case study, the purity spec is only 80% for this stream.) Available space for this manuscript limits more detailed elaboration about other alternative options herein.

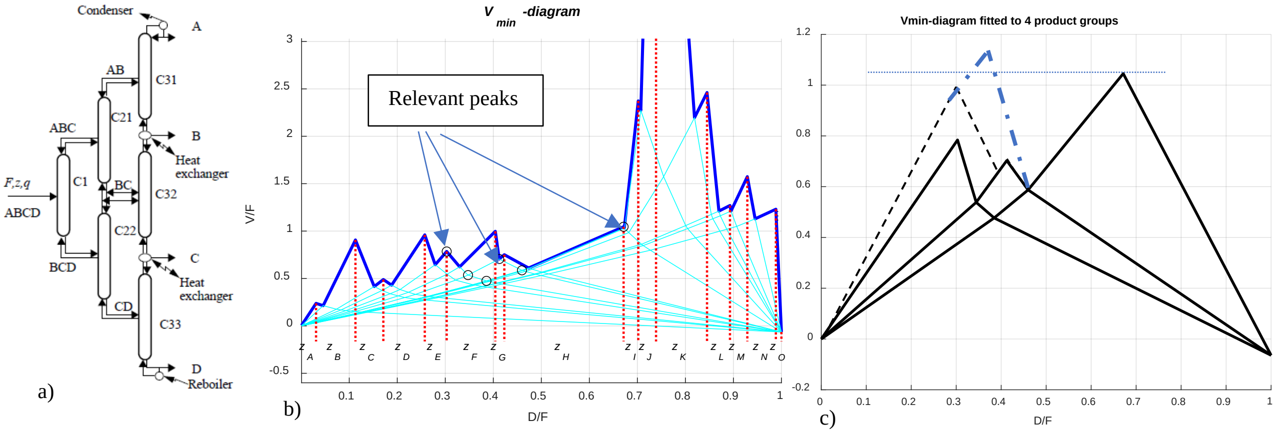

Figure 4. a) Four product separation in extended full flexible Petlyuk arrangement. b) Vmin-diagram for 15-component feed. c) Simplified 4-product Vmin-diagram (solid) fitted to the relevant points in the 15-component diagram. Dashed peaks indicate lifted peaks for top separation for alternative simplifications to the arrangement in Figure a): Dashed: C22 removed, Dash-dot: With Side rectifier for side product B. (C31 removed, and condensers placed on top of C21 and C32)

Conclusion

The Vmin-diagram is both a concept and a graphical tool for calculation and assessment of minimum energy operating conditions in multicomponent distillation. It is suitable in particular when applying the fully thermally coupled arrangements like Dividing Wall Columns (DWC). It can be used for characterization of the feed condition, and from that predict the overall minimum energy demand and how the internal flow rates can be set for obtaining the desired separations with minimum energy consumption. The diagram can also be used to assess possible simplifications to the generalized section arrangements for a class of feed properties without compromising the energy consumption. This gives and easier path to industrial realization of complex 4-5 product Dividing Wall Columns. The usage can both be based on the original ideal assumptions, based on feed data only, but a practitioner with an available rigorous process simulator can easily get to accurate results for real mixtures too. The Vmin-diagram can also provide good initializations.

References

1. Kaibel, G. *Distillation Columns with Vertical Partitions*. Chem. Eng. Technol. 1987, 10, 92-98.
2. Petlyuk, F.B., Platonov, V.M., Slavinskii, D.M. (1965). Thermodynamically optimal method for separating multicomponent mixtures. Int. Chem. Eng. Vol. 5, No. 3, pp 555-561
3. I. Dejanović, Lj. Matijašević, Ž. Olujić, *Dividing wall column—A breakthrough towards sustainable distilling*, Chem. Eng. and Processing: Process Intensification, Volume 49, Issue 6, 2010, Pages 559-580,
4. I.J. Halvorsen, *Minimum Energy Requirements Complex Distillation Arrangements*. NTNU Dr. ing. Thesis 2001:43. https://folk.ntnu.no/skoge/publications/thesis/2001_halvorsen/ThesisHalvorsen2001-www.pdf
5. I.J. Halvorsen and S. Skogestad, *Minimum energy consumption in multicomponent distillation*. Ind.Eng. Chem.Res., Volume 42 (2003), page 596-604 (part 1), page 605-615 (part 2), page 616-629 (part 3).
6. Underwood, A.J.V. (1948), *Fractional Distillation of Multi-Component Mixtures*. Chemical Engineering Progress, Vol. 44, no. 8, 1948
7. Z. Fidkowski and L. Krolikowski (1986). *Thermally Coupled System of Distillation Columns: Optimization Procedure*, AIChE Journal, Vol. 32, No. 4, 1986.
8. I. Dejanović, I. J. Halvorsen, S. Skogestad, H. Jansen and Ž. Olujić, Cost-effective design of energy efficient four-product dividing wall columns, Chemical Engineering Transactions, 35, 283-288 (2013)