Final Technical Report

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Table of Contents

List of Acronyms

BARON – Branch and Reduce Optimization Navigator
CPAT – Commercialization Projects Assessment Tool
MINLP—mixed-integer nonlinear program
NLP – nonlinear program

List of Tables & Figures

Executive Summary

In spite of the challenging nature of the tasks, all major tasks for this project were successfully accomplished. This has resulted in several 'firsts' for the distillation literature.

A long-standing problem in multicomponent distillation has been elucidation of all useful multicomponent distillation configurations to separate a feed mixture into its components. We developed an intuitive, easy to use step-by-step method that draws all basic and subcolumn distillation configurations for any non-azeotropic n-component mixture. Thus, now it is easy to draw the search space of thousands to millions of possible configurations as number of components in the feed increase from four to eight or higher.

Once the search space is available to a practitioner, finding the configuration that is optimal is a daunting task. This requires searching through thousands or even millions of configurations. Thus, we developed a two-tier strategy. In the first step, we algorithmically write governing equations for each of the configurations using Underwood's method to estimate heat duties. These equations are then solved using Branch and Reduce Optimization Navigator (BARON) solver to obtain guaranteed globally optimal solution for each configuration. This series of nonlinear programs (NLPs) provides us the ranklist of the entire search space based on the chosen criteria of energy consumption, exergy used, or total annualized cost including both energy and capital. In the second step, the top few identified configurations are then optimized using a detailed process simulator. We have confirmed the efficacy of our two-tier approach using several example case studies.

In order to make our method accessible to the industrial practitioners, we have developed a user interface for optimal distillation design, which allows thousands of drawings of our configurations to be instantly generated after running our optimization. The drawings produced by this program are interactive, showing flowrates, section vapor flows, and exchanger duties, and can be filtered based on a number of system properties including vapor duty, exergy loss, capital cost, number of transfer streams, number of thermally coupled streams, or the presence or absence of particular splits in the configuration.

An added benefit of this project has been that we were able to identify a hitherto-unknown class of heat and mass integrated distillation columns with lower heat duties! We also developed a method to draw these configurations for a given nonazeotropic n-component mixture.

The prevailing practice by industrial designers has been to design multicomponent distillation configurations based on heuristics and know-how. Since our work has shown that the search space contains thousands to millions of configurations, we clearly expect the prevailing practice to often result in suboptimal designs. Indeed when our method was applied to real industrial problems, in almost all cases it identified multicomponent distillation configurations that were 10% to 50% more energy efficient than the ones currently being used. For example, when applied to a case of crude oil separation, we have discovered configurations that have potential for up to 50% energy savings when compared to the existing separation train in a refinery. If applied on a global scale, these energy savings are comparable to the discovery of a new giant oil field (100 million barrels of oil) every year!

We have also disseminated the method and its findings through several presentations at international conferences, invited keynote and plenary lectures, presentations to chemical companies and publication of many papers in the high impact journals. An invited book chapter was written. Our crude distillation results have appeared in trade journals such as Chemical Processing, Hydrocarbon Processing, and Chemical Industry Digest. In relation to these results, the PI was interviewed by Lakeshore Public Radio about our findings.

Introduction: This project sought and successfully answered two big challenges facing the creation of low-energy, cost-effective, zeotropic multi-component distillation processes: first, identification of an efficient search space that includes all the useful distillation configurations and no undesired configurations; second, development of an algorithm to search the space efficiently and generate an array of low-energy options for industrial multi-component mixtures. Such mixtures are found in large-scale chemical and petroleum plants. Commercialization of our results was addressed by building a user interface allowing practical application of our methods for industrial problems by anyone with basic knowledge of distillation for a given problem. We also provided our algorithm to a major U.S. Chemical Company for use by the practitioners.

The successful execution of this program has provided methods and algorithms at the disposal of process engineers to readily generate low-energy solutions for a large class of multicomponent distillation problems in a typical chemical and petrochemical plant. In a petrochemical complex, the distillation trains within crude oil processing, hydrotreating units containing alkylation, isomerization, reformer, LPG (liquefied petroleum gas) and NGL (natural gas liquids) processing units can benefit from our results. Effluents from naphtha crackers and ethane-propane crackers typically contain mixtures of methane, ethylene, ethane, propylene, propane, butane and heavier hydrocarbons. We have shown that our systematic search method with a more complete search space, along with the optimization algorithm, has a potential to yield low-energy distillation configurations for all such applications with energy savings up to 50%.

Background: Prior to the execution of this project, past work on zeotropic multicomponent distillation configurations had generated a large body of extremely valuable information, but it was still unable to identify the low-energy distillation configurations for a given application. One problem had been that for many years, the search space for the distillation networks was incomplete. The superstructures reported were found to lack some configurations, and no systematic method to elucidate all distillation configurations from a network representation was available. The second problem with finding the optimum distillation configuration had been the enormous difficulty of the mathematical task and the size of the problem in terms of computational effort. This project successfully addressed the need for methods that provide quick screening to prune the search space before a more detailed assessment is carried out. The task of the initial screening ensured that all the low-energy candidate distillation networks are identified.

Results and Discussion of Project Tasks

Task 1 – Proof of Concept

In order to provide proof of our concept, the following subtasks were successfully completed.

1.A – Develop a paper algorithm and illustrate how it could be used to develop multiple distillation column configurations for multicomponent separation.

An algorithm was developed and then later used to generate multicomponent distillation column configurations. All possible four-component configurations are shown in Figure 1.

1.B – Demonstrate the economics and energy savings potential through a CPAT analysis on an example process.

A CPAT analysis was performed on a sample separation process. The process chosen was separation of ethylene from a hydrocarbon mixture, which we modeled as a system of four pseudocomponents:

A: Methane & lighter
B: Ethylene

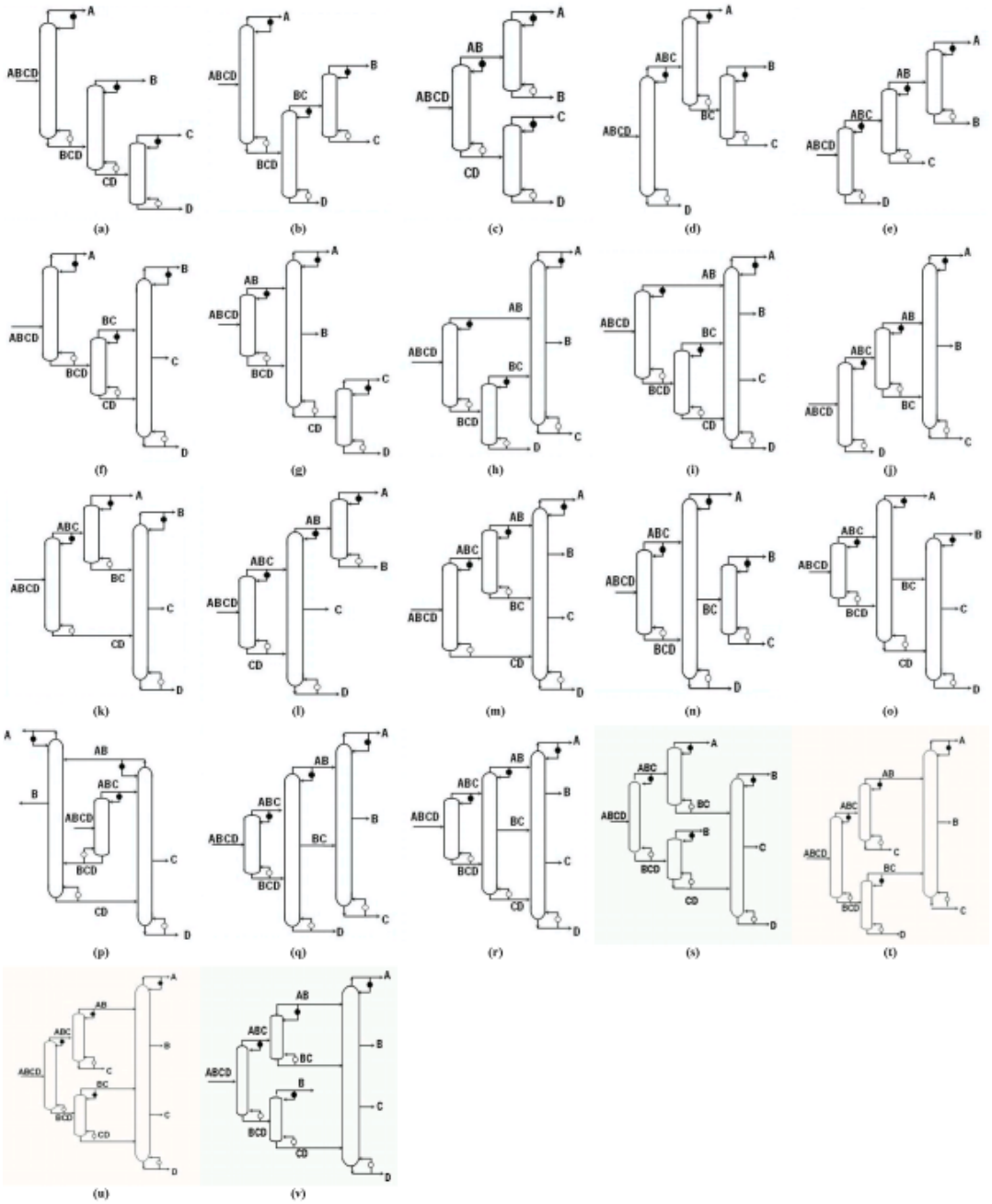

Figure 1: Possible four-component distillation configurations. (a)-(e) Sharp split basic configurations. (f)-(r) Non-sharp split basic configurations. (s)-(v) Nonbasic configurations.

C: Ethane
D: Propylene & lighter

The current configuration used in industry for this separation was identified. After looking through a number of candidate configurations to perform the same separation, it was found that compared to the current configuration, it was possible to achieve up to 35%-45% in heat duty savings. Since ethylene distillation is cryogenic and needs work input as opposed to heat input, the temperature levels at which cooling are required can significantly affect the viability of the

final configuration, a fact which we would later consider in task 3.H. As a whole though, this study allowed us to glimpse the potential of our method.

Task 2 – For an n-component mixture, identify a complete and compact search space such that no useful distillation configuration is excluded

Through the successful execution of this task, we have solved a long-standing chemical engineering problem. An intuitive and easy to use stepwise method was introduced to draw all possible basic and subcolumn configurations for the distillation of any given *n*-component mixture stream into *n* product streams. We introduced terms such as subcolumn configurations, regular column configurations, plus column configurations, basic and non-basic configurations to the chemical engineering literature. This is the first time that such a comprehensive methodology for drawing a complete search space of basic and subcolumn multicomponent distillation configurations is available in chemical engineering literature. The success of the new method and its importance is gauged from the fact that we were invited to write a chapter on this method for a three-volume distillation book being published next year (Distillation Fundamentals and Principles, Editors: A. Gorak and E. Sorensen, Publisher: Academy Press). Also, for this work the doctoral graduate student Vishesh H. Shah received the best graduate student research award for distillation by the Separations Division of the AIChE at its annual meeting in Salt Lake City, Utah in 2010.

2.A – Develop a method to evaluate the energy efficiency of the non-sharp-split basic configurations versus sharp-split basic configurations.

For an n-component separation, a sharp split basic configuration uses the fewest distillation sections (2(n-1)) and the fewest intercolumn transfer streams (n-2). For example, see configurations a-e in Figure 1. A non-sharp-split basic configuration requires between 2n and (n(n-1)) distillation sections and at least n-1 intercolumn transfer streams. For example, see configurations f-r in Figure 1. It thus seems likely that a sharp-split basic configuration will have a lower cost for capital and control. The aim of this task was to evaluate whether non-sharp-split basic configurations can provide energy savings sufficient to offset this increase in separation scheme complexity.

Table 1: Ratio of lowest non-sharp-split vapor flow to lowest sharp-split vapor flow within basic configurations (Giridhar & Agrawal, 2010a)

Split	Abcd	aBcd	abCd	abcD	aBCD	AbCD	ABcD	ABCd	abCD	aBcD	aBCd	AbcD	AbCd	ABcd	ABCD
eee	0.955	0.708	0.721	0.934	0.704	0.786	0.696	0.630	0.831	0.718	0.624	0.884	0.717	0.701	0.685
eed	0.865	0.783	0.945	0.994	0.975	0.984	0.950	0.892	0.992	0.945	0.906	1.002	0.931	0.798	0.958
ede	0.859	0.947	0.866	0.905	0.899	0.862	0.906	0.910	0.867	0.911	0.920	0.823	0.882	0.945	0.896
edd	0.769	0.905	0.546	0.998	0.697	0.811	0.850	0.718	0.812	0.878	0.716	0.984	0.599	0.895	0.706
dee	0.995	0.857	0.502	0.740	0.763	0.917	0.930	0.878	0.570	0.843	0.774	0.978	0.926	0.942	0.863
ded	0.947	0.790	0.869	0.953	0.682	0.705	0.672	0.625	0.912	0.598	0.542	0.595	0.560	0.869	0.563
dde	0.993	0.545	0.878	0.676	0.685	0.807	0.778	0.660	0.860	0.567	0.693	0.984	0.839	0.787	0.659
ddd	0.943	0.569	0.574	0.938	0.612	0.684	0.659	0.584	0.823	0.673	0.569	0.807	0.673	0.799	0.559

The method and results from this task were published in the paper “Synthesis of distillation configurations: I. Characteristics of a good search space” (Giridhar & Agrawal, 2010a). For a given feed condition, using Underwood’s method for calculating vapor flows at pinched, minimum reflux conditions, the non-sharp configuration with the lowest vapor flow was identified. Subsequently, for the same feed condition, the sharp-split configuration with the lowest vapor flow was identified. The ratio of the minimum vapor flows of these two configurations is shown below in Table 1 for a number of conditions. A total of 120 feed conditions were chosen to reflect the entire range of possible four-component separations, in terms of both ease of separation and feed compositions. The specific values of the feed

parameters are given in Tables 2 and 3. In Table 2, uppercase letters represent plentiful components, while lowercase letters represents other components. For example, Abcd denotes a feed rich in A but lean in the other three components. An equimolar mixture is denoted as ABCD. In Table 3, relative volatilities are denoted either as easy ('e', a ratio of 2.5 between adjacent components) or difficult ('d', a ratio of 1.1 between adjacent components). Thus an 'eed' split means the relative volatility between A/B and B/C are each 2.5 whereas the corresponding value between C/D is 1.1.

Table 2: Different feed compositions for a four-component feed stream used in this task (Giridhar & Agrawal, 2010a)

Feed	A	B	C	D
Abcd	85	5	5	5
aBcd	5	85	5	5
abCd	5	5	85	5
abcD	5	5	5	85
aBCD	5	31.7	31.7	31.7
AbCD	31.7	5	31.7	31.7
ABcD	31.7	31.7	5	31.7
ABCd	31.7	31.7	31.7	5
abCD	5	5	45	45
aBcD	5	45	5	45
aBCd	5	45	45	5
AbcD	45	5	5	45
AbCd	45	5	45	5
ABcd	45	45	5	5
ABCD	25	25	25	25

Table 3: Different feed relative volatilities for a four-component feed stream used in this task (Giridhar & Agrawal, 2010a)

Separability	α_{AB}	α_{BC}	α_{CD}
eee	2.5	2.5	2.5
eed	2.5	2.5	1.1
ede	2.5	1.1	2.5
edd	2.5	1.1	1.1
dee	1.1	2.5	2.5
ded	1.1	2.5	1.1
dde	1.1	1.1	2.5
ddd	1.1	1.1	1.1

For 119 out of 120 feed configurations used in Table 1, it was found that the sharp-split configuration with the lowest vapor flow had a higher total vapor flow than the non-sharp split configuration with the lowest vapor flow. In the one exceptional case, for feed AbcD with 'eed' split, only a 0.2% advantage was seen for the sharp-split configuration, compared to the non-sharp split. The energy savings of a non-sharp-split configuration vary from negligible to the order of 45%.

It was concluded that a complete, compact search space for distillation must include both sharp split configurations (due to their possible savings in capital and control costs) and non-sharp-split configurations (due to their demonstrated possibility for over 40% in operating cost savings).

2.B – Assess whether the search space should include non-basic distillation configurations.

Many complete formulations of the search space in previous work contain a number of non-basic distillation configurations (that is, those with more than n-1 columns; see configurations (s)-(v) in Figure 1). As the previous task suggests, these configurations have an increased burden in capital cost due to their additional columns and column sections. We wish to assess whether these configurations have an offsetting benefit that would lead to their inclusion in a compact search space. Similar to the sharp and nonsharp split configuration case, calculations were done to assess non-basic configurations for all 120 different four-component feed conditions. For each feed condition, the ratio of the minimum vapor flow

for the non-basic configuration with the least vapor flow to the minimum vapor flow for the basic configuration with the lowest vapor flow was calculated and is tabulated in Table 4.

Table 4: Ratio of the lowest vapor flow of non-basic configuration to the lowest vapor flow of basic configuration for each feed conditions (Giridhar & Agrawal, 2010a)

Split	Abcd	aBcd	abCd	abcD	aBCD	AbCD	ABcD	ABCd	abCD	aBcD	aBCd	AbcD	AbCd	ABcd	ABCD
eee	1.045	1.006	1.046	1.142	1.084	1.067	1.123	1.106	1.037	1.129	1.085	1.137	1.086	1.025	1.094
eed	1.073	1.053	1.002	1.023	1.010	1.020	1.064	1.023	1.010	1.054	1.010	1.083	1.016	1.071	1.025
ede	1.104	1.004	1.039	1.109	1.020	1.061	1.016	1.035	1.047	1.007	1.013	1.165	1.059	1.011	1.036
edd	1.186	1.005	1.044	1.047	1.041	1.041	1.059	1.116	1.038	1.036	1.104	1.118	1.053	1.026	1.052
dee	1.012	1.009	1.123	1.112	1.065	1.035	1.019	1.031	1.131	1.032	1.051	1.048	1.039	1.014	1.038
ded	1.043	1.027	1.008	1.053	1.029	1.029	1.039	1.042	1.024	1.050	1.048	1.080	1.048	1.030	1.047
dde	1.039	1.050	1.014	1.300	1.146	1.112	1.071	1.107	1.003	1.044	1.125	1.053	1.086	1.075	1.121
ddd	1.238	1.157	1.160	1.260	1.203	1.224	1.260	1.240	1.162	1.224	1.203	1.409	1.201	1.155	1.384

Since all the vapor flow ratios in Table 4 are greater than one, it is clear that for every feed condition considered, there exists no non-basic configuration that provides a lower vapor flow than the best possible basic configuration. Since the non-basic configurations already pay a penalty in capital cost, *we made the important conclusion that an ideal search space formulation should include basic configurations, and not include non-basic configurations*. Exclusion of non-basic configurations provides the additional benefit of significantly reducing the size of the search space we generated in part 2.C. A talk on this method and that of Task 2.A was given at the 2007 AIChE Spring National Meeting, entitled "New Energy-Efficient and Low-Cost Multicomponent Distillation Configurations".

2.C –Develop a framework that will redefine the search space such that all basic configurations can be drawn through a forward march through the network without generating any non-basic configurations.

Initially, in the paper "Synthesis of distillation configurations II: A search formulation for basic configurations" (Giridhar & Agrawal, 2010b), a supernetwork formulation based on integer programming was proposed. This formulation defined a configuration as a series of binary task variables – for example, $x_{ABC,AB}$ was a variable defined to be one if a column with a feed ABC and a product AB existed within a configuration. The constraints imposed to define the search space were as follows:

1) Ensure mass balance. If a node exists, it must have one distillate and one bottom. If a node does not exist, it cannot produce any other node.
2) Prevent redundant configurations. All components contained in the node must be present either in the distillate or the bottom.
3) Ensure basicity. Ensure that the configuration generated can be implemented in n-1 columns.

Taken together, these constraints provide an integer problem with multiple answers. Upon finding all solutions which satisfy these constraints, we have uniquely defined all basic configurations.

Subsequently this supernetwork formulation was recast into a step-by-step six-step synthesis method which allows for a simpler and more intuitive way to generate a complete and compact search space. The new method was published with the title "A Matrix Method for Multicomponent Distillation Sequences" in the AIChE Journal (Shah & Agrawal, 2010). In comparison to the supernetwork method, it is much easier to apply this method when the number of components increases beyond 5. The physical insights gained by this method helps to simplify the problem.

$$\begin{bmatrix} ABCDE & ABCD & ABC & AB & A \\ 0 & BCDE & BCD & BC & B \\ 0 & 0 & CDE & CD & C \\ 0 & 0 & 0 & DE & D \\ 0 & 0 & 0 & 0 & E \end{bmatrix}$$

Figure 2: Matrix for a five-component mixture

The heart of our step-by-step synthesis method is shown in Figure 2. An upper triangular matrix is generated which has n rows and n columns. The top left position in the matrix is occupied by the feed stream that is to be separated. The final pure products of the separation are listed in the final column of the matrix. All other spots in the triangle are filled by submixture streams – those mixtures of components which are somewhere between the feed mixture and the final products in terms of how much separation has been accomplished.

We notice that in any split with one feed and a top and bottom product, the only possible top products of the configuration are those found on a right-traveling horizontal line from the spot in the matrix representing the feed. For example, the only top products that can be produced from BCDE are BCD, BC, and B. Likewise, the only bottom products possible from a given feed are those that are found on a downward/right traveling along the diagonal line from the feed node (CDE, DE, or E from feed BCDE). We can also reverse this observation to note that the only feed nodes that can produce a given stream are those positioned horizontally to the left or diagonally to the left and up from the given stream's spot in the matrix.

In order to use this matrix to derive possible basic configurations, we create matrices of this form with each spot taken by a 0-1 binary variable. The feed stream (ABCDE) and product streams (A,B,C,D,E) will always be present and will thus always be represented by a 1. All submixture streams have either 1 (present) or 0 (absent). For Figure 2, where the number of submixture streams is 9, we can generate 2^9=512 candidate matrices. The next task is to draw a configuration from a given candidate matrix.

However, not every candidate matrix is a feasible basic configuration. For example, if every submixture spot in the matrix were represented by 0, there would exist no node capable of producing product B, product C, or product D. Thus, we must apply a number of checks to eliminate those matrices that do not have a feasible basic configuration associated with them. We do this with rules similar to those introduced by Giridhar & Agrawal.

Check 1. For every stream that exists, ensure that at least one stream that can act as its feed also exists. This excludes the feed node itself.
Check 2. For every node with a top and bottom product, ensure that all components contained in the node are also contained in one of the products. In other words, components must not disappear in a split.
Check 3. Ensure that at least n-2 submixtures are transferred.

Using these three checks formulated mathematically, we narrow the 512 candidate matrices for a 5 component mixture down to a total of 203 matrices representing basic configurations. This procedure can be performed for any n and after completion, the complete search space of basic configurations, including sharp and non-sharp splits, will be represented by the collection of matrices generated.

In order to draw a configuration from its corresponding matrix, we can simply identify each split that is present in the matrix and stack the splits properly within n-1 columns to arrive at a final drawing of the configuration. A 5-component example is provided in Figure 3. In 3a, a sample matrix is shown. In 3b, each 1 in the configuration is replaced by the stream it represents. In 3c, each individual split represented by the matrix is shown. In 3d, the circled products from 3c are combined and drawn from a single location, allowing a total of 10 splits to be performed in only 4 distillation columns.

At this point, we have successfully created a method for generating the complete set of basic configurations. For this task, it remains only to calculate the size of this set for any number of components in the feed. Table 5 shows the calculated values for an n value of 3 through 8.

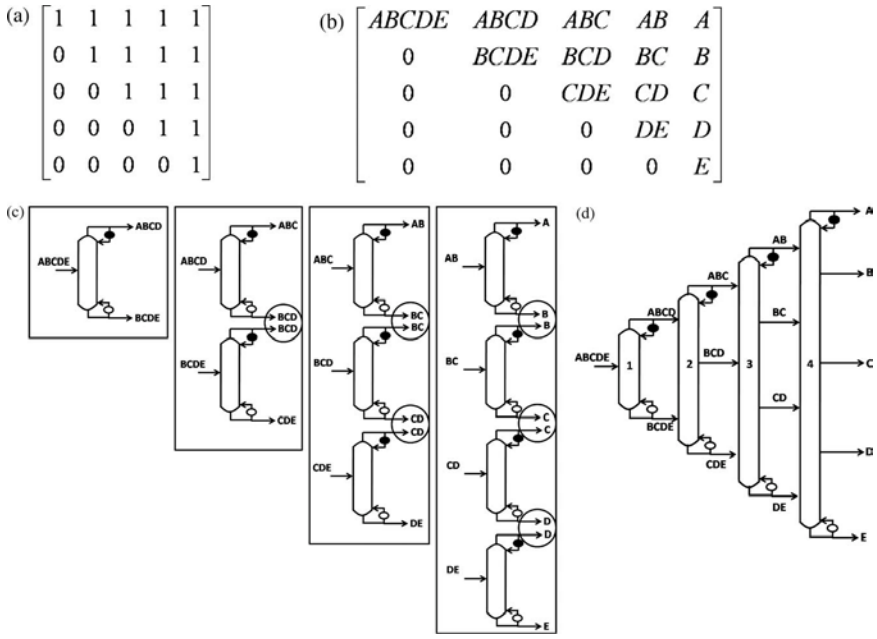

Figure 3: Drawing a 5-component configuration from a matrix

Table 5: Number of Basic Configurations as n grows

Number of Components in the Feed	Number of Basic Configurations
3	3
4	18
5	203
6	4373
7	185,421
8	15,767,207

This work has generated a substantial amount of interest after it was presented at the 2007 AIChE Annual Meeting entitled “Synthesis of Optimal Distillation Networks”, followed by “A Computationally Efficient Method to Generate a Complete Search Space for Multicomponent Distillation Sequences” at the 2008 AIChE Annual Meeting. The method is now being taught in chemical engineering classrooms of various universities and is soon to be published as a chapter in a distillation book..

2.D – Develop a framework to include distillation configurations with less than n-1 columns in the search space.

Due to the substantial possible advantages in installation and control costs, it is desirable to examine the potential of subcolumn configurations – that is, those column arrangements that perform an n-component separation in less than n-1 columns. This topic is covered by our group’s paper, “A Synthesis Method for Multicomponent Distillation Sequences with Fewer Columns” (Shenvi et al, 2012). This paper takes the six-step method presented in our previous work (Shah & Agrawal, 2010), and adds two additional steps to the formulation to arrive at the complete space of possible subcolumn configurations. To summarize these steps in a simple way, matrices that were previously disallowed are examined if the resulting configuration could be drawn with less than n-1 distillation columns. To ensure these new configurations are still feasible, they must have at least one side-stream product, must still have all product streams distinct from the feed streams of the column they are produced from, and cannot have two submixture streams transferred in opposite directions between columns if one is a product which can be derived from the other.

Interpretation of the matrices derived from this method requires caution. Proper drawing of one possible subcolumn configuration is shown in Figure 4.

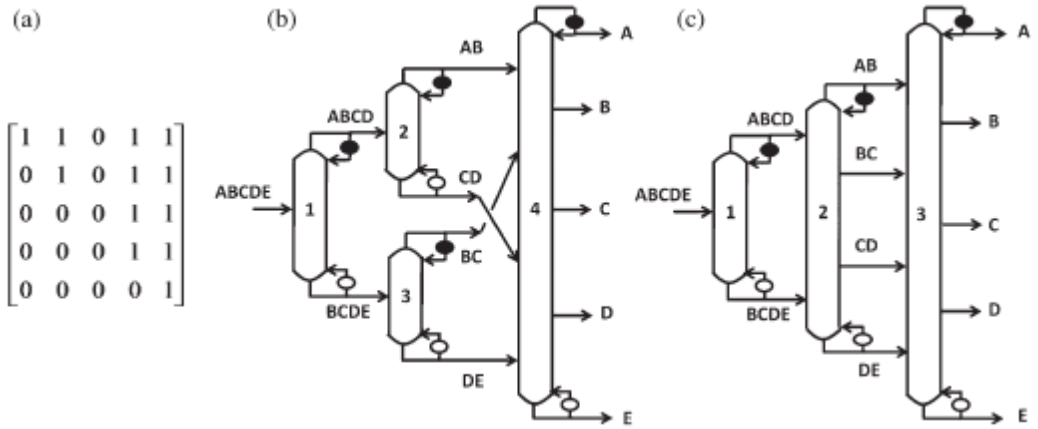

Figure 4: (a) sample subcolumn matrix. (b) splits contained within this matrix, as might be initially interpreted. (c) the same configuration, rearranged so that it contains less than n-1 columns (Shenvi et al, 2012)

Finally, as shown in Table 6, we can give the complete search space of subcolumn distillation configurations, including thermal coupling (see Task 4):\

Table 6: Number of subcolumn distillation configurations

Number of Components in the Feed	Number of Subcolumn Configurations without Thermal Coupling	Number of Additional Thermally Coupled Configurations
3	1	0
4	12	18
5	198	1279
6	5142	124,346
7	224,257	20,168,590
8	17,056,898	5,739,609,045

Task 3 – Develop an algorithm to sweep the search space and find an array of optimum distillation configurations for a given multicomponent feed

In order to utilize the multitude of novel configurations generated by the algorithm developed in step 2, it is important to be able to determine which configurations are energy efficient and which are not. Through the successful implementation of this task, we developed a unique, potent design tool which allows quick generation and screening of the full search space for any multicomponent separation. The developed algorithm was based on Underwood's method and requires as its input only the following: number of components, feed composition and state, and relative volatility for each component. The results of this screening tool were confirmed through rigorous process simulation using real thermodynamic data and tray counts, and alternative objective functions were developed that also apply Underwood's method to screen configurations based on thermodynamic efficiency or total annualized cost. Each of these objective functions was then paired with a first-of-its-kind global optimization algorithm which allows individual evaluation of each configuration to the globally optimal solution. Finally, a tool for practicing engineers was developed which allows visualization, further screening, and flowsheeting of all configurations in the search space.

3.A – Develop an algorithm to do first level screening using Underwood's method to calculate vapor flow in a distillation column.

For a given multicomponent feed distillation, having successfully listed the configurations present in the search space, we turn to the question of identifying which of these possibilities are attractive configurations. One first-level way to screen for attractive configurations is to find those with the minimum possible vapor flow. We choose vapor flow because it has ties to both the capital costs (size of heat exchangers and diameter of distillation columns scale with the vapor flow through the system) and the operating costs (more vapor generated means more reboiler duty, and also means more vapor condensed/more condenser duty). Another benefit of using vapor flow as an objective function is that it can be calculated quickly using Underwood's equations at minimum reflux. Using Underwood's equations as the central separation governing equation, we additionally write a series of mass balance equations to arrive at a nonlinear programming problem which we can solve for minimum vapor flow. We wrote an algorithm that generates all the pertaining equations for a configuration as it is generated from the method of Task 2. The equations for the configuration are then solved to give minimum vapor duty for that configuration. This step is repeated for all the configurations and in the end they are ranklisted according to their vapor flow requirements.

An example of a complete ranklist of the search space is provided in Shah & Agrawal (2010). The algorithm we have developed is tested by examining two cases – simplified versions of a light and heavy petroleum crude oil feed which are treated as five component mixtures. The conventionally used configuration for this separation is a spatial rearrangement (Figure 5a) of a configuration which is included in our search space – the fully thermally coupled indirect split sequence (Figure 5b).

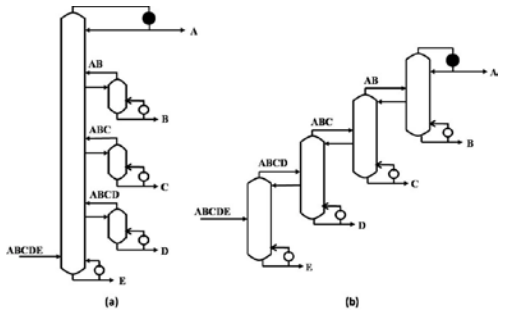

Figure 5: Conventional configuration for petroleum crude distillation.

We optimized the total vapor duty of this configuration for a light crude and a heavy crude. When we compared the calculated optimized vapor flows with other configurations in the entire search space, we observed that it is possible to find basic configurations (i.e., without thermal coupling) that have a much lower minimum vapor requirements. If we go on to allow thermal coupling (see task 4B), we observe that the best new configurations can reduce the total vapor duty of the system by over 48% for the light crude distillation and over 17% for the heavy crude distillation. Even if we are required to retain certain aspects of the original system, our method can still identify more energy-efficient candidates. For example, if it is required that component E (heavy residue) is removed from the mixture in the first column for purposes of preventing fouling, it is still possible to find configurations that can save 19.4% and 8.8% respectively in the vapor duties of light and heavy crude separation. This shows that by adjusting which types of configurations our method generates via mathematical constraints, we can provide a complete ranklist of the entire search space or a subspace of it for specific operational purposes.

Related results, including the case study described above, were presented at the 2009 AIChE Spring National Meeting as "Synthesis and quick identification of low-energy sequences for multicomponent distillation." Some of these results were also incorporated in the April 2008 presentation "Reducing Energy Consumption by New Distillation Configurations", which was presented at the 11th Topical on Refinery Processing at the 2008 AIChE Annual Spring Meeting. The early findings from this work were published as "Global Optimization of Multicomponent Distillation Configurations:1.Need for a Reliable Global Optimization Algorithm" in AIChE Journal (Nallasivam et al, 2013).

3.B – Develop methods to do screening with real thermodynamic data and tray counts in the distillation columns.

The method developed in 3.A uses Underwood's equations for estimating the vapor duty requirement of the configurations. Although the Underwood's equations are easy to use and provide a quick way of screening through a large number of configurations, they are based on several assumptions of ideal mixture separations. For widespread application of our screening tool, there is thus a need to validate the rank-list of configurations found by this method against a rank-list obtained using rigorous thermodynamic data and stage-to-stage calculation. Using an example case of ethylene distillation from a feed of mixed hydrocarbons, which will be treated as a four component separation, we simulated thirteen basic configurations using ASPEN Plus®.

Table 7: Validation of Screening Tool by Rigorous ASPEN Simulations

Rank	Configuration	
	Screening Tool	ASPEN Simulations
1	(n)	(n)
2	(l)	(l)
3	(h)	(k)
4	(k)	(h)
5	(j)	(i)
6	(i)	(f)
7	(f)	(e)
8	(e)	(j)
9	(b)	(b)
10	(a)	(a)
11	(c)	(c)
12	(m)	(m)
13	(d)	(d)

The total vapor requirement found via NLP optimization is normalized to the lowest value for the set of 13 configurations. Likewise, the heat duty requirement after optimization in ASPEN is normalized to that of the configuration with minimum heat duty. Then, the 13 configurations are ranked from lowest to highest in each metric. The results are shown in Table 7.

Each letter represents a specific configuration in the search space of four-component arrangements. We can see that the order of our NLP optimization ranklist is essentially preserved when performing detailed ASPEN calculations. The same configurations identified as the best four by our screening tool are identified as the best four by ASPEN. The same four middle configurations are still the middle configurations in both methods. Finally, the 5 configurations identified as the least efficient (as well as their order) are identical in both methods. Some slight shuffling in the ranklist occurs, but as a whole the order provided by our calculations using Underwood's equations are highly representative of those that would be obtained using detailed thermodynamic models. This is an important finding as it allows us to use the results from our first level screening NLP model as initial estimates for the ASPEN

simulation with the real thermodynamic data. In this manner, the likelihood of obtaining globally optimal solutions from ASPEN models is substantially increased.

3.C – Develop methods to account for cost and assess operability, manufacturability and potential for retrofit in an existing plant.

We have developed a formulation which uses the same global minimization algorithm as previously discussed in task 3.A to study total annualized cost of distillation configurations. This formulation still uses the Underwood equations, but additionally includes a number of correlations to calculate equipment sizing data from the system's vapor flow, relative volatility and recovery data. The constraints governing the system are identical to those used to optimize based on vapor flowrate. However, instead of an objective function summing all vapor requirements, the objective function is

$$\min\left(\sum_{s=1}^{ns} Ccol_s + \sum_{s=1}^{ns} Ctray_s + \sum_{c\in Reboiler_s} Creb_c + \sum_{c\in Condenser_s} Ccond_c + Cst\times \sum_{c\in Reboiler_s} Qreb_c + Ccw\times \sum_{c\in Reboiler_s} Qcond_c\right)$$

which contains individual terms for column exterior cost, column tray cost, reboiler and condenser capital cost, and operating cost for steam and cooling water. In the upcoming paper "Global Optimization of Multicomponent Distillation Configurations: 3. Economic Optimization Design for the Separation of Multicomponent Mixture" (Zhang et al), we compare this capital cost formulation to current literature practices, concluding that current practices may be faster to provide a single good solution, *but using our global minimization algorithm both guarantees a globally optimal solution that proved to have up to 5% lower costs in some cases, and gives a ranklist of all solutions rather than just picking one.*

In another important milestone of this project, in conjunction with the Rosen Center for Advanced Computing, we have developed a user interface which can take the results of any calculations we do to outline the search space and turn that data into a flowsheet-style interactive drawing of all the configurations in the search space. Each of these drawings comes with viewable tooltip information on flowrates, section vapor flows, and reboiler and condenser duties as calculated by our global minimization algorithm. Because of our desire to make this interface a helpful tool for distillation practitioners, we have included some filter tools which can allow the viewing of only configurations that meet certain operability and retrofit criteria. For example, if one wished to see all derivatives of a current configuration that retained the same first distillation column, a filter can be set to only view drawings that meet this criterion. Likewise, if a maximum of two thermal coupling links were desired, this maximum could be imposed through use of our filters. Development of this interface provides us a useful step forward in the use of our concepts by industrial practitioners by removing much of the expertise required to interpret and manipulate results from our mathematical formulation. Instead, the information is presented simply in a way that can be used for actual design of distillation columns, needing no prior experience with our methods.

3.D – Develop a computationally faster and robust NLP solver that will provide globally optimal solutions for heat duty.

The original solution method used to solve the NLP was the fmincon solver built into MATLAB. This method provided feasible solutions, but very often the solutions were computationally challenging to reach and got stuck at local minima within the optimization space. In other words, fmincon solver did not guarantee the global optimality of our calculated vapor flowrates. In order to achieve better, faster and guaranteed globally optimal solutions we added task 3.D, and then proceeded to address it by entering into collaboration with Prof. Mohit Tawarmalani of Krannert School of Management at Purdue University. Prof. Tawarmalani is a co-developer of the Branch and Reduce Optimization Navigator software, and we rebuilt our program to solve our generated NLP problems in this software, known as BARON. There are several advantages to using BARON. First, it contains a number of advanced feasible space range reduction features to ensure a faster solution. BARON can also provide excellent convex underestimators to nonconvex functions, which are present in our formulation. Using BARON, we were able to guarantee globally optimal solutions to all vapor duty screening problems for up to a 5 component search space containing 6,128 configurations (which includes thermally coupled configurations – see

Task 4). The program can also handle a higher number of components, but needs additional work to make it computationally faster.

In addition to implementing BARON, a number of specific improvements were made to increase robustness and convergence speed. The most notable of these was our Underwood Root Bounding routine, which went through detailed bound reduction measures to impose the tightest possible bounds on the crucial Underwood roots before attempting to solve the problem. This process of improving our optimization is discussed in a manuscript titled "Global Optimization of Multicomponent Distillation Configurations: 2. Enumeration based global minimization algorithm" which is currently undergoing final revision prior to submission to the AIChE Journal.

3.E – Develop equations to estimate heat duties of configurations with less than n-1 columns by calculating vapor flow rates..

In order to be screened in the same way as regular-column configurations, we require equations to estimate vapor duties of configurations with less than n-1 columns. A considerable amount of time was spent developing shortcut equations that were then tested against literature results. The literature results showed that the developed equations were consistent with detailed simulation for three component mixtures only. These equations were found to be unreliable for higher number of components and require future work.. Equipped with these verified equations, we can combine this result with task 2.D to screen for energy efficient subcolumn configurations.

3.F – Develop an algorithm to do first level screening of distillation configurations with less than n-1 columns on the basis of vapor flow rates.

The equations derived for task 3.E can be combined with our matrix method from task 2.D to create a complete screening tool for subcolumn configurations. This screening tool has been developed at a trial level, but has not yet been fully tested for case studies of specific processes.

Due to the smaller size of the search space for subcolumn configurations, it is anticipated that the total computational time required to ranklist the search space will be substantially less than that required by the regular-column search space for the same number of components in the feed. However, like the regular-column search space, the total number of configurations increases polynomially with the number of components (refer to Tables 5 and 6).

Our results related to distillation configurations with less than n-1 columns generated two presentations at national conferences. The first, given at the 2010 AIChE Annual Meeting, was "A Method for Multicomponent Distillation Sequences with Fewer Columns". It was followed up at the 2011 AIChE Annual Meeting with the related talk "A Method for Novel Multicomponent Distillation Sequences with Fewer Columns." A paper was also published in the AIChE Journal entitled "A Synthesis Method for Multicomponent Distillation Sequences with Fewer Columns" (Shenvi et al, 2012).

3.G – Develop equations to assess exergy consumption of basic distillation configurations.

Using minimum vapor as the objective function has the advantage of approximating both capital cost and operating cost; conversely, the temperature level at which vapor is generated is not considered. This could lead to a distillation configuration being regarded more efficient despite requiring generation of vapor at a much higher temperature than a rival configuration, driving down its true benefit.

Accounting for temperature levels in a distillation to derive a thermodynamic efficiency for a separation process has often been done through exergy analysis. Analysis based on thermal efficiency can often provide useful insights for design that would not be apparent otherwise.

For these reasons, we wish to examine what happens when we screen our search space based on exergy loss rather than vapor duty. Achieving this required us to add additional constraints that calculate the exergy loss of the system from the vapor flows and the stream flowrates in our NLP formulation. In the process of deriving the exergy loss, we take advantage of a very important relation between temperature and relative volatility to express the final expression in terms of only flows, relative volatilities, and mole fractions. More notably, this expression for efficiency which measures the effect of temperature can be calculated without a detailed calculation of temperature. The objective function for the optimization is shown below, where L_j and V_j are the liquid and vapor molar flowrates of the jth stream

respectively, $z_{f,i}$ is the mole fraction of component i in the feed, $x_{i,j}$ is the mole fraction of component i in the liquid stream j, α_i is the relative volatility of component i and q is the quality of a stream.

$$\min \left[\begin{array}{l} \sum_i z_{f,i} \ln z_{f,i} + \sum_{j=cond} L_j \int_0^1 [\ln(\sum_i \alpha_i x_{i,j})] dq \\ + \sum_{j=reb} V_j \int_0^1 [\ln(\sum_i \alpha_i x_{i,j})] dq \end{array} \right]$$

3.H – Develop an algorithm to do screening of distillation configurations by calculating exergy consumption under Task 3.G.

We are able to create a ranklist of all 6,128 configurations (which includes thermally coupled configurations – see Task 4) in the 5 component search space on the basis of exergy loss. When we compare this ranklist to that from our previous vapor duty objective function, we find that not all configurations which are desirable by one measure are desirable by another (Figure 6).

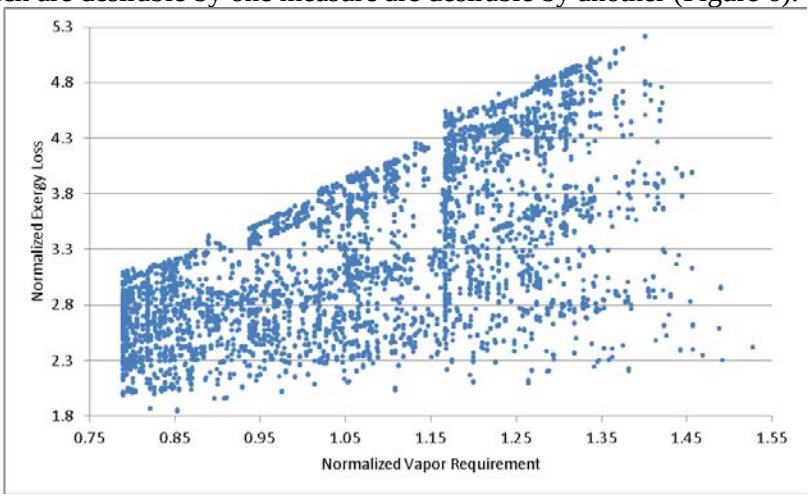

Figure 6: Five component search space, ranked by exergy loss and by vapor flow

Comparing two configurations in this space which are similar in thermodynamic efficiency but have different capital costs, or vice versa, shows that configurations which allow production of vapor to be moved to lower temperature reboilers and condensation of vapor to be moved to higher temperature condensers are favored thermodynamically. For example, in Figure 7, the two configurations shown have identical vapor duty, but the location of condensers in the second configuration allows a reduction of 34% in exergy loss without changing the vapor duty requirement. The data is provided in the form [Normalized Vapor Flow (Normalized Exergy Loss)] at each reboiler or condenser. Further discussion of this result can be found in the group's upcoming paper "A method for exergy minimization over the full search space of regular-column configurations" which is currently being revised (Huff & Agrawal).

The results of Figure 6 as well as the equations underlying the exergy screening method were presented at the 2012 AIChE Annual Meeting, a talk entitled "Design of Efficient Systems for Multicomponent Distillation."

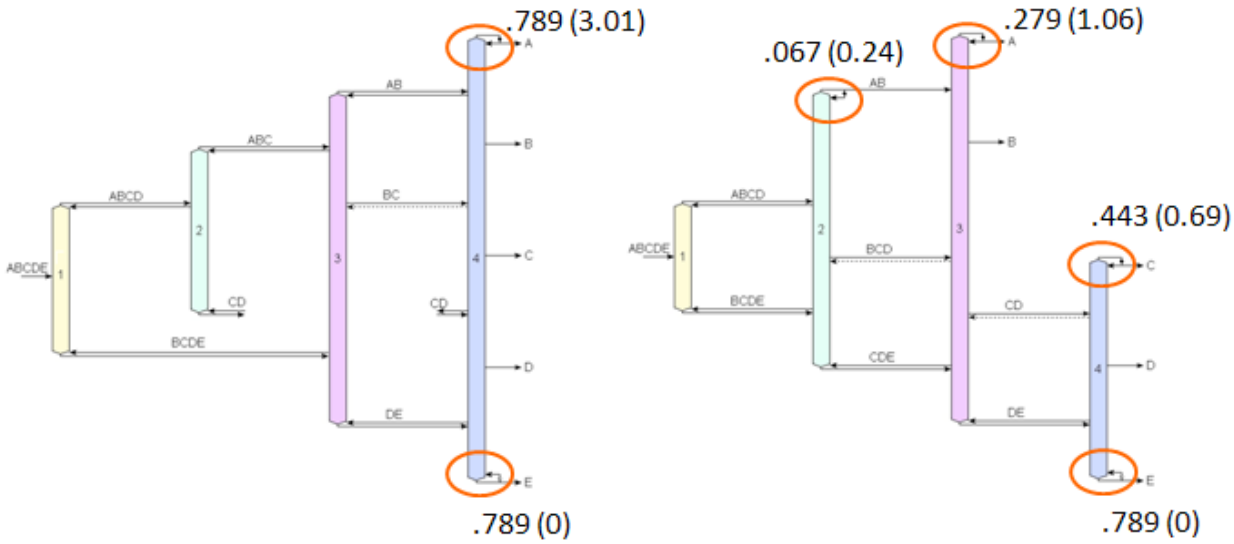

Figure 7: Comparison of cases with identical vapor requirements and different exergy losses. The numbers in the parenthesis are exergy losses.

<u>Task 4 – Develop an algorithm to sweep the search space and find an array of optimum thermally coupled distillation configurations for a given multicomponent feed</u>

All operations undertaken in Task 3 were for basic configurations, which are known to generally have a higher vapor requirement than configurations with thermally coupled links. In Task 4, the methods of Task 3 were successfully extended to configurations with thermally coupled links.

4.A – Define search space for thermal-coupling between the distillation columns and also develop relevant performance results.

Any basic configuration containing at least one submixture stream has at least one thermally coupled derivative configuration. Including these thermally coupled configurations in our search space can provide a number of very energy efficient configurations. The matrix method was thus modified to also include thermally coupled variants of its basic configurations. Using additional 0-1 integer variables to indicate the presence or absence of thermal couplings, we find that a basic configuration with *p* possible locations for thermal coupling has a total of 2^p-1 additional configurations which can be derived from it. Once we list all of these possibilities, the search space referred to in Table 5 expands; the expanded search space can be seen in Table 8. In this way, we have defined a complete yet compact search space that includes both basic and thermally coupled configurations, the first algorithm to do so in literature. This work was also included in the AIChE Journal paper of section 3.A (Shah & Agrawal, 2010).

Table 8: Search space including thermally coupled configurations

Number of Components in the Feed	Number of Basic Configurations	Number of Additional Configurations with Thermal Coupling
3	3	5
4	18	134
5	203	5925
6	4373	502,539
7	185,421	85,030,771
8	15,767,207	29,006,926,681

4.B – Develop an algorithm to do first level energy based screening using Underwood's method to calculate vapor flow in a distillation column.

In this task, the algorithm already developed for task 3.A was adapted to include the thermally coupled configurations generated in task 4.A. As noted in the description of task 3.A, many of the configurations that proved to be optimal, as well as the current configuration used for the separation of petroleum crude oil, are thermally coupled configurations. A detailed case study of the usefulness of thermally coupling links was performed and published in I&EC Research Journal by Shah & Agrawal (2011).

The results of Tasks 4.A and 4.B were presented nationally in the presentation "Thermal Coupling in Multicomponent Distillation Sequences" at the 2009 AIChE Annual Meeting in Nashville, TN. An extension of this method that discussed possible further improvements was given at the 2012 AIChE Annual Meeting, entitled "New Class of Thermal Coupling Links in Multicomponent Distillation.

4.C – Develop methods to do screening of thermally-coupled configurations with real thermodynamic data and tray counts in the distillation columns.

In a manner identical to that in task 3.B, we compare ASPEN simulations with the results obtained from our screening tool. We find that while there is again some variance in the specific positions in the ranklist, the two ranklists correlate highly. A configuration –whether basic or thermally coupled – identified as low in total vapor requirement by our NLP screening method will also be one of the top configurations when a complete simulation including detailed thermodynamic models is used. Once again this is an important finding that allows a screening of thousands of configurations with reasonable computational time and yet guarantees that the top few beneficial configurations will always be identified. Once the few top configurations are identified they are then subjected to detailed evaluation using real thermodynamic data.

4.D – Draw the attractive thermally-coupled configurations as operational systems.

In our work with the Rosen computing center, we were able to provide drawings of both basic and thermally coupled systems that contain interactive tooltips to display operational info about the system. This was limited to mass flows, liquid and vapor flows. Additional information regarding column pressures and controls has not yet been incorporated, but is still in our plans to aid in detailed design.

4.E – Develop methods to account for cost, assess operability, manufacturability and potential for retrofit in an existing plant as it relates to thermally coupled links.

This task was successfully completed in the same way as its corresponding Part 3 task. All of the capital cost formulation information in Task 3.C has been successfully implemented as well for thermally coupled configurations. This gives us a formulation that can compare both basic and thermally coupled configurations in terms of total annualized cost, which includes the capital cost of all columns, reboilers, and condensers as well as the operating costs associated with steam and cooling water.

The retrofit considerations designed into our user interface also apply to thermally coupled configurations. Just as with basic configurations, we can search for all thermally coupled configurations that contain certain splits, certain columns, or a certain number of submixture transfer streams. We are also capable of restricting our retrofit search to only those configurations with a certain number of thermally coupled streams. All this work is a part of a paper which is currently undergoing revision prior to submission (Zhang et al).

4.F – Develop a computationally faster and robust NLP solver that will provide globally optimal solutions for heat duty of thermally-coupled configurations.

Optimization of thermally coupled configurations tends to be the most computationally intensive task we can perform with our NLP solver. All of the improvements described in task 3.D can also be applied to this section. Use of the BARON solver allows the specific constraints associated with thermally coupled streams to experience the same advantage of range reduction and convex underestimation as the NLP for basic configurations. Before implementation of the speed and robustness improvements, it was a task that took many days to examine the complete search space for 5 components

(6,128 total configurations). After the improvements made to the global minimization algorithm, all 6,128 configurations could be solved to global optimality generally within hours, a remarkable achievement in computational speed! These remarkable results are the subject of the manuscript currently undergoing its final revision, “Global Optimization of Multicomponent Distillation Configurations: 2. Enumeration based global minimization algorithm” (Nallasivam et al).

4.G – Develop a computationally faster and robust NLP solver that will provide globally optimal solutions for heat duty of thermally-coupled configurations with less than n-1 columns.

The use of BARON solver and all constraints implemented to speed convergence also pay dividends when dealing with thermally coupled configurations with less than n-1 columns. As noted in 3.F, due to hurdles in task 3.E, this has not been applied to a large number of components or a specific case study; however, our group’s expertise in optimization ensures that when we do wish to perform a case study on subcolumn configurations, the convergence speed and stability should be excellent, and solutions will be guaranteed to global optimality.

While we were unable to develop easy to use equations for estimating minimum vapor flows for columns with multiple feeds and products (which is the key feature of columns within the space of configurations with less than n-1 columns), we had a remarkable success in another aspect of this task. While attempting to draw thermally coupled configurations for a subcolumn search space, we discovered a new class of heat and mass integrated column configurations. These configurations not only use lower than n-1 columns but are also highly energy efficient and provide an array of new configurations to practitioners in the field. Our paper submission to the AIChE Journal on this subject, “New Multicomponent Distillation Configurations with Simultaneous Heat and Mass Integration” (Shenvi et al, 2013), received such favorable reviews that it was put on exceptional fast track for publication by the journal.

4.H – Develop equations to assess exergy requirement of a thermally-coupled basic distillation configuration with n-1 distillation column.
4.I – Develop an algorithm to rank list thermally-coupled distillation configurations based on their exergy consumption from Task 4.H.

Tasks 4.H and 4.I were successfully completed. Replacing a reboiler or condenser with a thermally coupled link removed an opportunity for exergy to be input into or removed from the column. This means that the objective function was actually simpler for highly thermally coupled configurations; however, the offsetting complexity of NLP constraints associated with thermal coupling made most of the configurations equivalent in terms of calculation time.

The results of these tasks will be discussed in the upcoming paper “A method for exergy minimization over the full search space of regular-column configurations” (Huff et al). One of the key observations of this paper as it relates to thermally coupled configurations is that the fully thermally coupled configuration generates all its reboiler and condenser duty at the exchangers with the most extreme (and thus costly) temperatures. Thus, from a thermodynamic efficiency standpoint, it is possible to improve on the fully thermally coupled configuration with smart insertion of one or two exchangers at intermediate temperatures to handle part of the duty. For reference, the fully thermally coupled configuration is represented in Figure 6 by a dot with minimum vapor flow but maximum exergy loss among those with low vapor flow (that is, the top left dot on the configuration graph). This will be the first time in literature that thermodynamic efficiency analysis is combined with a complete, compact search space formulation.

4.J – Validate results of task 4.H in ASPEN using real thermodynamic data.
4.K – Validate results of task 4.I in ASPEN using real thermodynamic data.

Analysis of exergy-based equations and ranklists is still underway and has not yet produced definitive results.

5 – At the end of tasks 2, 3 and 4, the developed tools will be applied to three high-volume, high-impact industrial processes.

Our tool for generation of a complete search space and vapor duty based ranklist was applied to three high-volume, high-impact industrial processes. This was performed by one of our graduate researchers during a semester-long internship visit to a cost-sharing industrial partner, where he applied our tools to proprietary separations reflecting real life plant conditions. As expected based on our analysis of crude oil and ethylene separation case studies, the ranklist identified a number of configurations with more than 20% potential reduction in energy costs compared to the current configuration in use. The results of our analysis were then studied in more depth using detailed process modeling. While the method met exemplary success and results were of great use to the industrial partner, due to the proprietary nature of the separations we are unable to report the results here.

Benefits Assessment

The primary benefit of our findings lies in their adaptability and thoroughness. We are capable of designing a separation for any mixture of gases, liquids or both, as long as the mixture can be represented as *n* distinct components with known relative volatilities. The only information required to synthesize all possible regular-column and sub-column configurations is the number of components *n*. The only additional information required to provide a complete ranklist of all configurations based on vapor duty or thermodynamic efficiency is the feed composition and thermal quality. A complete ranklist based on total annualized cost can be produced with only this information plus specifications of certain cost estimation constants. We have proven through case studies that our configurations can reduce total energy consumption by 20 to 50 percent for a number of high-volume industrial cases such as crude oil separation, ethylene production and more.

We have the option to provide a complete ranklist of every configuration in the search space, ensuring that every option is considered. Issues of controllability or retrofit can be addressed by taking the top ten (or twenty, or any given number) configurations and performing more detailed studies on their properties – our primary goal in this case is the identification of desirable candidate configurations for further study. Additionally, we have shown through a case study that the results of our optimization line up extremely well with the results that would be achieved through detailed stage-to-stage optimization with real thermodynamic data in a program like ASPEN.

With 90 – 95% of all separations in the chemical and petrochemical plants, distillation is among the predominant unit operations. According to one estimate, there are approximately 40,000 distillation columns in operation in the U.S. with energy consumption equivalent to 1.2 million barrels of crude oil per day. A large fraction of the separations are done for mixtures containing four or more components using distillation trains containing multiple columns. Our developed method has a potential to reduce energy consumption by 10 to 50% for most of these applications and has a potential to make huge impact on energy consumption by the chemical and petroleum industry.

Commercialization

In the course of working with industrial partners on the case study in Task 5, a constant note we received was that the most effective road to commercialization would come through development of a simple, easy-to-understand user interface which translates the complex results of our optimizations into flowsheets with actual drawings of all configurations and operational data about each configuration. As a result, we developed the user interface program “Distview”, described in Task 3.C. This program provides flowsheet drawings of all configurations in our search space, and displays information on stream flows, column flows, and reboiler and

condenser duties. Additionally it allows sorting of all configurations based on vapor duty, thermodynamic efficiency or total annualized cost as well as structural criteria like number of transfer streams or number of thermally coupled streams. As a tool for retrofit or operability design the tool can filter through the configurations and only display those with certain characteristics (including presence of certain splits, a specific number or thermal couplings, or a specific number of transfer streams). As a whole, this tool moves our process forward from a difficult-to-interpret group of numerical results to a simple, efficient way of analyzing and designing configurations in an industrial setting. The development of 'Distview" is a critical step forward in the use of our technology by the individual practitioners.

In order to demonstrate the versatility of our method in an industrial setting, Anirudh Shenvi, a graduate student, spent four months at Eastman Chemicals. There he applied our technology to various existing industrial multicomponent distillations. It is remarkable that in all cases, the use of the method identified 10-30% reduction in heat duty. Our intention is to provide software to other chemical companies. Also, in order to make companies aware of our technology and the software, we plan to demonstrate it in the distillation sessions at the AIChE Spring meetings. Also, R. Agrawal (PI) is making presentations at multiple chemical and petroleum companies to increase awareness of the technology and the software.

Accomplishments

- Doctoral Student Vishesh H. Shah received the best graduate student research award for distillation by the Separations Division of the AIChE at its annual meeting in Salt Lake City, Utah in 2010.
- Two provisional patents were filed for energy efficient distillation processes – the first relating to ethylene distillation and the second to petroleum crude oil distillation.
- Three graduate students completed thesis dissertations on this topic, with two more still in progress. The thesis works produced by this group are
    - Synthesis of multicomponent distillation configurations (Arun Giridhar)
    - Energy savings in distillation via identification of useful configurations (Vishesh Shah)
    - Synthesis of energy efficient distillation configurations (Anirudh Shenvi)
- Ten student-led research papers and corresponding presentations were submitted and presented at major conferences including the AIChE Fall and Spring Meetings. Further details are given in the references.
- Seventeen invited lectures or PI-led research presentations were presented on the work including two keynote lectures and two plenary lectures. Further details are given in the references.
- We were invited to write a book chapter "Conceptual Design of Zeotropic Separation Processes" based on this work. This book chapter is included in an upcoming textbook titled "Distillation Processes and Principles", Volume 1, edited by A. Gorak and E. Sorensen and to be published by Elsevier..
- Seven papers on this topic were published in scientific journals – two in *Computers & chemical engineering*, one in *Industrial & Engineering*, and four in the *AIChE Journal*. For further details, see the references. Three additional papers are currently in preparation.
- Our crude distillation results have appeared in trade journals such as Chemical Processing, Hydrocarbon Processing, and Chemical Industry Digest.
- In relation to these results, the PI was interviewed by Lakeshore Public Radio about our findings.

- The technology was successfully demonstrated in industrial applications by industrial practitioners.
- A software titled "Distview" for visualization and screening of our results has been developed by the group and tested in select industrial applications by the practicing engineers.
- The first two papers published from this work, Giridhar and Agrawal in Computers in Chemical Engineering, were identified by the editor-in-chief to be among the most cited articles published in the Journal during the period 2010-2012. A certificate to this effect was given by the journal for each of the article.
- On the basis of the reviewers' enthusiastic comments, the article "New Multicomponent Distillation Configurations with Simultaneous Heat and Mass Integration" by Shenvi et al. was recognized as a fast track article by the editor of the AIChE Journal.

Conclusions

In this project, we sought to meet several long-standing demands in the field of process design. The *first* was the need for a quick and thorough method of enumerating the complete search space of distillation configurations. This was addressed via our mathematical step-by-step formulation which represents each of the thousands of configurations as a unique binary upper triangular matrix. When presented with a matrix, it is simple and user-friendly to draw the actual distillation sequence it corresponds to. Our step-by-step method was also designed to utilize thermally coupled links and enumerate all possible combinations thereof.

After enumerating all configurations that perform a separation, there was a *second* need to develop screening tools which allow evaluation of which ones are desirable. We have solved this problem on multiple fronts, using several objective functions by which the entire search space can be ranklisted: (i) minimizing total vapor generation requirement provides a simple, quick-to-solve objective function with ties to both capital and operating costs; (ii) thermodynamic efficiency minimization allows a detailed evaluation of operating costs including temperature levels; (iii) all of these objective functions were additionally replicated for systems with thermally coupled links.

A *third* important deliverable for this project was a robust, efficient algorithm for global optimization which guarantees the best possible solutions for configurations. By applying advanced techniques of nonlinear optimization and adopting the powerful and unique nonlinear program solver BARON, we have ensured that the solutions provided by our method are the best possible solutions given the objective function.

Finally, we have developed a user interface which allows visualization and screening of the results of our optimizations. Our method and the user interface have been applied to various real-life case studies and used in collaborations with industrial partners. This interface is a large step towards commercialization, as it is simple to use and can be utilized for any zeotropic liquid or gas separation without specific expertise in our methods. A number of included tools allow for screening of configurations based on operability, structural, or retrofit criteria.

Recommendations

To best move forward with this research, the following are some of the possibilities:

- Conduct laboratory or pilot scale experiments to verify the results produced by our modeling.
- Construct an interface between our Distview program and ASPEN Plus, with the capability to import our configurations directly into the process simulator for detailed analysis.

- Some work has been done in developing new configurations with multiple feeds to a single split. It has been shown that these configurations offer additional potential for energy savings – work has begun on derivations of equations to incorporate these configurations into our screening process.
- For successful commercialization, there is a need to implement more recent findings in the 'Distview' software to keep it up to date. Also, as it is used by the industrial practitioners, it will be required to input their findings/comments in the software.

References: Listing of papers, book chapter and presentations resulting from this research..

Papers published from this research

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