MODELLING AND SIMULATION

OF COMPLEX REFINERY

DISTILLATIONS

By

EDGARDO A. LOPEZ

Licenciado en Ingenieria Quimica
Universidad de Costa Rica
San Jose, Costa Rica
1981

Master of Science in Chemical Engineering
The University of Michigan
Ann Arbor, Michigan
1983

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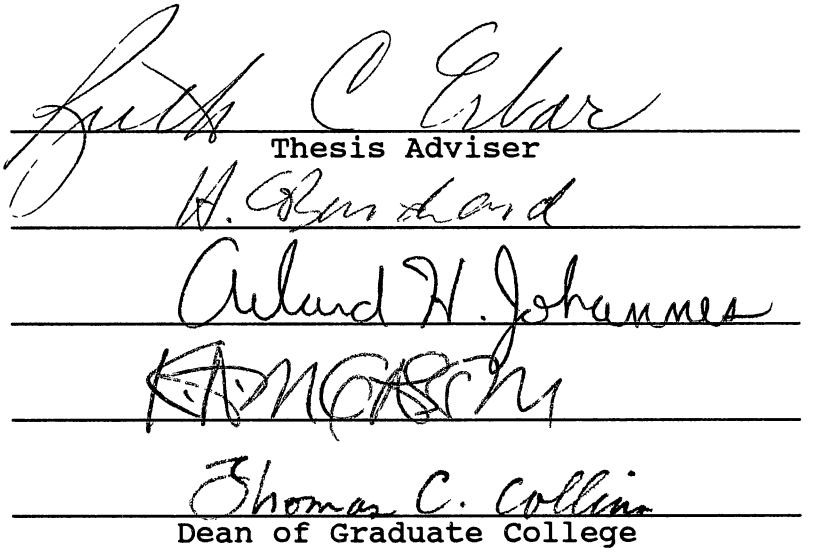

Thesis Adviser

Dean of Graduate College

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CHAPTER I

INTRODUCTION

A crude unit which separates a crude oil into various petroleum fractions, is one of the most complex units in the refining industry. They handle the most tonnage and consume the most energy of any industrial distillation. This situation has made the optimal design and operation of fractionation systems like these, an important priority in the oil industry.

Accurate models and computer simulations become very valuable tools for this purpose. Quite unfortunately, crude tower simulation is considered one of the most difficult ones.

The difficulty comes not from a single factor, but rather from a combination of elements that must be incorporated for a successful solution. These are:

a.- Thermodynamic modelling of crude oils. A crude oil is a complex mixture containing hundreds of components that must somehow be characterized so that relevant thermodynamic properties can be calculated.

b.- Complex system of towers and heat exchangers. A crude unit is an interlinked system of several towers and heat exchangers that must be modelled.

c.- Presence of water. Water is introduced to these towers in the form of stripping steam. It introduces non-idealities in the vapor and liquid phases which become an additional burden on the thermo-package. To make things worse, water may condense in some of the trays. The liquid-liquid equilibria that results is rarely solved. The location of the tray in which water drops is not known in advance, unless it is an existing unit.

d.- Flexibility of configuration and specifications: A useful simulator should provide the flexibility of changing easily the tower configuration and tower specifications, so that meaningful studies can be performed.

e.- High dimensionality: The simulation of a crude tower is among the biggest ones. The number of equations to be solved is in the hundreds. These equations are complex and highly non-linear. A robust and computationally efficient solution method becomes an important aspect of the problem.

f.- Friendliness: We have grown so accustomed to the friendliness of pc-software, that non-interactive programs are destined never to be used. Therefore, it is almost mandatory nowadays to provide a user interface to communicate with the user.

The purpose of this work was to develop an interactive simulator that successfully incorporate all the above ele-

ments in its design. Although developed with a crude tower in mind, it is flexible enough to simulate most of the separations encountered in an oil refinery: absorbers, reboiled-absorbers, distillation units and refluxed-absorbers.

Highlighting the simulator is the development of CRUDESIM, the user interface which integrates the four packages in the simulator, and FRAC, a new three phases solution algorithm that solves the whole crude unit as a full three phase problem. It detects by itself water condensation, and solves rigorously the L-L-V equilibria that results. A brief description follows.

CRUDESIM is a coherent system of about 70 screens and menus that provide access to the different programs, and organize the flow of information throughout the simulator. On line graphics capabilities are also provided, so that the user could easily check the results of his/her simulation. The four programs in the simulator are:

1.- VLE

Standard VLE calculations like flash, 3-phase phase, pure component vapor pressure, dew point, bubble point, etc, are available through this package. They can be used in the prediction mode, or the optimization mode. In this last option, EOS parameters are optimized to minimize an user defined objective function.

2.- THERMO

This is the thermo package for the simulator. It includes two EOS: the SRK (Soave,1972), and the PR (Peng,1976). It includes procedures to calculate K-values and enthalpies for all the components. Only the SRK can be used for crude oils, since no parameters for the PR are available in the open literature. Also included is a rigorous phase stability test based on tangent plane stability analysis (Michelsen,1982) to be used with the SRK for detecting water condensation.

3.- C6-PLUS

This is the oil characterization package. A crude oil or petroleum fraction can be characterized in any of four available ways: partial TBP distillation, ASTM distillation, Chromatographic distillation, or complete TBP, (Erbar and Maddox, 1983). Based on this information, the program generates all the necessary parameters to used the SRK EOS. It also generates the parameters to use the SRK to describe the water rich liquid phase if present.

4.- FRAC

This is the solution algorithm for the multicomponent fractionations. It belongs to the inside-out family of methods originally proposed by Boston (1970). In the inside loop, local models are used to calculate the thermodynamic properties. In the out-

side loop, convergence of the local models to the values predicted by the rigorous models is checked. The loops are repeated until convergence. The user defines if it want to use it in the three phase, or two phase mode. In the former mode, an stability test is introduced to test phase stability in the liquid phase. If a water rich phase appears, split calculations are introduced in both loops as described in full detail later.

Many strategies are used to solve the Material balance, Equilibrium relationships, Summation, and Heat balance equations (MESH equations) that describe a multi-component separation process. Chapter II presents a survey of the methods available in the open literature. Two and three phase applications are discussed simultaneously. A final section is presented on crude towers which reveals the very limited work published on this subject.

The concept of local models is introduced in Chapter III along with the modelling equations needed to use this concept. Of special interest are the different modifications needed to handle the second liquid phase, the pump-arounds, and the side strippers. This introduces the reader to the basic model and also provides the framework drawn upon in later chapters.

Chapter IV describes the solution algorithm in full, and the modifications implemented to handle the wide variety of problems that can be solved with our algorithm.

The thermodynamic package is described in Chapter V. Separated sections are presented on crude characterization, treatment of water-hydrocarbon mixtures with EOS, and stability analysis, in order to give the reader a complete picture of the scope of the models used. An important objective of this research was to provide rigorous methods for property generation. After all, even with the perfect tower algorithm, the results will not be better than the thermo-package used with it.

Next, a full description of the simulator is given in Chapter VI. Its structure and many of its option are presented in this section in some more detail.

A full validation of the simulator is presented in Chapter VII, where a wide variety of problems are solved and its results compared against published results. A summary of conclusions a recommendations is presented as a final chapter.

CHAPTER II

LITERATURE REVIEW

The "Science" of Distillation, as described by Seader (1989), dates back to 1893 when Sorel published his equilibrium stage model for simple, continuous, steady-state distillation.

Sorel's equations were too complicated for their time. It was until 1921 when they were first used in the form of a graphic solution technique for binary systems by Ponchon, and some time later by Savarit, who employed an enthalpy-concentration diagram. In 1925 a much simpler, but restricted graphic technique was developed by McCabe and Thiele. Since then, many solution methods have been proposed usually requiring the availability of computers.

The difficulties in solving Sorel's model for multicomponent systems have long been recognized. First, the size and the nature of the equation set. For instance, Seader (1989) mentions that with a 10 components and 30 equilibrium stages, the equations add to 690. Of these, 60% are non-linear, which makes it impossible to solve the equations directly. Secondly, the range of values covered by the variables. For example, the mole fraction of a very volatile component at the bottom of the column might be

very small, perhaps 10^{-50}, whereas the value of the total flow rate might be in the order of 10^{4}.

A final characteristic of Sorel's set of equations is its sparsity. That is, no one equation contains more than a small percentage of the variables. For example, for the case of 10 components and 30 stages, no equation contains even 7% of the variables. This sparsity is due to the fact that each stage is only directly connected to two adjacent stages, unless pump-arounds or interlinks are used as is the case of crude towers.

Over the years, a wide variety of computer methods have been developed to solve rigorously Sorel's model. This chapter provides a review of more recent developments in this area. The papers by Wang (1980), Boston (1980), and the book by Seader (1981), provide an excellent review of earlier works.

The different methods proposed, can be classified into five categories: Equation Decoupling, Simultaneous Correction, Relaxation, Reduced Order and Inside-Out or Local Model methods.

Equation Decoupling Methods

In these methods, the MESH equations are grouped either by stage or by type. These groups of equations are solved for a prescribed group of variables while holding the remaining variables constant. The iteration variables are updated by direct substitution or some other updating

algorithm. The procedure is repeated until all the equations are satisfied.

Stage by stage Procedures

The classical Lewis-Matheson (1932) and Thiele-Geddes (1933) methods are of this type. The MESH equations are grouped by stage and solved stage by stage from both ends of the column. These methods are prone to a buildup of truncation errors and are seldom used.

The development of the "theta method" by Holland and coworkers (1963) significantly improved the utility of stage by stage procedures. A detailed exposition of the method and its variations can be found in Holland (1981).

Decoupling by type

Amudson and Pontinen (1958) were the first to proposed a decoupling by type procedure for distillation calculations. But perhaps the best known example of this approach is the method by Wang and Henke (1966), also called Bubble Point method, BP. Here the main iteration variables are the stage temperatures and phase flow rates. The temperatures are calculated from the combined summation and equilibrium equations, and the flow rates are obtained from the combined enthalpy and total mass balances. Unfortunately, this pairing of variables is effective only for relatively narrow boiling systems. The method frequently fails for wide boiling systems. Further, the procedure involves a

lag of the K-value dependence from iteration to iteration, which makes the method unsuitable when the composition dependance is strong.

The sum of rates method, SR, by Sujata (1961), uses the same iteration variables, but reverses the pairing of equations and variables. The temperatures are obtained from the enthalpy balances, while the flow rates are calculated from the solution of the combined component mass balance and equilibrium equations. This method is effective for wide boiling systems, such as absorbers, but not for narrow boiling systems. Friday and Smith (1964) discussed the capabilities and limitations of the BP and SR methods.

Tomich (1970) presented a method in which the pairing issue is avoided by solving for the temperatures and flow rates simultaneously in each iteration. The corrections in the variables is determined by considering simultaneously the combined enthalpy and total mass balance, and the combined summation and phase equilibrium equations. The Jacobian of this system is initially calculated by finite differences approximations, and its inverse updated by the Quasi Newton method of Broyden (1965). However, there is still a composition lag like that of the Wang and Henke method which makes it unsuitable for highly non-ideal systems.

Simultaneous Correction Methods

In these methods, the MESH equations are linearized and solved simultaneously using a Newton-Raphson technique. The resulting system of linear equations is solved for a set of iteration variable corrections, which are then applied to obtain a new estimate. The procedure is repeated until the magnitudes of the corrections are sufficiently small.

The system Jacobian has a sparse structure. SC methods take advantage from the fact that the sparsity pattern is known a priori, to develop very efficient solution procedures. In most cases, the Jacobian has a block tridiagonal structure which can be exploited as first shown by Naphtali and Sandholm (1971). Hofeling and Seader (1978), Buzzi Ferraris (1981) and others have presented efficient sparse algorithms for cases in which the block tridiagonal structure has been destroyed due to interlinks and pumparounds.

Many variations of the Newton-Raphson appeared since the 1970's on this approach for single towers (Gentry, 1970; Roche, 1970; Gallum and Holland, 1976; Kubicek et al., 1976; Hess et al., 1977), as well as on interlinked towers. Wayburn and Seader (1984) give an excellent review of the work done on interlinked towers.

There are several advantages to the simultaneous correction method. The NR method results in quadratic convergence as the solution is approached. The method

accommodates non-standard specifications directly and it is not limited to certain kind of problems. On the negative side, this method has the highest computational load and requires the most storage space of any other method. It also fails to converge when the initial guesses are outside the domain of convergence, which can be quite small when the system is strongly nonlinear. A number of strategies have been proposed to increase the robustness of the overall iterative procedure. These include: damping of the Newton steps, the use of the steepest descent direction, relaxation and continuation.

The use of homotopy continuation methods to solve difficult distillation problems, has gained a lot of attention in recent years. Detailed discussions of the method are given by Wayburn and Seader (1984), Seydel and Hlavacek (1987), and Hlavacek and Rompay (1985), here is a basic description as presented by Swartz (1987).

The problem to be solved is used to defined a new problem continuous in a parameter. This homotopy is constructed to have a known or easily calculated solution at the initial value of the continuation parameter, and to coincide with the original problem when the parameter reaches its final value.

Consider the solution of the equation system $F(X) = 0$. A commonly used form for the transformed function is the convex linear homotopy

$$H(X,t) = t\,F(X) + (1 - t)\,G(X) \qquad (2.1)$$

with $t \in [0,1]$.

Typical choices for G(X) are X-X0 and F(X)-F(X0), giving the fixed point and Newton homotopies respectively. The solution of H(X,t) at t=0 for these homotopies is simply the initial vector X0.

A simple strategy for progressing along the continuation path is to subdivide the range of t into equal intervals and solve the homotopy system iteratively at each step, using as the initial guess the values obtained at the previous step. Bhargava and Hlavacek (1984) report success with this approach. An improved guess at each step may be obtained by applying an explicit Euler integration step to the homotopy equation differentiated with respect to the continuation parameter, Salgovic and Hlavacek (1981). The above approaches fail if the Jacobian becomes singular along the homotopy path. This problem can be avoided by differentiating then integrating with respect to the arc-lenght, Wayburn and Seader (1984).

The above types of homotopy methods have been successfully applied to distillation problems. A drawback of this approach however, is that the variables may take on meaningless values such as negative mole fractions along the homotopy path, resulting in possible failure of the thermodynamic subroutines. The paper by Wayburn and Seader (1984) describes the use of absolute values to deal with this problem. A possible deleterious effect of the

discontinuities induced by the absolute value function was not encountered in their examples.

Vickery and Taylor (1986) present a homotopy based on the system thermodynamics. Since it is the composition dependance of the K-values and enthalpies that cause most of the computational difficulties, these authors proposed a "thermodynamic homotopy" in which the problem was simplified to one involving a thermodynamically ideal mixture for which the model is a lot easier to converge. The composition dependance was then introduced in such a way as to make the difficult problem solvable. The variables in this case remain physically meaningful, and success with this approach is reported. Vickery et al. (1988) have also used stage efficiency as a continuation parameter.

Relaxation Methods

These methods solve the MESH equations in their unsteady state form, and consequently appear to have a large domain of convergence. The various methods differ in the simplifying assumptions made in the transient formulation and in the type of integration method use. Discussions of these methods are found in Wang and Wang (1981), and King (1980).

Ketchum (1979) proposed an algorithm combining the relaxation method and the NR method. The unsteady-state MESH equations are formulated in terms of the variables: x,L,V,T at time $t + \Delta t$, and the relaxation factor ϕ. Then,

the system is the solved by the NR method. This algorithm works as a relaxation method for small ϕ, and as NR for large ϕ. Ketchum applied the algorithm successfully to systems with pump-arounds and inter connected columns.

Relaxation methods are extremely stable, and converge to the solution for all type of problems. However, the rate of convergence is usually slower than the other methods, situation which have prevented its wide application.

Reduced Order Methods

As pointed out before, one of the main problems with mathematical models of staged separation systems is the large dimensionality of the process model. A recent development which particularly address this aspect, has been the concept of reduced models for separation processes.

The method was first presented by Wong and Luss (1980), and has been subsequently developed by two teams of researchers: that of Steward and coworkers (1985, 1986, 1987), and that of Joseph and coworkers (1983 a,b, 1984 a,b, 1985, 1987 a,b). Swartz (1987) presents an excellent review of all related methods to this approach. A short description of the method follows, the reader is referred to the original paper by Steward et al. (1985) for a more detailed description.

The basic idea is to approximate the tower variables by polynomials using $n \leq N$ interior grid points, s_j, along

with the entry points, s_0 for the liquid states and s_{n+1} for the vapor states. Any basis can be chosen for the approximating polynomials. However, the choice will affect the numerical properties and the convenience of the implementation.

Monomials $\{x^i\}$ are not well conditioned, particularly at high orders. The conditioning reflects the effect of perturbations of the coefficients on the function value. When small perturbations in the coefficients produce large changes in the function values, the representation is said to be poorly conditioned. Lagrange polynomials provide a better conditioned basis. This choice gives the following approximation for the tower variables:

$$\tilde{\underline{l}}(s) = \sum_{J=o}^{n} W_{lj}(s)\tilde{\underline{l}}\ (s_j) \qquad o \le s \le n \tag{2.2}$$

$$\tilde{\underline{v}}(s) = \sum_{j=1}^{n+1} W_{vj}(s)v(s_j) \qquad 1 \le s \le n+1 \tag{2.3}$$

$$\tilde{L}(s)\tilde{h}(s) = \sum_{j=0}^{n} W_{lj}(s)\tilde{L}(s_j)\tilde{h}(s_j) \qquad o \le s \le n \tag{2.4}$$

$$\tilde{V}(s)\tilde{H}(s) = \sum_{j=1}^{n} W_{nj}(s)\tilde{V}(s_j)\tilde{H}(s_j) \qquad 1 \le s \le n+1 \tag{2.5}$$

with

$$\tilde{L}(s) = \sum_{i=1}^{c} \tilde{l}_i(s) \tag{2.6}$$

$$\tilde{V}(s) = \sum_{i=1}^{c} \tilde{v}_i(s) \tag{2.7}$$

The W functions in the equations above are Lagrange polynomials given by:

$$W_{1j}(s) = \prod_{\substack{k=0 \\ k\neq j}}^{n} \frac{(s-s_k)}{(s_j-s_k)} \qquad j=0,\ldots,n \tag{2.9}$$

$$W_{nj}(s) = \prod_{\substack{k=0 \\ k\neq j}}^{n+1} \frac{(s-s_k)}{(s_j-s_k)} \qquad j=1,\ldots,n+1 \tag{2.10}$$

Substitution of the approximating functions into the MESH equations yields a corresponding set of residual functions, interpolable as continuous functions of s. The collocation equations are obtained by setting the interpolated residuals to zero at the interior grid points s_1, $s_2,\ldots\ldots,s_n$:

$$\tilde{\underline{l}}(s_j-1) + \tilde{v}\ (j+1) - \underline{l}(\tilde{s}_j) - \underline{v}(\tilde{s}_j) = 0 \tag{2.11}$$

$$\tilde{\underline{y}}(s_j) - \tilde{\underline{y}}(s_j+1) - \tilde{E}_{nv}\{y-\underline{y}(s_j+1)\} = 0 \tag{2.12}$$

for j=1,...,n, where :

$$\tilde{\underline{y}}(s) = \frac{\tilde{\underline{v}}(s)}{\tilde{V}(s)} \tag{2.13}$$

$$\tilde{\underline{x}}(s) = \frac{\tilde{\underline{l}}(s)}{\tilde{L}(s)} \tag{2.14}$$

and

$$\tilde{L}(s_j-1)\tilde{h}(s_j-1)+\tilde{V}(s_j+1)\tilde{H}(s_j+1)-\tilde{L}(s_j)\tilde{h}(s_j)-$$

$$\tilde{V}(s_j)\tilde{H}(s_j) = 0 \qquad j=1,\ldots,n \tag{2.15}$$

The placement of the collocation points determine the accuracy of the approximation. Villadsen and Michelsen (1978) showed that choosing the collocation points as zero of orthogonal polynomials leads to significant improvement in the accuracy of the solution. Cho and Joseph (1983) have used Jacobi polynomials for this purpose, whereas Steward et al. (1985) used Hahn polynomials. This last choice has the nice property that the reduced model converge to the full order model when the number of collocation points equals the number of trays. Srivastava and Joseph (1985) review this matter of selection of collocation points in further detail.

Once the collocation points are selected, the equations are solved by a suitable method to obtained the tower variables at the grid points. The full tower profile is then obtained by interpolation.

Inside-Out or Local Model Methods

In computer simulation, a considerable amount of time is spent evaluating thermodynamic properties and their derivatives. Local model methods are the first to recognize this fact to generate a very efficient family of methods.

The basic idea is to use simple approximate models for the thermodynamic properties, and to restructure the calculation procedure in terms of the simple models. A two level procedure result from this idea. In an outside loop, model parameters are calculated from rigorous models. On the inside loop, the separation problem is solved based on these approximate models. The sequence is repeated until convergence is reached. In theory, any of the previous methods could be used to converge the inner loop, even a simultaneous correction method.

Boston and Sullivan (1974) were the first to suggest a procedure like this. They called their approach Inside-Out technique, although the denomination Local Models will be used in this work. Boston selects the volatility and energy parameters as his successive approximation variables. These are the parameters of the approximate models which are updated on the outside loop. An important attribute of these variables is that they are very week functions of variables for which initial estimates may be very poor, such as temperatures, interstage phase rates, and liquid and vapor mole fractions. Successive approximations were obtained by solving the model equations, followed by updating the parameters from the rigorous models. The procedure converges very rapidly with exceptional stability.

Instead of using stage temperature, and liquid and vapor flows as independent variables for the inner loop,

Boston introduces the stripping factors. In this way, difficulties associate with interactions between these other variables are avoided.

The calculations are organized in the form of a very stable and efficient method of the Bubble Point type. Component Material balances are solved first. Temperatures are calculated from the bubble point equations. Next, interstage vapor and liquid rates are obtained from the specification equations and enthalpy balances. This allows calculation of the stripping factors which are checked against the assumed values for convergence. Broyden's quasi Newton method is used to determine new values for the next iteration. Since its introduction, Boston (1980) has extended the algorithm to handle absorption, reboiled absorption, highly non ideal mixtures, water-hydrocarbon systems and three phase systems, Boston and Shah (1979).

A major improvement in the method was introduced by Russell (1983). This author converges the inner loop variables using a quasi Newton approach to achieve all enthalpy balance and specifications directly. The K_b formula provides the stage temperatures, and the summation equations give the interstage flow rates. The errors in the variables result in enthalpy imbalances and specifications errors.

These errors mean that the initial Jacobian must be obtained numerically (first time only), and variables updated. Thereafter, the Broyden method is used to update

the Inverse. The outer loop is the same as that of the Boston-Sullivan method. The main advantage of this modification is the capability to work with many different type of specifications without introducing any additional difficulty.

This approach has been actively pursued for commercialization by software companies, and continuous to be expanded in its applications, see for example Morris et al. (1988). Venkataraman et al. (1990) gives details of an inside out method for reactive distillation using Aspen Plus. In this implementation, the Newton's method is used to converge all the inner loop variables simultaneously.

Multicomponent Three Phase Distillation

Three phase distillation has been a very active field of research during the past years. Table I taken from Cairns and Furzer (1990), presents a summary of the three phase applications found in the open literature. Most of the examples are limited to ternary systems. Only the most recent studies have investigated multicomponent systems with up to four and five components.

The first methods for three phase distillation were basically a series of three phase flashes. Since then, many of the strategies applied to homogeneous distillation have been tried with the three phase case. The major improvement in recent years has been the introduction of

TABLE I

SUMMARY OF THREE PHASE
DISTILLATION EXAMPLES

#	SYSTEM	REFERENCE
1	ethanol/water/ethyl acetate	Bril et al.(1975)
2	2-propanol/water/ benzene	Bril et al.(1975)
3	butanol/water/propanol	Block and Hegner(1976) Ross and Seider(1981) Swartz and Steward(1987)
4	butanol/water/ butyl acetate	Block and Hegner(1976)
5	butanol/water/ ethanol	Ross and Seider(1981) Schuil and Bool(1985) Ross (1979)
6	propylene/benzene/ n-hexane	Boston and Shah(1979)
7	acetone/chloroform/ water	Boston and Shah(1979)
8	butanol/water/butyl acetate	Boston and Shah(1979)
9	acrylonitrile/ acetonitrile/water	Buzzi and Morbidelli(1982 Swartz and Steward(1987)
10	acetonitrile/water/ trichloroethylene	Pratt (1942)
11	benzene/water/ethanol	Baden (1984)
12	propane/butane/ pentane/methanol/ hydrogen sulfide	Baden (1984)
13	water/acetona/ ehanol/butanol	Pucci et al.(1986)
14	ethanol/water/ cyclohexane	Baumgartner et al.(1985)
15	sec-butyl alcohol/ di-sec-butyl ether/ water/butylenes/ methyl ethyl ketone	Kovach and Seider(1987)

stability tests. They determine the number of liquid phases in a given tray and automatically incorporate this aspect of the problem in the solution algorithm. A short review of the available methods is given next.

Successive Flash Methods

These methods simulate the tower as a series of three phase flashes. The approach, although extremely stable, usually requires many iterations, and therefore large computing times, even when compare with simultaneous correction methods.

Ferraris and Morbidelli (1981) present a version of this method. They introduce different sequences in which the flashes could be solved, but recommend one in which each stage is considered as separated from the others. At each iteration, the value of all the variables are simultaneously changed. The authors use the method to verify the results of two other methods they proposed. These other methods require a previous knowledge of the stages with three phases, and therefore use the successive flash method as a sort of stability test. Other difficulty mentioned by Ferraris and Morbidelli is the strong attraction to the trivial root when solving the three phase flash. They solved this problem by restricting the value of the liquid mol fraction in each phase. This strategy however, assumes a previous knowledge of the range of the solution, which limits its use on a general purpose algorithm.

A more recent implementation of the method is given by Pucci et al. (1986). Their algorithm consists of carrying out a series of flashes first from the reboiler up to the overhead condenser, then from the top to the bottom of the column, and so on until convergence conditions are satisfied. For any stage j, the MESH equations describing that stage, are solved simultaneously by a Newton-Raphson method.

Their isenthalpic flash calculation acts as an stability test in the following way. First a two phase flash is done, Next, the isoactivity criterion is solved for the liquid. If a solution is found, the mixture is considered three phase, and a full three phase calculation done. If no LLE solution is found, the mixture is stable and the two phase results are used. The authors point out the strong attraction to the trivial solution, and proposed a technique based on infinite dilution activity coefficients to initialize the LLE calculations.

Equation Decoupling Methods

Block and Hegner (1976) presented a decoupling algorithm of the Bubble Point type. These authors use the overall liquid composition as iteration variables, breaking the equations in several groups. First the isoactivity condition is solved to give equilibrium compositions and L-L ratio. If no solution is found, the mixture is considered stable. Next, the bubble point equations are solved

for the temperature and the vapor fraction. Then, the energy balances and overall material balances are solved for V, L′ and L". Finally, Block and Hegner use the residuals of the component material balances to generate a Newton Raphson correction to update the iteration variables. The procedure is repeated until convergence.

Ferraris and Morbidelli (1981) also developed an algorithm of this type. They split their equations in three groups. The iteration variables are the overall liquid compositions. The first system of equations consist of the equilibrium equations, and it is solved for T, and the equilibrium compositions. The second system consist of the overall material balances and the energy balances. The structure is block tridiagonal, and therefore is easily solved. The last system consists of the component material balance, and it is solved by a method similar to that of Boston and Sullivan (1972). This approach needs a priori knowledge of phase separation. Therefore, it is used by these authors in conjunction with their successive flash approach.

Other algorithms belonging to this category have also been presented by Kinoshita et al. (1983) and Baumgartner et al. (1985). The basic problem with all these approaches is their inability to accommodate different set of specifications, and the weak treatment of the stability issue. The problems address by Friday and Smith (1964) also applied here.

Simultaneous Correction Methods

Ferraris and Morbidelli (1981) also developed a method of this type. Their algorithm solves all the equations simultaneously by the NR method. The resulting system has a block tridiagonal structure, similar to that for the two phase case, Naphtali and Sandholm (1971). The method requires a previous knowledge of the phase split; therefore, the authors used it with their multiflash method in order to arrive to a solution.

Niedzwieki et al. (1980) developed a technique for a modified K-value that accounts for the additional equilibrium expressions of a L-L-V system. The method has become known as the mixed K-value model. It avoids the addition of the extra equilibrium expressions to the MESH so that existing computer programs for the simulation of vapor-liquid columns can be used for three phase systems. Several researchers have used this technique in combination with the simultaneous correction approach to simulate three phase distillation.

Schuil and Bool (1985) extent the mixed K-value technique to make it applicable to system with distribution of all components over both liquid phases. The basic expressions are described next. For any component i, the equilibrium ratio is given by:

$$k_i = \frac{y_i}{x_i} \qquad (2.16)$$

When the component i is distributed over two liquids, the K-value is given by the following expression:

$$k_i = \frac{k_i' \, k_i''}{a k_i'' + (1-a) k_i'} \tag{2.17}$$

where

$$a = \frac{L'}{L' + L''} \tag{2.18}$$

where the equilibrium ratios between the vapor and the first and the second liquid phases are given by k_i' and k_i'', respectively. Equation (2.17) is the general equation for the mixed K-value model. This equation is used in those equations in which two liquid phases are formed. Any of the available stability test could be used to determine phase split.

Baden and Michelsen (1987) used a form of the mixed K-value model in combination with a simultaneous correction approach to simulate three phase separations. In their implementation, the general equations forming the framework of the standard Naphtali-Sandholm method remain unchanged. The only modifications needed are the calculation of liquid phase thermodynamic properties. A stability test is needed to decide whether or not to base the K value, and its derivatives, on the mixed or standard equilibrium ratio.

These authors used the test by Michelsen (1982 a,b) for this purpose.

Cairns and Furzer (1990 b) have recently presented a similar implementation. They used the mixed K-value model with a form of the Naphtali and Sandholm algorithm. This particular algorithm assumes constant molar overflow, and therefore only the MES equations are considered.

Recently, Kovach and Seader (1987) presented a homotophy-continuation method for three phase distillation. The method solves in full (no mixed K-values) all the equations describing the distillation, and can successfully get the multiple steady states that have been reported for some of these towers. The authors extended the homotopy of Allgower and Georg in order to follow very closely the homotopy path. This is very important in heterogeneous distillation because some of the solution are located very close to the limit points.

Kovach and Seader ordered the MESH equations in the same way as Wayburn and Seader (1984): first the component material balances, then the energy balances, and last the equilibrium equations. Furthermore, V_{ij} are the first variables, followed by T_i, l'_{ij} and l''_{ij} (when applicable). The model equations are solved simultaneously by the NR method to some given tolerance.

After the iteration variables are updated, by either the Euler predictor or Newton correction steps, the stream enthalpies are calculated, and the liquid phases are

checked for stability. If a stable phase is detected, the second-phase flow rate is added to the first and dropped from the iteration variable vector.

The stability test consist of a check against a polynomial fit of the binodal curve. This checking is bypass for large systems. When this checking is positive or bypass, the split is calculated with a two phase LLE homotopy method. The method seems to be very robust for solutions inside the binodal region. For the outside region however, the algorithm converges some times to a solution with negative flow rates instead of the trivial solution.

Reduced Order Methods

Swartz and Steward (1987 b) extent the reduced order approach to the case of multiphase distillation. These authors proposed the use of separate modules, or finite elements, to represent each multiphase region. The adjustable module lengths are treated as continuous variables with their sum constrained to be consistent with the physical dimensions of the column. These locations are calculated simultaneously with the other system variables, thus greatly facilitating the solution of such a system.

The conditions at the boundary are analogous to the bubble point condition. Based on this, the authors proposed equations for the linkage of the modules. The expanded equation set allows the introduction of additional variables: the second liquid compositions and the module

length. The solution procedure involves obtaining an initial distribution of breakpoints from a two phase solution. A stability test is applied to the liquid phase at the collocation points. The test of Boston and Shah (1979) was used for this purpose. Column sections containing phase discontinuities were then subdivided into modules. Guesses for the states at the new collocation points were obtained by interpolation. The complete system of model equations was solved by a damped Newton method.

Local Model Methods

Boston and Shah (1979) extended the inside-out technique of Boston and Sullivan (1974) to the case of multiphase distillation. As in homogeneous distillation, the variables are the parameters of the local models for the thermodynamic properties. An extra iteration loop is introduced however, for the ratio of the two liquid phases in each tray. A significant contribution of this algorithm was the development of a stability test to detect phase splitting in the tower. The test is based on a minimization of the Gibbs free energy, and a phase initialization base on what the authors call "maximum effective infinite dilution activity". More details are given in Chapter V.

Ross and Seider (1981) also presented a similar algorithm based on the local models of Boston and Sullivan (1974). However, these authors modify the structure of the

inner loop, and use the primitive variables (T, x_i, L and V) as iteration variables. By proceeding this way, they loose the great stability provided by using the stripping factors as variables. The authors also find necessary to provide damping in the overall liquid composition. Ross and Seider use the split algorithm of Gautam and Seider (1979). This approach differs from the Boston and Shah (1979) stability test, in that a different initialization is used, and the rand test is employed to minimize the Gibbs free energy. More details are given in chapter V.

Schuil and Bool (1985) have also presented an approach in which they combined the local model concept with the mixed K-value model explained in a previous section.

Crude Towers

Although petroleum distillation has been practiced for over a century, there has been very little published literature in the field. In fact, the first comprehensive book on design procedures did not appeared until 1973 with Watkins's book "Petroleum Refinery Distillation". This book is an excellent source on hand calculation procedures.

On the area of computer simulation, the situation is not any better. Amudson et al. (1959) were the first to model a distillation column with a side stripper using an algorithm of the Bubble Point type. The method involved a separate convergence of the main column assuming composi-

tions of the vapor return streams from the side strippers. After that, each side strippers was converged, and the revised vapor streams were used to converge the main column again.

Cechetti at al. (1963) presented the first full simulation of a crude unit. In this work, the main column and side strippers were solved simultaneously with the $\ominus$ method. There was a limited treatment of the water, since it was regarded to be present in the vapor phase alone, except for the condenser.

Hess et al. presented the multi $\ominus$ method for modelling of absorber-type pipestills since the $\ominus$ method had failed to converge for towers of this type. The method uses a NR procedure to solve the model equations in a way similar to that of Tomich (1970). Water was considered as distributed between the vapor and the liquid phases on all stages except for the condenser, where it was considered as an immiscible liquid. These authors run the same example of Cechetti to demonstrate their method. More details on this tower are given in Chapter VI. Disadvantages of this method are the need for good initial estimates in order to converge successfully, excessive time to invert the Jacobian with stages go beyond 30, and composition lag when calculating K-values.

Russel (1983) used his modification of the Boston and Sullivan method to simulate several crude towers including the tower of Cechetti. However, he provides no results or

information on the quality of the answer in his article. This author focuses more in describing the algorithm, although some comparisons of execution times are made. No details are given with regard to the handling of water.

Morris et al. (1988) describes the results of their implementation of the Russel algorithm in HYSIM, a process flowsheet simulator by Hyprotech Ltd. of Canada. These authors present the simulation results of three different crude units, and compare the results obtained by the Peng Robinson EOS with those of the Chao-Seader method, as obtained on another unspecified simulator. No information is provided however, on the tower specifications or the crude oil characterization needed in order to try to reproduce these results. No details are provided either with regard to the handling of water.

One of the main points made by these authors is with regard to the approach needed for PC implementations. They first tried with a modification of the Ishii and Otto (1973) simultaneous correction approach and concluded: " While this approach proved to be quite workable on a main frame and exhibited reasonable convergence properties, it simply requires too much memory and took too long to run on a PC ". They favor the Russell algorithm, a form of which is implemented on their flowsheet simulator.

Hsie (1989) presented a relaxation approach to the steady state simulation of crude towers, and illustrated its application by solving Cecchetti's example. Hsie

reduced the dimensionality and stiffness of the system by dividing the components in three types: separated lights, separated heavies, and distributed components.

This author noted that the less volatile components disappear very rapidly in the few stages above the feed tray. These heavy components having small K-values and liquid phase composition less than 10^{-20} are called "separated heavy components". The ODE's describing these components are eliminated for the upper stages of the column. However the author does not mention if this is done automatically by the program or has to be set up by the programer. This is an important point since it alters the structure of the Jacobian and solution procedures.

In this work, the equations are solved in groups as in the equation decoupling approach. Hsie found that the pairing of equations and variables corresponding to the Bubble Point method does not work unless the initial guess is very accurate. Therefore, he recommends the pairing corresponding to the Sum of Rates method. However, the author reports that the dynamic characteristics of the tower are better represented by the Bubble Point method after a correct steady state condition was determined from the SR version. Hsie tried to ODE solvers and found Gear's BDF integration method more efficient than the semi implicit Runge Kutta methods.

The advantages of this work are its stability and capability to do dynamic simulation. The disadvantages are

large execution times, inability to deal with different set of specifications, and apparently some previous knowledge of the solution in order to separate the components in the three categories introduced by the author, and therefore be able to used the separated component concept.

More recently, Lang et al. (1991) presented an equation decoupling method which combines the Bubble Point method, and the Sum of Rates method in a new way for the simulation of crude towers.

In this algorithm, the Wang and Henke (1966) method is used for the modelling the upper rectifying section (plates above the feed plate) of the main column. For simulating the lower stripping section of the main column and the side strippers, the Sum of Rates method of Burningham and Otto (1967) is suggested. Water may be regarded as being distributed between the vapor and the liquid phases or as a single phase light component (present only in the vapor). Liquid-Liquid equilibrium is never considered. The authors illustrate their method by comparing product compositions of the simulation against experimental results. The agreement is good. However, no comparisons of the temperature profile or the interphase flow rates is provided in the article. Not included either is the crude oil distillation or crude oil characterization.

This algorithm offers the advantages of the decoupling techniques, that is low memory requirements, but also its

disadvantages: lack of flexibility to accommodate more general specifications.

One of the specific purposes of this project is to provide a general purpose algorithm capable of handling these type of petroleum distillation. A rigorous treatment of the water with an EOS approach will be provided in order to solve for the concentrations of hydrocarbon in the water phase. An option to treat the crude unit as a full three phase problem is also targeted for development. This provides the algorithm with a capability to predict water drop out anywhere in the tower. This characteristic is not presently available in any crude tower model, and it is an important one when checking a final design. For this purpose rigorous stability tests based on EOS will be included in the thermo-package. The simulator is designed for small machines in the 386 range. Therefore, an important consideration will be to decrease the memory requirements while still providing the capacity to simulate towers with a great variety of specifications.

CHAPTER III

MATHEMATICAL MODEL

The full stagewise model considered in this study is first described. Then, a degrees of freedom analysis is developed. The concept of Local Models in process simulation is thereafter introduced. Finally, the model equations are expressed in terms of the specific local models used in this work.

The Steady-State Model

The following assumptions are normally made when modelling stagewise separations

(i) The vapor and liquid leaving a stage are well mixed.

(ii) Thermal equilibrium between the phases leaving each stage.

(iii) A definite relationship (not necessarily equilibrium) between the liquid and vapor compositions leaving each stage.

(iv) No vapor or liquid entrainment.

Under the above assumptions the steady-state operation of a column is described by four sets of equations. These are

the well known MESH equations. With the notation illustrated in Figure 1 the equations are:

Material balance equations:

$$v_{ij}\left(1+\frac{W_j}{V_j}\right) + l_{ij}\left(1+\frac{U_j}{L_j}\right) - l_{i,j+1} = f_{ij} \qquad (3.1)$$

Equilibrium or **E**fficiency relations:

$$v_{ij} = E_j\left(\frac{K_{ij}\, V_j}{L_j}\right) l_{ij} \qquad (3.2)$$

where E_j is the vaporization efficiency, Holland (1981). If $E_j = 1.0$ then equation (3.2) is reduced to the equilibrium relationship.

Summation equations:

$$L_j = \sum_{i=1}^{c} l_{ij} \qquad (3.3)$$

$$V_j = \sum_{i=1}^{c} v_{ij} \qquad (3.4)$$

Heat balances:

$$L_{j-1}\, h_{j-1} + H_{j+1} - (V_j + W_j)\, H_j - (L_j + U_j)\, h_j + F_j\, H_{fj} + Q_j = 0 \qquad (3.5)$$

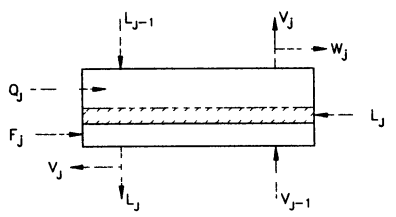


Figure 1: Schematic of a Single Stage

Degrees of Freedom Analysis

The degrees of freedom of a system represent the number of process variables that must be set in order to completely describe the system. A degrees of freedom analysis is a systematic way to determine these variables. There are different ways of doing it, the analysis below follows the procedure by Erbar (1983).

The degrees of freedom (N_S) are given by the following expression

$$N_S = N_V - N_r + N_t \tag{3.6}$$

where:

N_V = total number of variables in the process

N_r = the number of variables fixed by restraints on the process

N_t = number of recurring variables in the process.

Applying this procedure to a simple equilibrium stage similar to that of Figure 1, the degrees of freedom are determined to be $N_S = 2C+6$. The results of this simple stage could be combined to produce the value for a group of equilibrium stages like a simple absorber or a rectifying section. These bigger elements could subsequently be combined to provide the results for more complex units. Using this method for the distillation column shown in Figure 2, the following results are obtained:

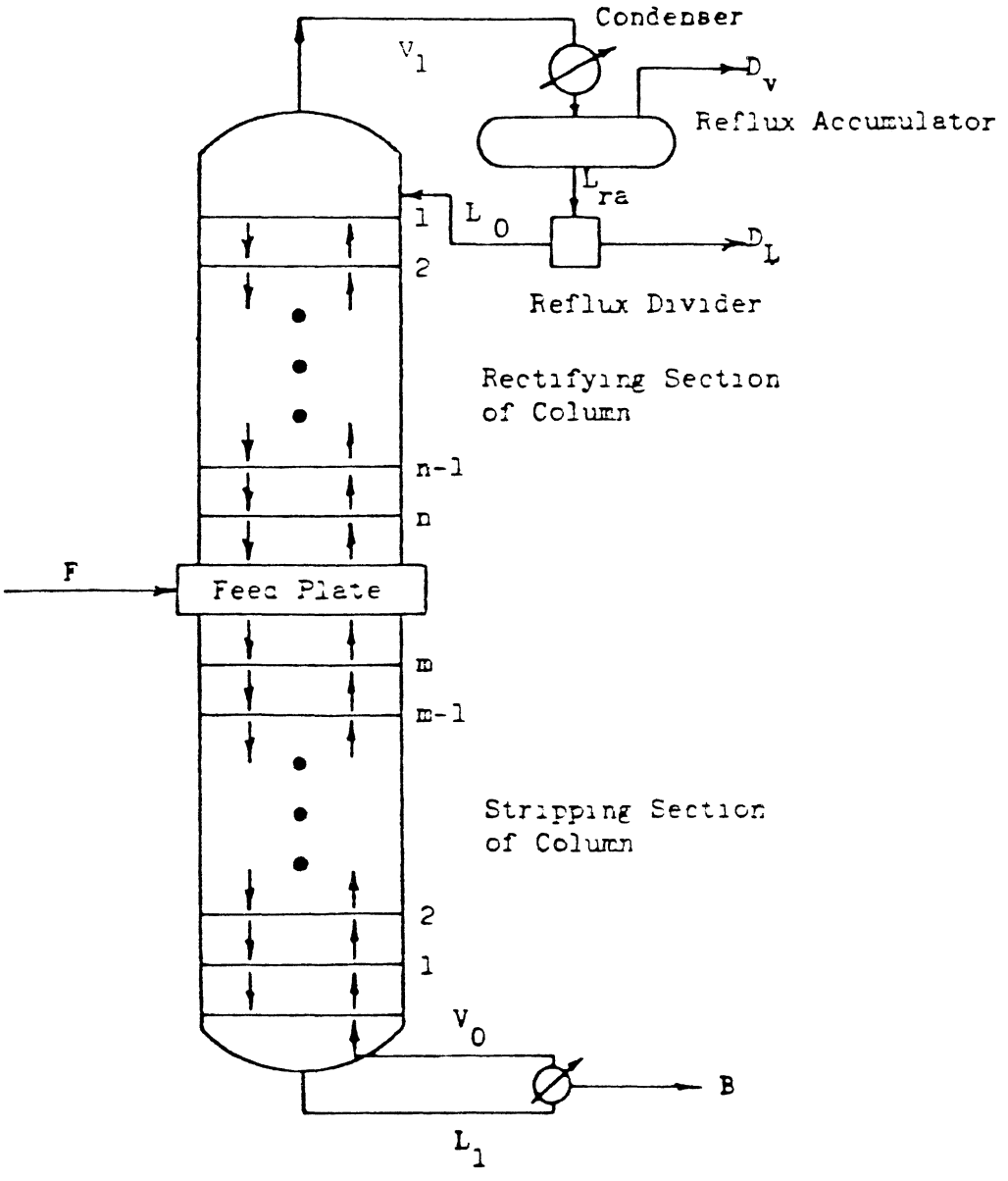


Figure 2: Schematic Diagram of a Simple Fractionator

Independent Variable	N_v
Rectifying section	2c+2n+5
Stripping section	2c+2m+5
Condenser	c+4
Feed plate	3c+8
Reflux divider	c+5
Reboiler	c+4
	10c+2(m+n)+31

the implied restrains are the number of variables in the interconnecting streams among the modules described above.

Restraint	N_r
Inter-connecting streams	9(c+2)
	9c + 18

Therefore, the degrees of freedom or design variables are

$$N_s = (10c + 2(m+n) + 31) - (9c + 18)$$

$$= c + 2(m+n) + 13$$

where m is the # of stages in the rectifying section and n is that in the stripping section. Normally, the variables shown in Table II are known, or can be easily calculated before running the simulation.

The remaining variables are the number of specifications that must be given to be able to solve the problem. In the case of the column of Figure 2, the number of necessary specifications is N_{sp} = {c+2(m+n)+13} - {3+2(m+n)+10} = 3 which could be chosen from the following list:

1. Total distillate flow rate
2. Ratio of vapor distillate to liquid distillate
3. Reflux ratio
4. Condenser heat duty
5. Reboiler heat duty
6. Recovery or mole fraction of one component bottoms
7. Recovery or mole fraction of one component in distillate

TABLE II

VARIABLES ALWAYS SPECIFIED FOR
A STAGEWISE SEPARATION

Type of Variables	Number of Variables
Component flow rates in feed, f_i	C
Feed pressure, P_{Fj}	1
Feed temperature, T_{Fj}	1
Stage pressure, P_j	m+n+3
Heat leaks, Q_j	m+n+1
Number of trays in rectifying and stripping sections	2
Pressure in reflux divider	1
Heat leak in divider	1
Total	c+2(m+n)+10

The interphase subprogram developed for our simulator automatically sets up the specifications for the user. Whenever extra equipment is added, like heat exchangers, side strippers, pump-arounds, etc., additional specifications are established. An option is also provided to substitute any of the basic specifications for any of 12 types of specifications available. More details of this feature are given in Chapter VI.

Each tower specification gives rise to an additional equation. For instance, if the vapor distillate rate is specified to be a value D, then the following equation is added

$$\sum_{i=1}^{c} v_{o1} - D = 0.0 \qquad (3.7)$$

The specification equations and the MESH equations form now an expanded equation set that must be solved by any of the methods given in Chapter II.

Local Models in Process Simulation

Each year more sophisticated thermodynamic models are introduced which can more accurately predict the thermophysical properties of process flows. At the same time however, they become computationally more expensive. Property evaluation is costly because models are implicit, complicated and highly nonlinear. Therefore, methods which are more efficient in their use of these models are needed. This is particularly important considering that 70-90% of

the time is spent on thermodynamic and physical property estimations, Hillestad et al. (1989).

The concept of Local Models in process simulation is introduced as a strategy to take advantage of this particular aspect. Several methods have been presented that use this concept for distillation simulation, for instance, Boston and Sullivan (1974), Russel (1983), etc. Nevertheless, these authors employed other framework to explain their ideas. The Local Model framework, however, offers the best one to present the distinctive characteristics of this family of methods. It was originally introduced by Chimowltz et al. (1984) as an approach to solve VLE calculations.

The Local Model approach involves the use of approximate models for representing the thermophysical properties of the components, and the restructuring of the calculation procedure in two levels or loops as indicated in Figure 3.

On the outside level or loop, the parameters of the local models are obtained from the rigorous values provided by the thermodynamic models. These parameters are either estimated or calculated initially, then updated, if necessary, at each solution of the simulation problem.

On the lower level or inside loop, the model equations are solved by any of the methods described in Chapter II, using the local models for property estimation. With this

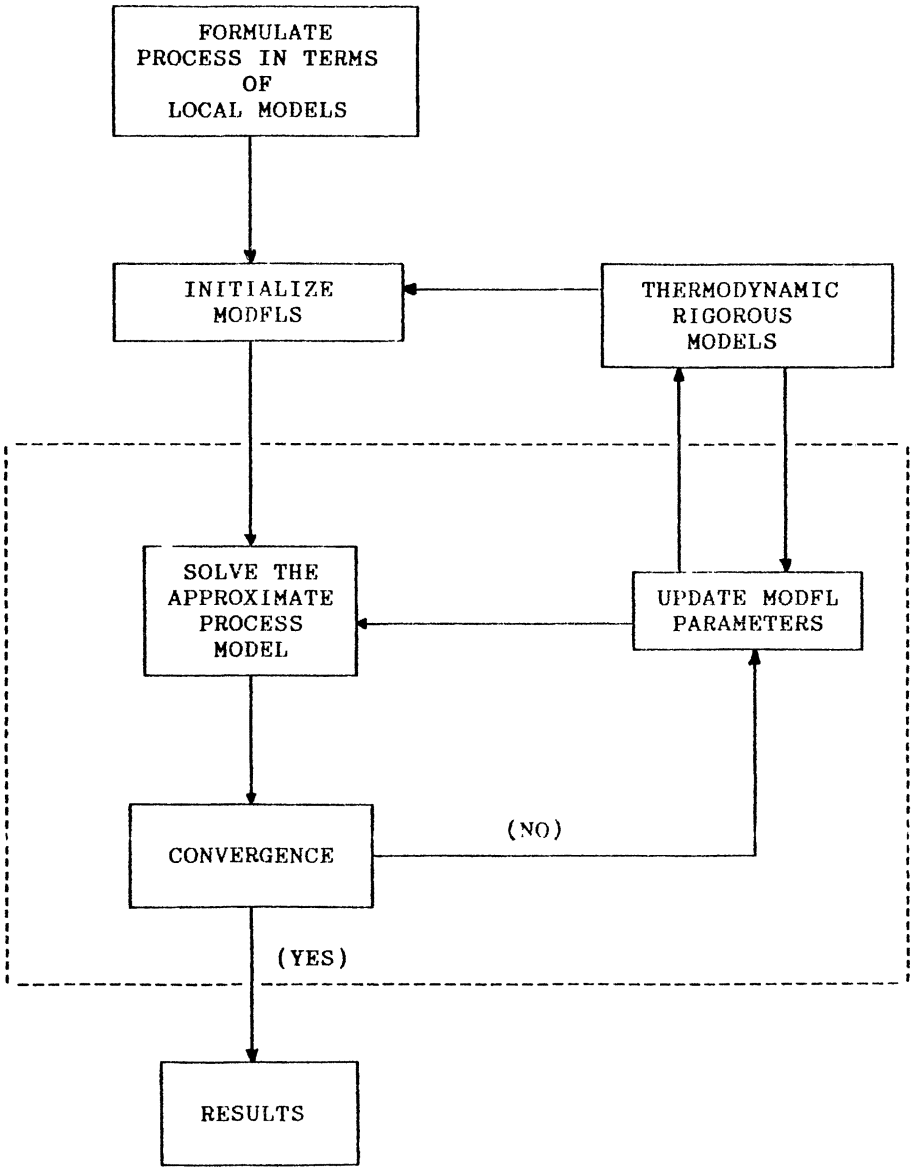


Figure 3: Local Model Approach

method, a sequence of problems is solved which has, in the limit, the same solution as the original one.

This approach possesses several important advantages. The total number of rigorous thermophysical property evaluations can be substantially reduced. The local models can easily be incorporated into the process model equations and their form is independent of the particular rigorous method used to obtain values for thermodynamic properties. It also provides very straight forward derivatives of various thermodynamic properties if the inner loop is solved with the Newton-Raphson method. The principal disadvantage of applying local models is that it requires more additional information to be stored, specially if sophisticated algorithms are used for updating the parameters.

The key to using this approach lies in the formulation of accurate yet simple local models to represent the thermodynamic properties. Chimowltz et al. (1983) and Boston (1980) provide reviews of the local models available for process simulation. It is essential that the local models have an explicit structure. The local approximation could be a polynomial or other arbitrary functions. However, local models based on physical considerations will be more efficient as they are valid over a much larger region before the parameters need to be revised. Major effects should be represented by an approximately correct mathematical structure, whereas minor effects are represented by

the adjustable parameters. It is also desirable to have as few parameters as possible.

In this work, local models are used for the k-values and the enthalpy departure functions. The local model for k-values is based on the popular k_b-model concept. Russell (1983) used a version of this model given by Boston and Britt (1978). However, this implementation will require more calls to the rigorous thermodynamic models when updating the parameters. Therefore the original models as described by Boston and Sullivan (1974) are preferred in this work.

The equilibrium ratio of component i on the stage j is given by the following expression

$$K_{i,j} = \alpha_{i,j}\ k_{bj} \tag{3.8}$$

where $\alpha_{i,j}$ is the relative volatility of component i on stage j. K_{bj} is temperature dependent and is given by the relationship

$$\text{Ln } K_{bj} = A_j - \frac{B_j}{T_j} \tag{3.9}$$

The coefficients of the K_b model are unique for each stage and are updated after each convergence of the inner loop. The coefficient B_j is determined from

$$B_j = -\sum_{i=1}^{c} y_{ij}\left(\frac{\partial \ln K_{i,j}}{\partial(1/T)}\right)_{x,y} \tag{3.10}$$

For scaling purposes, the value of A_j is initially evaluated by

$$A_j = \sum_{i=1}^{c} y_{ij} \ln(k_{i,j}) + \frac{B_j}{T_j} \tag{3.11}$$

However, at each successive update, its value is taken from

$$A_j = \ln K_{bj} + \frac{B_j}{T_j} \tag{3.12}$$

Local models for the enthalpy are also needed in order to solve the energy balances. The models given by Boston and Sullivan (1974) are more complex than needed. Russell (1983) suggested several models but did not say which one he used. Boston and Britt (1978) suggest another model that again is complicated. Therefore the model suggested by Boston (1980) is chosen in this work, since it is the simplest of all of them.

When Equation of State methods are used for enthalpies, they are calculated from the general equations

$$H_V = H_V^o - \Delta H_V \tag{3.13}$$

$$H_L = H_L^o - \Delta H_L \tag{3.14}$$

Where H_V and H_L are the vapor and liquid enthalpies per mol of mixture, and H_N^o and H_N^o are ideal gas enthalpies for the phases given from

$$H_V^o = \sum_{i=j}^{c} y_i \, h_i^o \tag{3.15}$$

$$H_L^o = \sum_{i=1}^{c} x_i \, h_i^o \tag{3.16}$$

The ideal gas enthalpies, h_i^o, are polynomial functions of temperature, so they are evaluated as needed using little computing time.

The departure functions are modelled as simple linear functions of the temperature in units of energy per mass base

$$\Delta H_V = C + D \, (T-T^*) \tag{3.17}$$

$$\Delta H_L = E + F \, (T-T^*) \tag{3.18}$$

where T* is a reference temperature, which in this work is taken to be the initial temperature profile. The parameter D and F represent mean residual heat capacities for the vapor and liquid mixtures, respectively, over the temperature range from T* to T. C represents the vapor enthalpy departure at T*, and E the liquid enthalpy departure at T*. Note again that the departure functions are modelled in terms of energy per unit mass rather than per mol.

Model Equations

In this section a summary of the modelling equations in terms of the local models is presented. A detailed derivation of the equations is included for reference in Appendix A. The notation of this appendix applies to all these equations.

Single Stage with Water Condensation

For all this section, the component material balance is given first, and then the energy balance

$$-l_{i,j-1} + \{RL_j + E_j \alpha_{ij} S_b S_{rj} Rv_j + \beta_j K_{ij}^D\} l_{ij} - \{E_{j+1} \alpha_{i,j+1} S_b S_{rj+1}\} l_{i,j+1} = f_{ij} \quad (3.19)$$

$$L_{j-1} h_{j-1} + V_{j+1} H_{j+1} - (V_j + W_j) H_j - (L_j + U_j) h_j + F_j HF_j + Q_j - L_j h_w = 0 \quad (3.20)$$

where:

$$L_j = \sum_{i=1}^{c} l_{ij} \quad (3.21)$$

$$V_j = \sum_{i=1}^{c} \{E_j \alpha_{ij} S_b S_{rj}\} l_{ij} \quad (3.22)$$

$$L_j'' = \sum_{i=1}^{c} \{\beta_j K_{ij}^D\} l_{ij} \quad (3.23)$$

$$W_j = V_j (RV_j - 1) \quad (3.24)$$

$$U_j = L_j (RL_j - 1) \quad (3.25)$$

$$H_j = \sum_{i=1}^{c} y_{ij}\, h_i^o - (C_j + D_j\,[T_j - T_j^*]) \qquad (3.26)$$

$$h_j = \sum_{i=1}^{c} y_{ij}\, h_i^o - (E_j + F_j\,[T_j - T_j^*]) \qquad (3.27)$$

Pump-Around

The presence of a pump-around affects two stages in the tower, the sending stage and the receiving stage. For the receiving stage:

$$-l_{i,j-1} + \{RL_j + E_j\,\alpha_{ij}\,S_b\,S_{rj}\,Rv_j + \beta_j K_{ij}^D\} l_{ij} - \{E_{j+1}\,\alpha_{i,j+1}\,S_b\,S_{rj+1}\}\, l_{i,j+1} - \left(\frac{G_s}{L_s}\right) l_{i,s} = f_{i,j} \qquad (3.28)$$

where the subindex s denotes sending sage.

$$L_{j-1}h_{j-1} + V_{j+1}\,H_{j+1} + F_j\,HF_j + G_s\,h_s - (V_j + W_j)H_j - (L_j + U_j)h_j - L_j''h_w + Q_p = 0 \qquad (3.29)$$

the heat exchanger if present, is installed in the receiving tray.

For the sending tray:

$$-l_{i,j-1} + \{RL_j + E_j\,\alpha_{ij}\,S_b\,S_{rj}\,RV_j + \beta_j\,K_{ij}^D + \frac{G_j}{L_j}\}l_{ij} - \{E_{j+1}\,\alpha_{i,j+1}\}l_{i,j+1} = f_{ij} \qquad (3.30)$$

$$L_{j-1}\,h_{j-1} + V_{j+1}\,H_{j+1} + F_j\,HF_j - (V_j + W_j)H_j - (L_j + U_j + G_j)h_j - L_j''h_w + Q_j = 0 \qquad (3.31)$$

Side-Strippers

The addition of a side stripper introduces more stages into the column which are described by the equations (3.19) and (3.20). However, three different stages must be modified to fully account for the presence of the side stripper: the sending tray in the main fractionator (SMF),, the receiving tray on the main tower (RMF), and the top tray of the side strippers (TSS). The reader is referred to Appendix A for the complete details and notation.

For the sending tray (SMF):

$$-l_{i,j-1} + \{RL_j + E_j \alpha_{ij} S_b S_{rj} RV_j + \beta_j K_{ij}^{D} + \frac{SS_j}{L_j}\}l_{ij} - \{E_{j+1} \alpha_{i,j+1} S_b S_{rj+1}\}l_{i,j+1} = f_{ij} \qquad (3.32)$$

$$L_{j-1}h_{j-1} + V_{j+1} H_{j+1} - (V_j + W_j)H_j - (L_j + U_j + SS_j)h_j + F_j HF_j + Q_j + L_j^{"}h_w = 0 \qquad (3.33)$$

For the top tray in the Side Stripper (TSS):

$$\{RL_j + E_j \alpha_{ij} S_b S_{rj} RV_j + \beta_j K_{ij}^{D}\}l_{ij} - \{E_{j+1} \alpha_{i,j+1} S_b S_{rj+1}\}l_{i,j+1} - \left(\frac{SS_{SMF}}{L_{SMF}}\right) l_{i,SMF} = f_{ij} \qquad (3.34)$$

$$SS_{SMF}\, h_{SMF} + V_{j+1} H_{j+1} - (V_j + W_j) H_j - (L_j + U_j)h_j + F_j HF_j + Q_j - L_j^{"}h_w = 0 \qquad (3.35)$$

For the receiving tray on the main fractionator (RMF):

$$-l_{i,j-1} + \{RL_j + E_j \alpha_{ij} S_b S_{rj} Rv_j + \beta_j K^D_{ij}\} l_{ij} - \{E_{j+1} \alpha_{i,j+1} S_b S_{rj+1}\} li,_{j+1} - \{E_{TSS} \alpha_{i,TSS} S_b S_{rTSS}\} l_{i,TSS} = f_{ij} \quad (3.36)$$

$$L_{j-1} h_{j-1} + V_{j+1} H_{j+1} + V_{TSS} H_{TSS} - (V_j + W_j) H_j - (L_j + U_j) h_j + F_j HF_j + Q_j - L''_j h_w = 0 \quad (3.37)$$

A final modification is made to the towers with side strippers. The last stage of the main fractionator, and the last stage of the side strippers have no vapor flow coming from the stage j+1, that is, $V_{j+1} = 0$. The stripping steam, if present, enters the tower as a feed at the respective stage, F_j.

CHAPTER IV

SOLUTION ALGORITHM

In this chapter, the algorithm formulated to implement the Local Model approach described previously is presented. The same algorithm is used to solve all type of towers: absorbers, reboiled absorbers, distillation and refluxed absorption towers. Enough "intelligence" has been programmed in the simulator to identify the particular tower type and to make the necessary adjustments.

Different tower types introduce differences concerning the inner loop variables, type and number of specifications, and type of scaling procedure to be used. this last aspect will be explained in more detail later in this Chapter. On the other hand, for the simulation of an homogeneous tower, the stability test and the split calculations are bypassed in both the inner and outer loop. The full algorithm is summarized in Figure 4.

The algorithm is designed to run with just a few estimates of flow rates and temperatures. An initialization procedure has been included that generates the initial profiles of composition, flow rates and temperature needed to start the calculations. With some minor differences,

1. Estimate $\bar{x}$, y, L, V, T.

2. Apply the Stability Test and make split calculations to obtain x', x", L', L", b.

3. Calculate parameter for local models.

4. Adjusted initial S-factors by scaling.

5. Solve the combined material and equilibrium equations.

6. Compute L', L", V, x, x" and y form the summation equations.

7. Given $\bar{L}$=L' + L" and $\bar{x}$, solve for the liquid-liquid equilibrium. Compute: b, x', x", L', L".

8. Update k_b-models and calculate Bubble Point Temperatures.

9. Compute stream enthalpies from Local Models.

10. Calculate errors in the heat balances and specification equations.

11. If the Jacobian is not available or need to be recalculated, then: Compute Jacobian numerically and invert it.

12. Predict changes to inner loop variables using current Jacobian Inverse and current errors.

13. Repeat inner loop calculations (steps 5 to 10). If the euclidean norm of the error vector is reduced continue. If not, reduce size of corrections and repeat inner loop calculations.

16. Update the Jacobian Inverse by Broyden's Method.

17. Repeat inner loop until convergence.

18. For the new profiles:
    - check for phase stability
    - revise split calculations
    - calculate new local model parameters.

19. Check for convergence:
    no → go to 4
    yes → continue.

20. Give tower results.

Figure 4: Proposed Algorithm

the procedure is basically the same as that of Boston and Sullivan (1974), and is included for reference in Appendix B.

Based on these initial profiles, the initial value of the local model parameters are evaluated as it is also explained in Appendix B. However, in the case of multi-phase distillation, a stability analysis is done on the liquid phase to determine if the second liquid phase is formed. The stability test of Michelsen (1986) is used for this purpose. The complete details of the stability analysis are given in Chapter V.

The inner loop calculations are described from steps 4 to 17. It begins with the solution of the combined component material balance and equilibrium or efficiency relationships. This equation set is normally tridiagonal in matrix form and can be solved with the Thomas algorithm. However, if side-strippers or pump-arounds are present, off diagonal elements are introduced to the matrix and sparse algorithms are needed to solve the system. The simulator is capable of recognizing this fact and switches from one equation solver to the other according to the tower configuration. The particular sparse equation solver used in this work is described in a later section in this Chapter.

After calculating the total flow rates from the summation equations, the vapor and liquid component mol fraction can be evaluated. For those trays in which two liquids are present, the liquid-liquid equilibrium is calculated to

obtain revised values for the liquid compositions in each of the liquid phase.

The LLE is solved in a form similar to the VLE flash. For a tray with a water side draw, the problem is reduced to solving the following expression:

$$f(\beta_j) = \sum_{j=1}^{c} \frac{(RL_j + \beta_j)\ (1-k_{ij}^{D})\ \bar{x}_{ij}}{(RL_j + \beta_j\ k_{ij}^{D})} = 0 \qquad (4.1)$$

where:

$$k_{ij}^{D} = \frac{k_{ij}'}{k_{ij}''} \qquad (4.2)$$

$$\beta_j = \frac{L_j''}{L_j'} \qquad (4.3)$$

A detail derivation of this expression is presented for reference in Appendix C. Equation (4.1) is solved for β_j by a Newton-Raphson method, and new values of x_{ij}', x_{ij}'', L_j'' and L_j' are computed for the respective tray. Note that k_{ij}^{D} are fixed to prevent oscillations during iterations of the inner loop as suggested by Ross (1979).

One of the important advantages of using the K_b-models is that they allow to calculate explicitly the stage temperature without any iterative calculation.

Given the new liquid compositions, the bubble point relation $\sum_i y_{ij} = \sum_i k_{ij}\, x_{ij} = 1.0$ may be rearranged to:

$$k_{bj} = \frac{1}{\sum_{i=1}^{c} \alpha_{ij}\, x_{ij}} \tag{4.4}$$

From the results of equation (4.4), the temperature can be calculated directly from the local model.

$$T_j = \frac{B_j}{A_j - \ln\,(k_{bj})} \tag{4.5}$$

Finally, the stream enthalpies are calculated from the local model and the errors in the energy balances and specification equations are evaluated. The convergence problem is to determine the set of Sr_j, RL_j, and RV_j so that the stage heat balances plus specification equations hold.

For this purpose the procedure by Russell (1983) is followed in this work. This author uses a damped quasi-Newton method with the well known Broyden's update. The corrections in the iteration variables are accepted only if they reduce the eucledean norm of the error vector as explained by Conte and De Boor (1980).

As the actual convergence variables, Russell uses the logarithms of the relative stripping factors for all stages plus the logarithms of V_j/L_j or W_j/V_j for each side stream product. This choice of iteration variables improves the

convergence and stability of the calculation algorithm and, therefore, were also adopted in this work.

When a pump-around is installed in the column, a new variable is needed. As can be seen from equation (3.28), this new variable is G_S/L_S or rather the logarithm of that value. Likewise, the installation of a side stripper introduces an extra variable in the iteration set, which in this case is the logarithm of SS_j/L_j as shown in equation (3.22).

The inner loop is considered to have converged when the average normalized errors in the enthalpy balances and specification equations is less than 0.05%. The enthalpy balances are normalized by dividing the equation by the sum of all input stream enthalpies. Similarly, the specifications are divided by a normalization factor which is usually the value of the specification. The convergence criteria is tighter than reported in the literature Jelinek (1988), but necessary in order to get accurate results.

Once the inner loop has converged, the parameters of the local models are updated based on the results of the rigorous thermodynamic models. Procedures similar to those used by Boston and Sullivan (1979) and Boston (1980) are used for this purpose.

When the algorithm is run as a multiphase tower, a stability test is applied to the overall liquid phase in the tray to determine if a water rich phase is present in that stage. In that case, a rigorous liquid-liquid equi-

librium calculation is done to determine the compositions in each phase. Equation (4.1) is used again in this task, but now the value of k_{ij}^{D} is updated at each iteration.

Since the stability calculations are time consuming, it is not applied to all the stages, but only to those trays with temperatures below 280 °F. There is no particular reason to choose this value other than it seems a safe value.

The problem is considered to have converged when the average relative error between the properties predicted by the rigorous models and those predicted by the local models is less than 0.05%.

The good convergence characteristics of this algorithm allow to satisfy this high criteria within a reasonable number of iterations.

Scaling of S-Factors

Poor estimates of interstage flows and temperatures and the resulting stripping factors, are the cause of initial maldistribution of components. In turn, this gives inaccurate bubble-point temperatures, and product compositions that are drastically different from specifications. It is not surprising that some methods fail to converge to composition specifications unless initial estimates are accurate.

To counter the effects of poor estimates, the scaling technique proposed by Boston and Sullivan (1979) is used in

this work. The stripping factors themselves are not the variables for the inner loop, but rather the relative stripping factors:

$$S_j = S_b \, Sr_j \tag{4.6}$$

where s_b is a scalar which value is adjusted to satisfy certain criteria that would otherwise be satisfied only by the final converged solution. The particular criteria depends on the type of tower. For distillation towers the criteria of Boston and Sullivan (1974) is used. For absorbers and reboiled-absorbers, that of Boston (1970) is employed. For refluxed-absorbers (crude towers) a new criteria has to be developed since none of the previous ones are satisfactory. The complete details are given in Appendix D.

Boston and Sullivan (1974) apply the scaling at each new iteration of the inner loop, while Russell (1983) does this, only in the first one. However, this last author gives no details of the scaling procedures he is using. In this work, it was found that the scaling procedures acts as an acceleration procedure decreasing the number of iterations needed to reach the answer. In particular, it decreases the number of times the Jacobian has to be evaluated introducing therefore a significant saving in computer time for some problems. Thus, the procedure is done at the beginning of each new iteration of the inner loop.

The net result is that very few estimates are needed to run the program. The S_b-scaling moves the material up or down the column so as to put the starting point of the convergence procedure in the vicinity of the solution.

Sparse Matrix Solver

The presence of side-strippers and pump-arounds in a separation column introduces off-band elements is the coefficient matrix of the component mass balances. The popular Thomas algorithm cannot be applied directly here, and a sparse matrix solver is needed to solve this problem.

Since the location of the off-band elements in known in advance, vary efficient methods can be developed to solve this kind of systems. Kubicek et al. (1976), Browne et al. (1977), Harclerde and Gentry (1972), Wayburn (1983), and Stadtherr and Malachowski (1982) have all presented alternative algorithms to handle this problem.

For simultaneous correction approaches, the methods of Stadtherr and Malachowski have the advantage of reducing significantly the storage requirements. This issue is not so important for decoupling techniques and most of the methods will work fine. Russell (1983) used the method by Hofeling and Seader (1978), however, the method by Kubicek et al. (1976) is preferred in this work because it is more structured and easier to set up. A short description of the method follows, the reader is referred to the original paper for more details.

The algorithm is based on the technique of modified matrices. For the linear equation

$$\bar{T}x = b \tag{4.7}$$

where $\bar{T} = T + R$, here T is a multidiagonal matrix n x n and R is a matrix of low rank. Let us define

$$R = R_1 R_2^T \tag{4.8}$$

where R_1, R_2 are n x m matrices. The matrix R_1 is composed of nonzero columns $j_1, j_2, \ldots, j_m$ of $T-\bar{T}$. The matrix R_2 is formed from the unit vectors $e_{j1}, e_{j2}, \ldots, e_{jm}$. The algorithm performs the following steps:

1. Given a matrix V(n x m) and a vector y satisfying:

$$TV = R_1 \tag{4.9}$$

$$Ty = b \tag{4.10}$$

A modified Thomas-Gauss algorithm is used to split T=LU, and V and y are calculating by back solving m + 1 times.

2. Form a matrix A(m x m)

$$A = I + R_2^T V \tag{4.11}$$

and a vector

$$w = R_2^T y \tag{4.12}$$

3. Solve

$$Az = w \text{ for } z \tag{4.13}$$

4. Finally, the solution to the original system is given by:

$$x = y - Vz \tag{4.14}$$

CHAPTER V

THERMODYNAMIC MODELS

This chapter provides a full description of the thermodynamic models which form part of this simulator. The first section deals with the equations of state included in the package and describes the component data base. The crude oil characterization procedures are described next. This is followed by a discussion on the treatment of water-hydrocarbon mixtures with equation of state. The remainder of the chapter focuses specifically on the phase stability analysis.

Equations of State

Thermodynamic prediction methods represent the heart of any process simulation. In fact, the simulation results will not be any better than the accuracy of the thermodynamic package used.

One of the strongest points of CRUDESIM, the simulator developed in this work, is the accuracy and robustness of the thermodynamic package. Equations of state methods have become the standard for predicting the properties of hydrocarbon mixtures. Two of the most popular EOS have

been programmed in our package: The Peng-Robinson (1978) and the Soave-Redlish-Kwong (Soave, 1972).

The necessary expressions to program these two equations are presented in Figures 5 and 6. The book by Maddox and Erbar (1982) provides an excellent review on the use of EOS methods for property predictions. The user is referred to this source for a description on the solution methods.

The reference state chosen for enthalpy calculations is the ideal gas state of the component at zero absolute temperature. The ideal gas state enthalpy constants are taken from the work by Passut and Danmer (1972). Liquid densities, when needed, can be calculated from the method proposed by Hankinson and Thompson (1979).

Binary interaction parameters are usually needed to provide an accurate representation of all thermodynamic properties with equations of state. These coefficients are provided only for the SRK, and therefore is the recommended method to use with the simulation of distillation problems. The PR can be used, however, the user is responsible for providing all the necessary coefficients. Alternatively, the user could use the VLE calculations in the optimization mode (as described in Chapter VI) to analyze binary systems and generate the binary coefficients. The values used with the SRK were calculated from the generalized correlations by Elliot and Daubert (1985).

The performance of the EOS models was validated by comparing the results of equilibrium calculation against

Standard form

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)} \quad (1)$$

Parameters

$$a = 0\ 42747R^2T_c^2/P_c, \quad (2)$$

$$b = 0\ 08664RT_c/P_c, \quad (3)$$

$$\alpha = [1 + (0\ 48508 + 1\ 55171\omega - 0\ 15613\omega^2)(1 - T_r^{0.5})]^2, \quad (4)$$

$$\alpha = 1\ 202\ \exp(-0\ 30288T_r)$$
for hydrogen (Graboski & Daubert 1979), (5)

$$A = a\alpha P/R^2T^2 = 0\ 42747\alpha P_r/T_r^2, \quad (6)$$

$$B = bP/RT = 0\ 08664P_r/T_r \quad (7)$$

Polynomial forms

$$V^3 - \frac{RT}{P}V^2 + \frac{1}{P}(a\alpha - bRT - Pb^2)V - \frac{a\alpha b}{P} = 0, \quad (8)$$

$$z^3 - z^2 + (A - B - B^2)z - AB = 0 \quad (9)$$

Partly reduced form (see Example 1 16)

$$P_r = \frac{3T_r}{V_r - 0\ 2599} - \frac{3\ 8473\alpha}{V_r(V_r + 0\ 2599)} \quad (10)$$

Mixtures

$$a\alpha = \Sigma\Sigma y_i y_j (a\alpha)_{ij} \quad (11)$$

$$b = \Sigma y_i b_i, \quad (12)$$

$$A = \Sigma\Sigma y_i y_j A_{ij}, \quad (13)$$

$$B = \Sigma y_i B_i \quad (14)$$

Cross-parameters

$$(a\alpha)_{ij} = (1 - k_{ij})\sqrt{(a\alpha)_i(a\alpha)_j}, \quad (15)$$

k_{ij} in Table 1 12, (16)

$k_{ij} = 0$ for hydrocarbon pairs and hydrogen. (17)

Fugacity coefficients are in Tables 3 3 and 3 4 Residual properties are in Table 11 3

$$\ln \hat{\phi}_i = \frac{b_i}{b}(z-1) - \ln\left[z\left(1 - \frac{b}{V}\right)\right] + \frac{a\alpha}{bRT}\left[\frac{b_i}{b} - \frac{2}{a\alpha}\sum_j y_j(a\alpha)_{ij}\right]\ln\left(1 + \frac{b}{V}\right)$$

$$= \frac{B_i}{B}(z-1) - \ln(z-B) + \frac{A}{B}\left[\frac{B_i}{B} - \frac{2}{a\alpha}\sum_j y_j(a\alpha)_{ij}\right]\ln\left(1 + \frac{B}{z}\right)$$

$$D_i = -T\frac{d(a\alpha)_i}{dT} = \left[m(a\alpha)\sqrt{T_r/\alpha}\right]_i,$$

$$D = \sum_i \sum_j y_i y_j m_j (1 - k_{ij})\sqrt{a_i\alpha_i}\sqrt{a_j T_{rj}},$$

$$\Delta\frac{H'}{RT} = 1 - z + \frac{1}{bRT}(a\alpha + D)\ln(1 + b/V),$$

$$= 1 - z + \frac{A}{B}\left(1 + \frac{D}{a\alpha}\right)\ln(1 + B/z),$$

Figure 5: SRK Equation of State

The Peng-Robinson Equation of State (Peng & Robinson 1976)

Standard form

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V^2 + 2bV - b^2} \tag{1}$$

Parameters

$$a = 0\ 45724 R^2 T_c^2 / P_c, \tag{2}$$

$$b = 0\ 07780 R T_c / P_c, \tag{3}$$

$$\alpha = [1 + (0\ 37464 + 1\ 54226\omega - 0\ 26992\omega^2)(1 - T_r^{0\ 5})]^2, \tag{4}$$

$$A = a\alpha P / R^2 T^2 = 0\ 45724 \alpha P_r / T_r^2, \tag{5}$$

$$B = bP/RT = 0\ 07780 P_r / T_r \tag{6}$$

Polynomial form

$$z^3 - (1-B) z^2 + (A - 3B^2 - 2B) z - (AB - B^2 - B^3) = 0 \tag{7}$$

Mixtures

$$a\alpha = \Sigma\Sigma y_i y_j (a\alpha)_{ij}, \tag{8}$$

$$b = \Sigma y_i b_i, \tag{9}$$

$$(a\alpha)_{ij} = (1 - k_{ij}) \sqrt{(a\alpha)_i (a\alpha)_j}, \tag{10}$$

$$A = \Sigma\Sigma y_i y_j A_{ij}, \tag{11}$$

$$B = \Sigma y_i B_i, \tag{12}$$

$$A_{ij} = (1 - k_{ij})(A_i A_j)^{0\ 5} \tag{13}$$

$$k_{ii} = 0 \tag{14}$$

$$\ln \hat{\phi}_i = \frac{B_i}{B}(z-1) - \ln(z-B) + \frac{A}{2\ 828B}\left[\frac{B_i}{B} - \frac{2}{a\alpha}\sum_j y_j (a\alpha)_{ij}\right] \ln\left[\frac{z + 2\ 414B}{z - 0\ 414B}\right]$$

$$\Delta \frac{H'}{RT} = 1 - z + \frac{A}{2\ 828B}\left(1 + \frac{D}{a\alpha}\right) \ln \frac{z + 2\ 414B}{z - 0\ 414B}$$

Figure 6: PR Equation of State

those of MAXIMIN, a process flowsheet simulator developed at Oklahoma State University. The details of this comparison are presented in Appendix E. As can be noticed, there is excellent agreement between the results from both programs.

A component data base or library of the 61 most frequently encountered components in hydrocarbon processing, is provided with the simulator. Table III list all the components included. The physical properties and coefficients needed to use these components with EOS methods form the component data base. Figure 7 presents a summary of the information needed for each component. Most of the data are taken from Edmister and Lee (1984).

Although information exists for only 61 components, the data base can be easily extended to accommodate any number of components, provided that there is enough memory in the computer for this purpose.

The properties needed to describe the crude oil pseudo- components are generated at execution time by means of correlations, and do not need to be included in the component data base. This is the subject of the next section in this chapter.

Crude Oil Characterization

The presence of petroleum fractions in refinery distillation makes the simulation of this system far more complex than the usual distillation with defined

TABLE III

COMPONENT LIBRARY

No.	Name	No.	Name
1.	hydrogen	32.	1-pentene
2.	Methane	33.	eis-2-pentene
3.	Ethane	34.	trans-2-pentene
4.	Propane	35.	2-mehtyl-1-1-butene
5.	N-Butane	36.	3-mehtyl-1-butene
6.	Iso-Butane	37.	2-methyl-2-butene
7.	N-Pentane	38.	1-hexene
8.	Iso-Pentane	39.	1-heptene
9.	2,2-Dimethyl propane	40.	propadiene
10.	N-Hexane	41.	1,2-butadiene
11.	2-Methylpentane	42.	1,3-butadiene
12.	3-Methylpentane	43.	cyclopentane
13.	2,2-Dimethylbutane	44.	methylcyclopentane
14.	2,3-Dimethylbutane	45.	Ethylcyclopentane
15.	N-Heptane	46.	Cyclohexane
16.	N-Octane	47.	Methylcyclohexane
17.	N-Nonane	48.	Ethylcyclohexane
18.	N-Decane	49.	Benzene
19.	N-Undecane	50.	Toluene
20.	N-Dodecane	51.	Ethylbenzene
21.	N-Tridecane	52.	O-Xylene
22.	N-Tetradecane	53.	M-Xylene
23.	N-Pentadecane	54.	P-Xylene
24.	N-hexadecane	55.	Nitrogen
25.	N-Heptededcane	56.	Oxygen
26.	Ethene	57.	Carbon Monoxide
27.	Propene	58.	Carbon Dioxide
28.	Isobutene	59.	Hydrogen Sulfide
29.	I-butene	60.	Sulfur Dioxide
30.	cis-2-butene	61.	Water
31.	trans-2-butene		

Name	Component Name
MW	Molecular Weight
SG	Specific Gravity
TC	Critical Temperature, degree F
PC	Critical Pressure, psia
W	Acentric factor
W_{SRK}	Acentric factor for H-T method
V*	Characteristic Volume, liter/mole for H-T method
δ_i	Solubility parameter, $(cal/ml)^{1/2}$
A, B, C, D, E, F, G	Ideal gas enthalpy coefficients
K_{ij}	Binary interaction coefficients for HC rich phase
(1) K_{wj} (2) K_{wj}	Binary interaction coefficients for the water rich phase
ID	Component identification number
TB	Normal boiling point, degree F

Figure 7: Component Data Base

components. Crude oils are complex mixtures of different hydrocarbons that must somehow be characterized in order to run the simulation. This is regarded as difficult due to the lack of experimental data and the need for representing the complex heavy fractions by means of a few model compounds or parameters.

There are different characterization methods available to predict the thermodynamic properties of these mixtures. Basically, all these methods cut the oil in a number of "pseudo-components" and estimate a given number of parameters for each one. The parameters are particular to each method, for instance:

- Cubic EOS (SRK, PR) require Tc, Pc, and W
- BWRS equation requires Tc, Pc, w and Vc
- Chao-seader (or Grayson-Streut) method requires Tc, Pc, w, δ_i, $\underline{V}$

EOS methods have become the standard for predicting the properties of hydrocarbons mixtures, usually including binary interaction parameters to increase the accuracy of the prediction. Petersen and Stenby (1991), Petersen et al. (1984, a, b; 1985), Erbar (1977) and Morris et al. (1988) have all proposed characterization procedures using cubic EOS. In this work the characterization method by Erbar is used. A general description of the method is presented next. The reader is referred to the original sources, Erbar (1977) and Maddox and Erbar (1982), for an evaluation of the accuracy of this procedure.

The method assumes some minimum information for each pseudo-component: average boiling point, specific gravity and molecular weight. If some of these data are not available, they could be estimated as explained in Chapter VI. With this information, the component is characterized as follows:

1. Estimate the PNA analysis of the fraction. This can be done by using a procedure similar to that of Hopke and Lin (1974).
2. Estimate the critical temperature of the PNA portions. Calculate the pseudo-critical temperature of the fraction using Kay's combining rule.
3. Estimate the critical pressure of the PNA portions and calculate the psuedo-critical pressure of the fraction like in step 2.
4. Estimate the Acentric factor. This can be done in two ways: from a correlation, like that of Kesler and Lee (1976), or better yet, from the equation of state by iterating on w until the equilibrium condition $f_i^L = f_i^L$ is satisfied at the normal boiling point.
5. Estimate the solubility parameter which is given by the following expression:

$$\delta_i = \left(\frac{H^V - RT}{V} \right)^{1/2} \qquad (5.1)$$

The heat of vaporization at the boiling point can be estimated from the following expression by Kistiakowsky:

$$\frac{H^{V}_{BPT}}{T_b} = 7.58 + 4.571 \log T_b \qquad (5.2)$$

This value can now be adjusted to obtain the value at 25 °C by the next expression:

$$H^{V}_{25} = H^{V}_{BPT} \left[\frac{T_c - 537}{T_c - T_b} \right]^{0.38}$$

6. Estimate the ideal gas enthalpy coefficients. The equations by Kesler and Lee (1976) are used in this work.

$$C_p^{*} = A + BT + CT^2 + CF\,(A' + B' + C'T^2) \qquad (5.4)$$

$$A = -0.32646 + 0.02678K$$

$$B = (1.3892 - 1.2122K + 0.03803K^2) * 10^{-4}$$

$$C = -1.5393 * 10^{-7}$$

$$A' = 0.084773 + 0.080809\ SG$$

$$B' = (2.1773 - 2.0826\ SG) * 10^{-4}$$

$$C' = -(0.78649 - 0.70423\ SG) * 10^{-7}$$

$$CF = \left[\left(\frac{12.8}{K} - 1\right) \times \left(\frac{10}{K} - 1\right) * 100\right]^2$$

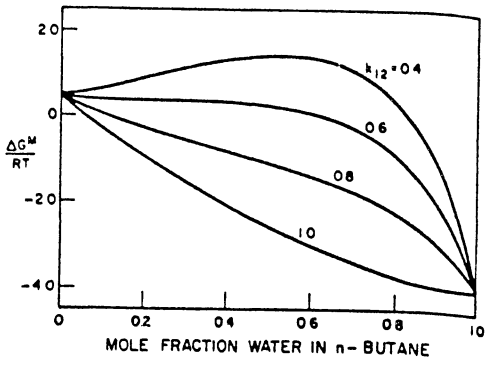
SG = Specific gravity

K = Watson characterization factor

Water-hydrocarbon Mixtures

Three-phase equilibria occur with some frequency in the production and processing of natural gas and petroleum, wherever considerable amounts of water are present. This has promoted a significant interest to extend the property prediction methods to describe this kind of systems.

Erbar (1973) was one of the first researchers to proposed a model for water-hydrocarbon mixtures. This author used a split approach with the Relich-Kwong EOS for the gas phase and the Scatchard-Hilderbrand activity coefficient for the liquid phase. Heidemann (1974) was the first to apply a pure EOS approach. He showed that the cubic EOS can predict liquid unstability by adjusting the binary interaction parameter. Figure 8 presents free energy of mixing curves for n-butane and water as obtained by Heidemann. If a line can be drawn tangent to the free energy of mixing curve at two points, any mixture of composition between the two points must, at equilibrium, separate in two phases which have the end point compositions. Figure 8 shows that it is possible to draw such a tangent line to each of the curves, except for k_{12}= 1.0. Note that the water rich phase is almost pure water. Heidemann also proved the impossibility of predicting both mutual solubilities adequately by adjusting a single value of the binary interaction parameters.



T=289 °F
P=100 psia

Figure 8: Standard Free Energy of Mixing for Water-N-Butane

Erbar et al. (1980) presented a generalized model for the treatment of water-hydrocarbon mixtures based on the SRK. By defining two binary interaction parameters, one for the HC-rich phase and other for the water-rich phase, the authors were able to predict the mutual solubilities with great accuracy. Furthermore, the binary interaction parameter for the water rich phase was made temperature dependent.

Many more authors follow on the same idea. For instance, Boston and Mathias (1980) mentioned the use on ASPEN of a version of the PR EOS with temperature dependant binary parameters. Robinson et al. (1985) presented two modifications to the PR EOS for the application to water-hydrocarbon mixtures: a new function for $\alpha(T)$, and a new temperature dependent interaction parameter for the aqueous

phase. Firoozabodi et al. (1988) applies the same idea to the Schmidt-Wenzel EOS, and Kabadi and Danner (1979) to the SRK and PR.

A serious limitation of all these works is the lack of a generalized model. Parameters are provided just for a few binary systems in which the approach was tested but nothing more. Therefore their approaches cannot be considered for a general purpose simulator.

Recognizing this limitation Kabadi and Danner (1988) presented a new approach that they were able to generalize. This work is the most comprehensive in the open literature, it covered 32 water hydrocarbon systems at 91 temperatures. The approach makes two modifications to the SRK. A new α-function is used for the water

$$\alpha^{1/2} = 1 + 0.6620\ (1-T_r^{0.8}) \tag{5.5}$$

And a new form of the a-parameter is employed for the pair water-hydrocarbon:

$$a_{wi} = a'_{wi} + a''_{wi}\, x_w \tag{5.6}$$

where:

$$a'_{wi} = 2(a_w\, a_i)^{1/2}\ (1 - k_{wi}) \tag{5.7}$$

$$a''_{wi} = G_i\ \left[1- \left(\frac{T}{T_{cw}} \right)^{c1}\right] \tag{5.8}$$

k_{wi} is a constant with different values for each homologous series, c_1 is a constant, and G_i is obtained from a group contribution technique.

This last approach seems to have an accuracy similar to that of the method by Erbar et al. (1980). However, it is limited to defined components and cannot be extended to pseudo-components.

The work by Erbar et al. (1980) has been chosen for the prediction of thermodynamic properties of water-hydrocarbon mixtures. The reader is referred to the original paper, or the book by Maddox and Erbar (1982) for a full evaluation of the method. A general description of the method is given in the rest of this section.

The basic modification done to the SRK was the introduction of two binary interaction coefficients: K^1_{ij} for the hydrocarbon rich phase, and K^2_{ij} for the water-rich phase.

The hydrocarbon phase parameter was usually set in the range between 0.4-0.6. The k^2_{ij}'s were found to be nearly linear functions of temperature.

$$K_{ij}{}^2 = a_o + a_1 \left(\frac{T}{1000} \right) \qquad (5.9)$$

The "standard" hydrocarbon k^1_{ij}'s are assumed to be applicable to the water phase when the binary pair does not contain water. For systems for which k^2_{ij} is not available, a four step procedure is followed:

1. Estimate the PNA analysis of the component (if it is a defined component, use the classical organic chemistry definition).

2. Estimate the slope of the k^2_{ij} equation from

$$a_1 = x_p\, a_{1p} + x_N\, a_{yN} + x_A\, a_{1A} \qquad (5.10)$$

where a_{1p}, a_{1N} and a_{1A} are constants.

3. Estimate k^2_{ij} at 100°F for the component from

$$k^2_{ij}\,(100) = b_o + b_1 \ln\left(\frac{V_i(\delta_i - 22.3)^2}{618}\right) \qquad (5.11)$$

where V_i and δ_i are the specific volume and the solubility parameters respectively. The constants b_o and b_i have different values for the paraffinic, naphtene or aromatic components. If the component is a C_{6+} fraction, k^2_{ij} is given as a molar average.

$$k^2_{ij}(100) = X_p\, k^2_p + x_N\, k^2_N + x_A\, k^2_A \qquad (5.12)$$

4. Finally, the intercept of the equation for k^2_{ij}, is obtained from

$$a_o = k^2_{ij}(100) - a_1\,(0.55967) \qquad (5.13)$$

If the value of k^2_{ij} exceeds the value for k^1_{ij}, k^2_{ij} is reset to a value equal to k^1_{ij}.

Phase Stability Analysis

Liquid-liquid flash or phase splitting are necessary calculations during the simulation of three-phase distillation towers. However, the calculations are complicated by the fact that there are multiple solutions to the equation set describing this problem.

Adding to the problem is the existence of a trivial solution. It is possible for the equilibrium calculation to fail and converge to the so called "trivial solution", with both phases having the same composition and density. When this happens, the sizes of the phases are indefinite, and the phase fractions can take any value. In practice, it is found that the domain of convergence to the trivial solution is large. Whether this solution or the correct solution is found, depends on the computational procedure and phase split initialization.

Cairns and Furzer (1991, a) and Swank and Mullins (1986) present extensive reviews on this subject. Some of the mathematical properties of phase equilibrium models are investigated by Burchard et al. (1980).

There are basically three approaches to solve the multiphase flash problem. The conventional approach is to solve the equation set describing the problem directly from an initial estimate of the phase split. If a trivial solution is found from this or a series of starting points, the mixture is considered to be homogeneous. A second approach consists of formulating the equilibrium

calculation as a Gibbs energy minimization problem, (Gautam and Seader, 1979).

Both approaches can fail if the initial estimate of the interation variables is not too accurate, and both may require a substantial amount of computation only to arrive to the trivial solution.

The third approach is currently recognized as the best one. It involves performing a stability test to decide whether or not the mixture is capable of existing as two liquid phases before attempting to solve the phase split equations. Methods like this have been proposed by Boston and Shah (1979), and Michelsen (1982 a,b).

In the method by Boston and Shah, the initial liquid phase is split on two trial phases by an initialization algorithm. This procedure is based on the concept of the "maximum effective infinite dilusion activity." Then the Gibbs energy of the split system is calculated and compared to the original homogeneous mixture free energy. If after 10 iterations of their algorithm the free energy of the system was not reduced, the mixture was considered stable. It is conceivable however, that an erroneous result could be obtained with this method, by the two phase region being "missed."

The method by Michelsen (1982 a,b) is arguably the best one. It is theoretically sounder, its solution simultaneously generates very good initial conditions for the phase split calculations, and it detects the metastable

regions as unstable. The reader is referred to the original papers for all the details, here a short description of the method is given.

The stability of a mixture requires that its Gibbs energy be at the global minimum. Given a mixture of composition z_i and chemical potential μ_i^o, then stability requires that for any other trial phase with composition y_i and chemical potential $\mu_i(y)$, the following criteria be satisfied.

$$F(y) = \sum_{i=1}^{nc} y_i \quad [\mu_i(y) - \mu_i^o] \geq 0 \qquad (5.12)$$

The geometrical significance of (5.12) is that F(y) represents the vertical distance from the tangent hyperplane to the molar Gibbs energy surface at composition z, to the energy surface at the test phase composition y. This is illustrated in Figure 9 for a binary mixture. Stability requires that the tangent hyperplane at no point lies above the energy surface.

Michelsen argues that stability can be checked by evaluating the left-hand side of expression (5.12) at the stationary points only, that is, where the derivatives with respect to all independent variables equal zero.

For equation of state calculation, it is more convenient to work in terms of fugacity coefficients. Then,

$$g(y) = \frac{F(y)}{RT_o} = \sum_i y_i \ (\ln y_i + \ln \phi_i - h_i) \geq 0 \qquad (5.13)$$

where: $\phi_i = \phi_i(y)$ and $h_i = \ln z_i + \ln \phi_i(z)$

Michelsen shows that finding the stationary points of (5.13) reduces to solving

$$\ln y_i + \ln \phi_i - h_i = k \quad (i=1,2, \ldots, M) \qquad (5.14)$$

Furthermore, at the stationary points of g(y), the tangent hyperplane to the energy surface is parallel to the hyperplane at z, with k representing the vertical distance between the two planes. This is illustrated in Figure 10. The original mixture is stable provided that k in non-negative at all stationary points. At the trivial solution (z), k will be equal to zero as shown in Figure 10. Clearly, the mixture in this figure is unstable.

Introducing new variables $Y_i = y_i \exp(-k)$, equation (5.14) becomes

$$\ln Y_i + \ln \phi_i - h_i = k \quad (i=1,2,\ldots, m) \qquad (5.15)$$

The new independent variables Y_i can be interpreted as mole numbers, the corresponding mole fractions being $y_i = Y_i/\sum_i Y_i$.

In summary, the method reduces to finding the solutions of equation (5.15). The mixture is stable if at all stationary points $k \geq 0$, which corresponds to $\sum_i Y_i \leq 1$.

That is

a) if at all solutions $\sum_i Y_i \leq 1. \Rightarrow$ stable

b) if at some of the solutions $\sum_i Y_i > 1 \Rightarrow$ unstable

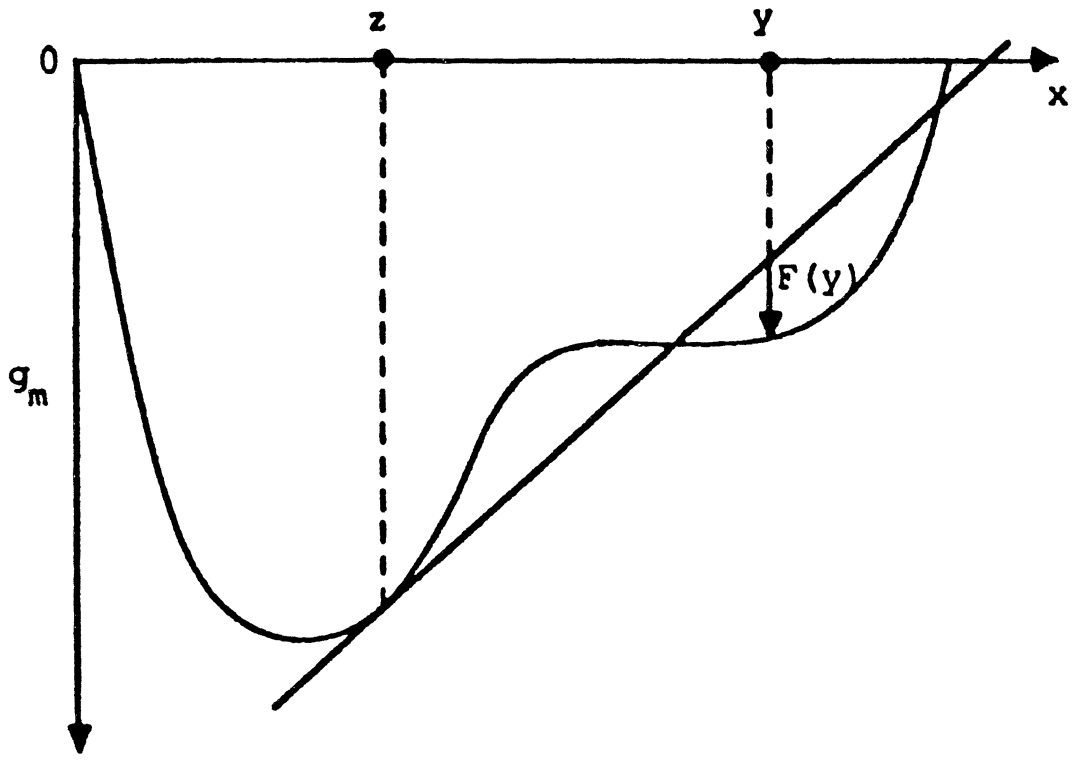


Figure 9: Tangent Plane Stability Analysis

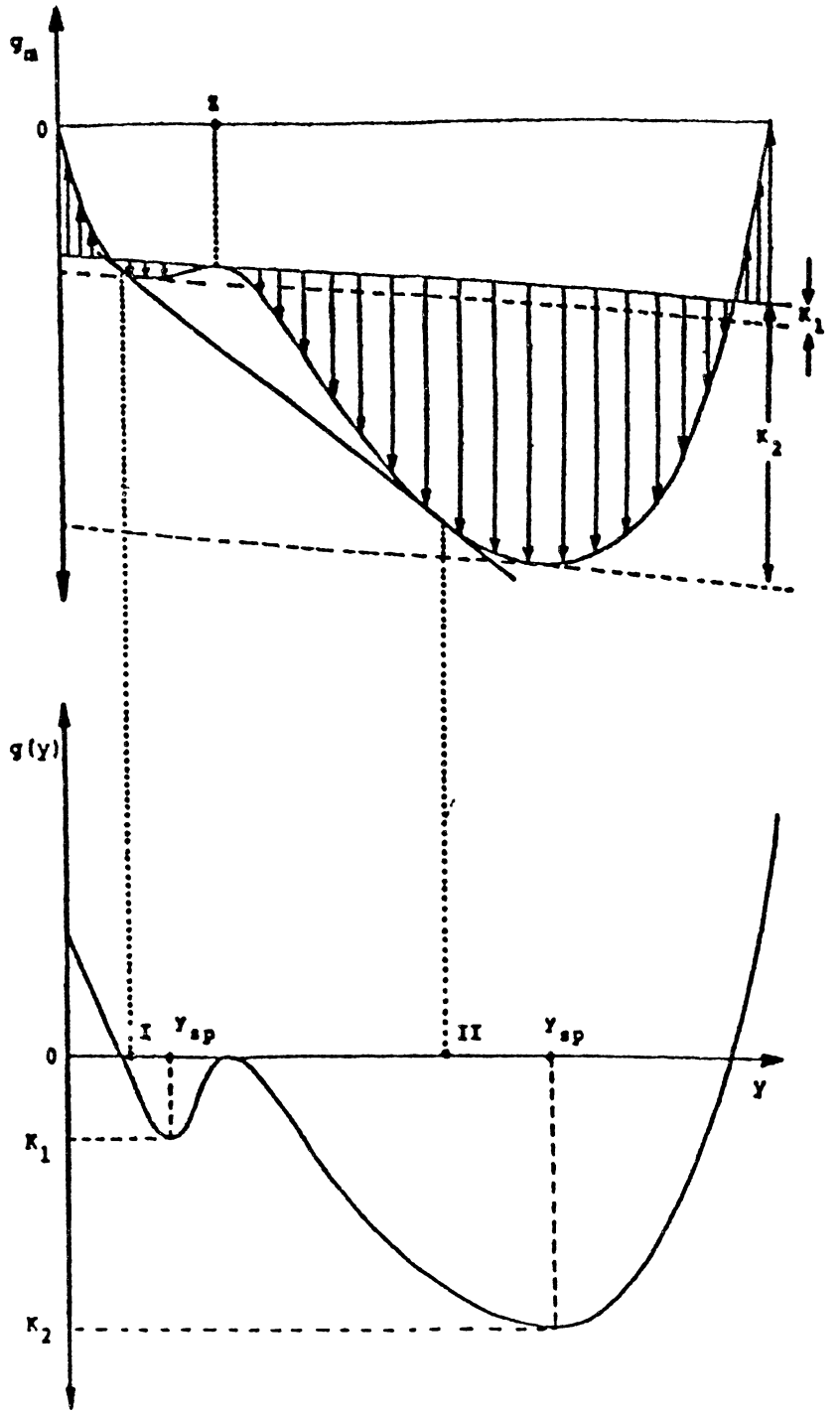


Figure 10: Tangent Plane Stationary Point Method

If the mixture is unstable, the stationary points are excellent estimates of the phase split. This can be seen in Figure 10, where the stationary points (y_{sp}) are close to the final split compositions I and II.

Michelsen (1982 a,b) examined a variety of numerical techniques for implementing this method. The direct substitution method is chosen for this work:

$$\ln Y_i^{(k+1)} = h_i - \ln \phi_i^{(k)} \qquad (5.16)$$

Michelsen noted that this scheme works well for systems in which the k-values are weak function of composition. For systems in which this is not true or exhibit a narrow immiscibility region, acceleration methods like the General Dominant Eigenvalue Method using one or two terms are recommended.

Michelsen converged (5.16) by starting with as many initial estimates as there are components in the system. Each initial guess for the trial phase is taken to be a pure component. A different approach is followed in this work, only two initial guesses are generated. The first consists of pure water, and the second trial phase consists of all the rest of the hydrocarbons in the system. Numerical experience with this method showed that is reliable for both stable and unstable mixtures.

CHAPTER VI

CRUDESIM: AN INTERACTIVE SIMULATOR FOR REFINERY DISTILLATIONS

In addition to the theoretical or engineering aspects of a simulation package, there is still an important issue to be covered, that of the user interaction.

A simulation program is a tool for engineering work, and unless it is convenient to use, no one will ever do anything with it. This is especially true nowadays where computer users have grown so accustomed to the friendliness of PC-software.

PC-based simulators therefore, require a user interface in line with the interactive nature of the machine. Possible choices include fill-in forms, menus, command driven systems, and conversational systems. Each one has its own merits, but a combination of menus and fill-in forms have been chosen for this work. The net result was CRUDESIM, a system of about 70 screens and menus that provide the desired degree of interaction with the user. Upon completion of the simulation, the user interface can also be used to examine the results. For instance, the user could write tables to the screen, display plots with profiles or print files to save the results for later use.

CRUDESIM is more than a distillation program. It provides the user with much more power and capabilities than the simple distillation program. To give a better idea, the rest of chapter presents a short description of the simulator options. This should also serve as reference material to CRUDESIM users.

The user starts the simulation by setting up the simulation options. General options like type of EOS, type of units, two-phase or three-phase distillation are set up in this screen. A short description of the input expected is given in the bottom line of the screen for each input field.

Next, the components to be included in the simulation are selected. A component is selected by typing its identification number in the proper field. If the user is not sure of the ID, he could invoke the component library and scroll on the list until he finds the desired component. The basic simulation input is finished by defining the feed. Up to 10 feeds or 50 equilibrium data points can be given to the program.

Once this step is done, the program has set up the basic simulation data base, which contains all the information for the components in the simulation. Options to save or retrieve different simulation cases are provided at this level. If a given component is identified by a number between 62 and 100, the simulator automatically recognizes this component as a crude oil and invokes the Crude Oil

Characterization module. Four characterization procedures are provided:

1. Complete TBP Analysis
2. Partial TBP Analysis
3. ASTM (D158 or equivalent) Analysis
4. Chromatographic Analysis

A complete TBP analysis provides the normal boiling point, specific gravity and molecular weight for each fraction in the characterization. This is all the information needed for apply the methods of Chapter V. The MW is optional, if not provided, it is estimated by a correlation.

The other three options consist of empirical procedures to generate the data of the complete TBP analysis from the respective starting information. The reader is referred to Chapter V of the book by Maddox and Erbar (1982) for a detailed description of these procedures.

The user is encouraged to provide as much information as is available for the respective crude oil. For instance, if bulk properties are known, then an adjustment procedure can be included so that bulk properties can be reproduced from the resulting characterization. This procedure is transparent to the user, since the program is "intelligent" enough to decide what to do. The characterization results are presented to the user in two forms: tables and plots. Any changes confirmed in the tables are included in the characterization at this time.

Options are provided to save and retrieve crude oil characterizations. This allows for the creation of crude oil libraries to use with simulation studies.

Two options are provided to leave the characterization module: In the first one the simulation data base is expanded to include all the information for the defined pseudo-components. In the second one, the C6-plus program is abandoned without any change. This last option allows access to the characterization routine without altering current simulation parameters.

Compositions of pseudo-components in the feed are automatically calculated by the program. The simulator also allows the user to input a light ends analysis in which case the composition of the whole stream is calculated by the simulator. This option is very convenient when simulating crude oil towers, since the light ends analysis is usually a standard part of the crude assay.

Upon return to the program, there are two calculation options available to the user: VLE calculations and Fractionation simulations. The following VLE calculations have been included in the program:

- Flash (fixed P and T)
- Pure Component Vapor Pressure
- Bubble Point P., and Bubble Point T
- Dew Point T., and Dew Point P
- Three-Phase Flash

Three operation modes are available: Simulation, Performance and Optimization. In the simulation mode the selected VLE calculation is done on the Feed. The other two modes are available only for binary systems. In the performance mode, the results of any of the VLE calculations are compared against the experimental data provided by the user. A whole series of statistics is calculated to give an idea of the model performance. A sample of the output is provided for reference in Appendix F.

In the optimization mode, the binary interaction parameters are optimized by a non-linear regression subroutine based on a Marquat procedure, Gasem (1986). The objective function is taken as the sum of the squared normalized errors. However, the user can choose which variables to include and how much weight to give to each one. More details on this data reduction procedure are given by Gasem (1986).

All the algorithms used for the VLE calculations are described by Maddox and Erbar (1982), except for the three phase flash. This option can be used only in the simulation mode, and was included in the simulator with the purpose of testing the phase stability subprogram. This program calculates first a two-phase flash on the feed. Then, it takes the liquid phase and tests its stability base on the methods described in Chapter V. If the liquid is unstable, a full three-phase flash is done taking the initial split from the results of the stability test. This

procedure has been found to be efficient, although it takes a little longer to converge that the two-phase flash.

Once the results are obtained from any of the VLE calculations, the user has the option of saving them in a file for later use, printing tables to the screen for inspection, or displaying the error plots that are relevant to his/her problem.

The other major calculation option provided by the simulator is the fractionation or tower simulation. Four types of towers can be simulated with the program: Distillation, Absorbers, Reboiled Absorbers and Refluxed Absorbers.

Columns are solved with very little information given by the user (profiles not required). All that is needed are the pressure at the top and the bottom, estimates of the top and bottom temperatures, product flow rates and a few other estimates. All types of condensers are allowed in the simulation.

The built-in "intelligence" in the program figures out a default set of specifications from this input. The number of specifications can be changed only by adding or deleting equipment from the tower. This procedure makes it difficult to under- or over-specify the tower. Any of the default specifications can be substituted with any of a group of 12 alternatives provided in the package. These are:

1. Product flow
2. Reflux Ratio
3. Component Recovery
4. Temperature in any stage
5. Exchanger duty on any tray
6. Mole fraction in any stream
7. Component flow in any stream
8. Pump-Around Temperature
9. Pump-Around Rate
10. Side-Stripper product flow rate
11. Side-Draw flow rate in vapor or liquid, on any tray
12. Total stream flow rate on any tray

The great flexibility provided by this feature, makes it also possible to give the algorithm a group of specifications which have no physical solution. Therefore, this flexibility should be used intelligently by the user.

More complex configurations are obtained by adding equipment to the column. A menu option is provided for adding: heat exchangers, pump-arounds, side-strippers, side-draws, and side-water-draws. CRUDESIM adds specifications automatically as the user reconfigure the tower. Any configuration option should be installed first before any modification is done for any of the specifications relating to these items.

At this point, options are provided to save and retrieve the specific tower configuration. This feature

allows one to run different alternatives of specification/ configuration for the same simulation problem.

The tower calculations start by generating an initial guess for the tower calculation as described in Appendix B. These profiles are presented to the user for confirmation. If there is some previous knowledge of the tower, the initial profiles can be improved at this time to speed up convergence.

After this, the calculations continue, and some basic information is given regarding what the program is doing. A status line continuously indicates the specific procedure that the column is solving. Additionally, a summary table is refreshed periodically on the screen to monitor the progress in the inner and outer loops. During the calculations, a history file is generated with all the important results of each iteration. This feature is very valuable when investigating convergence problems.

Upon solution of the tower, the program enters an output-menu providing different options to check the results. As before, the simulation results could be saved in a file or displayed in the form of tables. However the best option is to create graphs with the tower profiles. The following profiles are available:

- Temperature
- Total flow rates
- Stream enthalpies

- Component compositions in either the vapor, or liquid phase. Up to three component profiles can be displayed simultaneously on the screen at any given time

There are three options to leave the output section: quit the program, run another case or do a RERUN. This last option will take the converged answer as the initial guess for the next case to be solved. This feature is very convenient when solving a tower with difficult specifications. One strategy to solve this type of tower is to solve the problem for a simpler, easier set of specifications, and then take this solution as the starting point to solve the difficult problem.

Finally, it is recommended to solve first any of the test problems of the next chapter before proceeding with your first simulation.

CHAPTER VII

RESULTS AND DISCUSSION

In this chapter, CRUDESIM is used to solve a series of test problems and its results are compared with those from the literature. Distillation, absorbers, reboiled absorbers and crude towers are all considered in these problems.

Test Problem 1: Distillation

This distillation problem is described in Section 6 of the Manual for Hysim (1987). It describes a depropanizer, consisting of 12 stages with a partial condenser. A propane mole fraction of 0.02 is required for the bottom product and the overhead reflux is fixed at 1.0. The composition of the feed and the tower specifications are presented in Table IV. The pressure in the condenser and the reboiler are 200 and 205 psia respectively. A linear pressure profile is assumed for this problem. The product coming out of the condenser is all vapor. Its flow rate is initially estimated at 30 lbmol/hr. The initial estimate of the temperature in the condenser is 40°F, and 200°F for the reboiler. The feed is introduced in stage 6.

TABLE IV

TEST PROBLEM NO 1: FEED COMPOSITION
AND TOWER SPECIFICATIONS

Components		Flow Rate (lbmol/hr)
Methane		12.2332
Ethane		10.5976
Propane		8.1487
i-Butane		8.3864
m-Butane		7.6607
i-Pentane		6.9242
n-Pentane		5.9612
n-Hexane		4.9959
n-Heptane		3.9996
n-Octene		3.000
Feed Conditions:	Temperature	47.2522°F
	Pressure	480 psia

Tower Specifications:

1. Propane concentration in liquid out of stage 12: 0.02 % mol.
2. Reflux ratio of 1.

Although it is not clear from the problem description, it seems that the PR-EOS was used to obtain the simulation results.

A summary of the results produced by CRUDESIM is presented for reference in Appendix G. The problem converges in 6 iterations of the outer loop with an average of 1.7 inner loop interactions.

A comparison of the product compositions and heat loads is presented in Table V. As can be seen, the results from CRUDEISM are in good agreement with those from Hysim.

The temperature profiles are presented in Figure 11. The differences between the two profiles are within one degree on all the trays. The same situation is observed for the total flow rates as can be seen in Figure 12. The numerical values can be found in Appendix G. It should be noticed that the program was able to converge quite smoothly when using purity specifications.

Test Problem 2: Distillation With Pump Around

This problem is described by Waggoner and Loud (1977). These authors introduced some modifications to the theta method of Holland to make it capable of dealing with pump-arounds. The column consists of a 20 stage tower with a total condenser. The tower pressure is constant at 300 psia. The feed is introduced on stage 10 at its bubble

TABLE V

A COMPARISON OF PRODUCT FLOW RATES

Components	Top Product		Bottom Product	
	This Work	Hysim (1987)	This Work	Hysim (1987)
C1	12.233	12.233	0.000	0.000
C2	10.594	10.594	0.004	0.004
C3	7.322	7.319	0.826	0.830
$C\text{-}C_d$	0.385	0.373	8.000	8.014
n-C4	0.049	0.048	7.612	7.612
i-C5	0.000	0.000	6.924	6.924
n-C5	0.000	0.000	5.961	5.961
C6	0.000	0.000	4.996	4.996
C7	0.000	0.000	4.000	4.000
C8	0.000	0.000	3.000	3.000
Total	30.58	30.567	41.32	41.341

	Heat Duty (BTU/hr)	
	This work	Hysim (1987)
Condenser	$-0.2257*10^6$	$-0.2238*10^6$
Reboiler	$0.7284*10^6$	$0.7166*10^6$

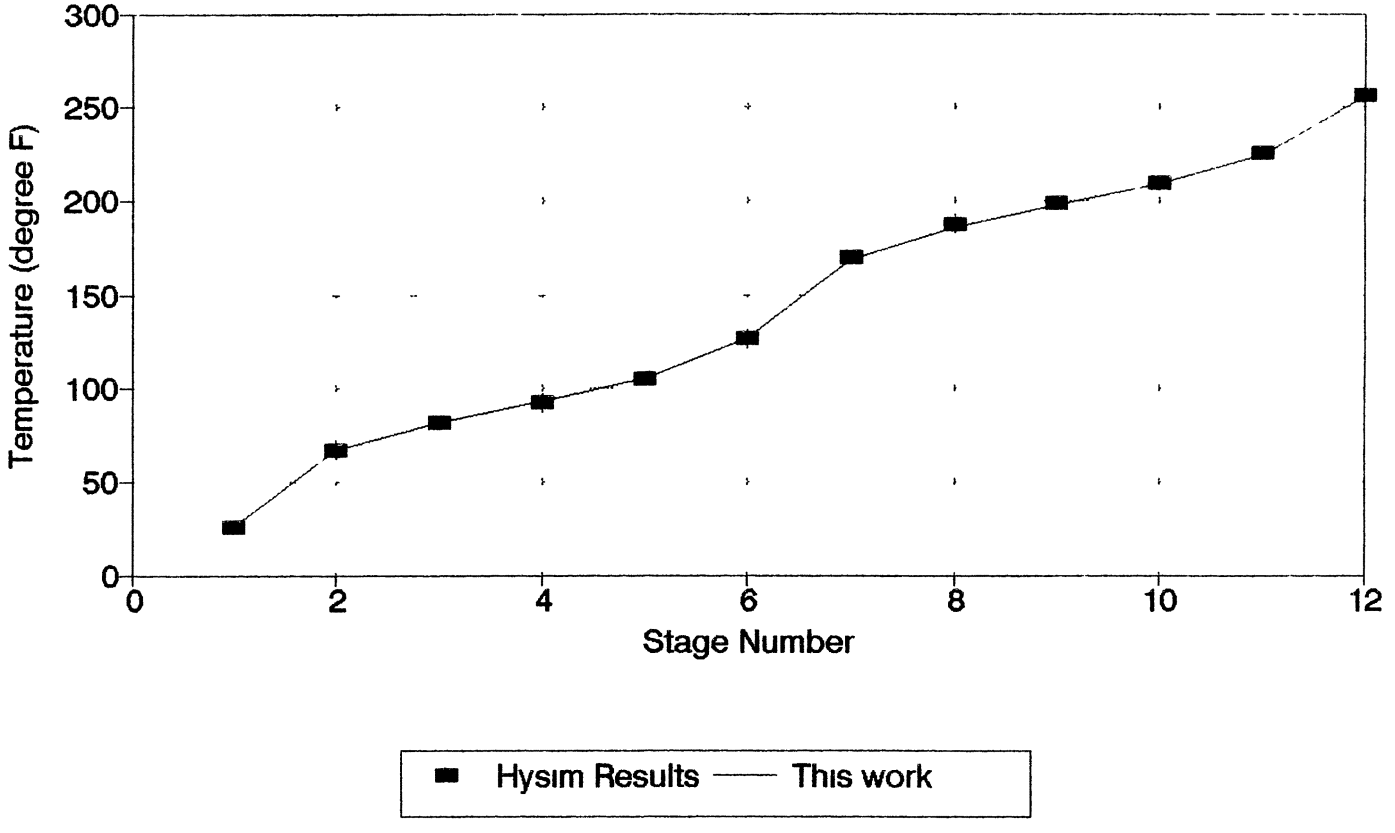


Figure 11: Temperature Profile

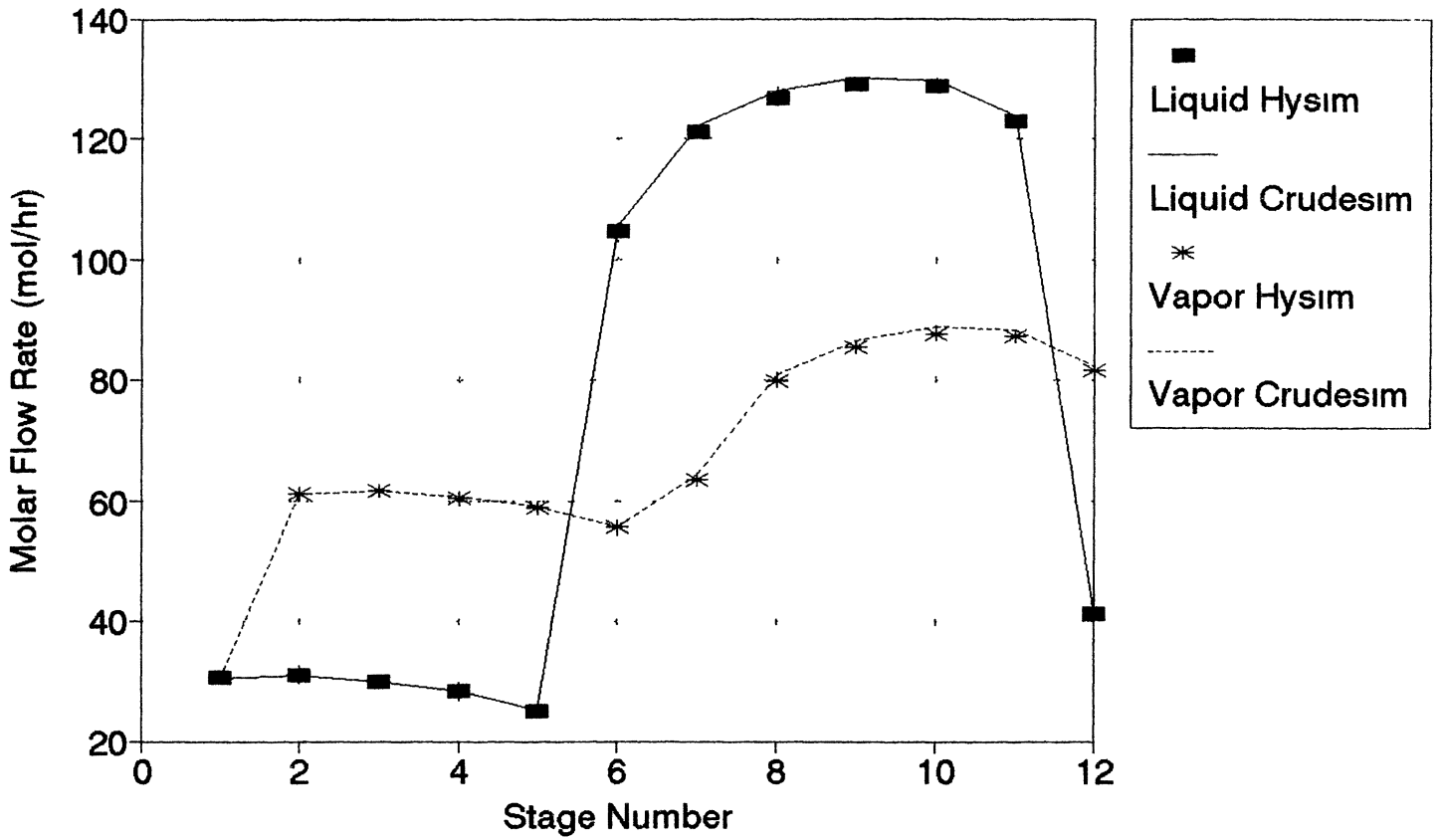


Figure 12: Flow Profiles

point. The feed composition and tower specifications are shown in Table VI. The pump-around goes from stage 16 to stage 5. Initial estimates for the temperature are 140 and 270°F, for the pump-around cases the bottom temperature was reduced to 260°F.

Waggoner and Loud presented three different simulations of this problem with three different pump-around rates: 0, 80 and 450 mol/hr. These authors do not give the precise details of the thermodynamic package used but mention that polynomials were used for the enthalpy and equilibrium ratios. As is typical also of the work by Holland, these are probably polynomials in temperature. Consequently, some differences are expected, as reflected by different bubble points in Table VI. The SRK equation of state has been used throughout all the examples in this chapter.

The liquid flow profiles for each one of the three cases are shown in Figure 13. The results presented by Waggoner and Loud (1977) are also shown for comparison. As can be seen the agreement is very good. The vapor flow profiles are presented in Figure 14. Only the simulation results with CRUDESIM are shown since Waggoner and Loud do not report the vapor flow rates. A summary of the numberical results from the simulations is included in Appendix H for reference.

TABLE VI

TEST PROBLEM NO. 2: FEED COMPOSITION AND TOWER SPECIFICATIONS

COMPONENTS	FLOW RATE (Mol/hr)
C3	325
i-C_4	50
N-C4	50
N-C5	75

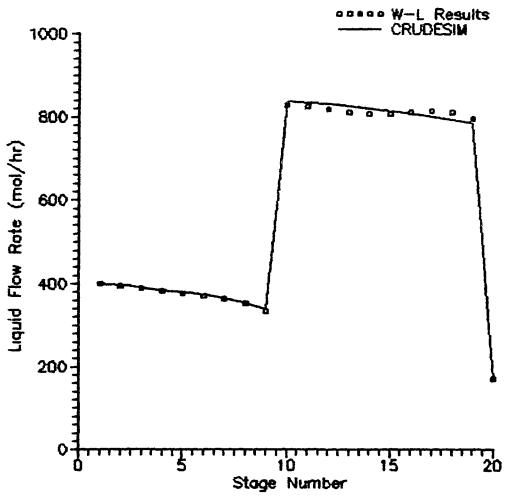
Feed Conditions

Bubble point: 168°F CRUDESIM: 170.8°F

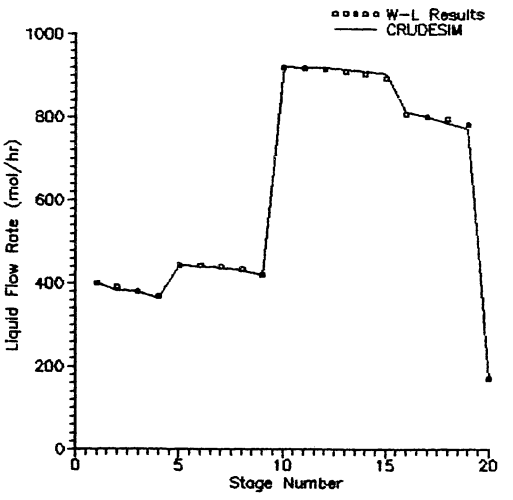
Pressure: 300 psia

Tower Specifications

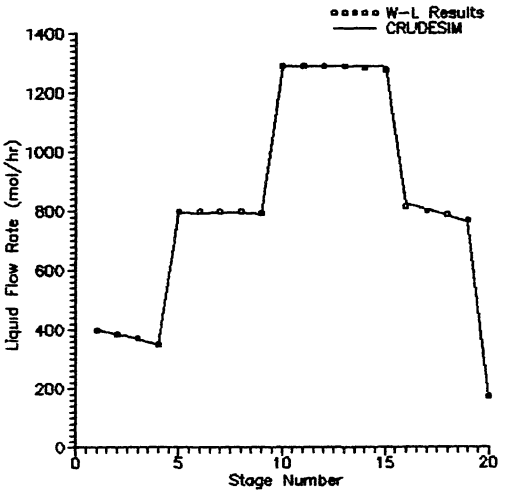
1. Distillate rate: 328 mol/hr
2. Reflux rate: 400 mol/hr
3. Pump-Around rate: 0, 80, and 450 mol/hr



(a) Profile with no Pump-Around



(b) Profile with a Pump-Around Rate of 80



(c) Profile with a Pump-Around Rate of 450

Figure 13: Liquid Flow Profiles

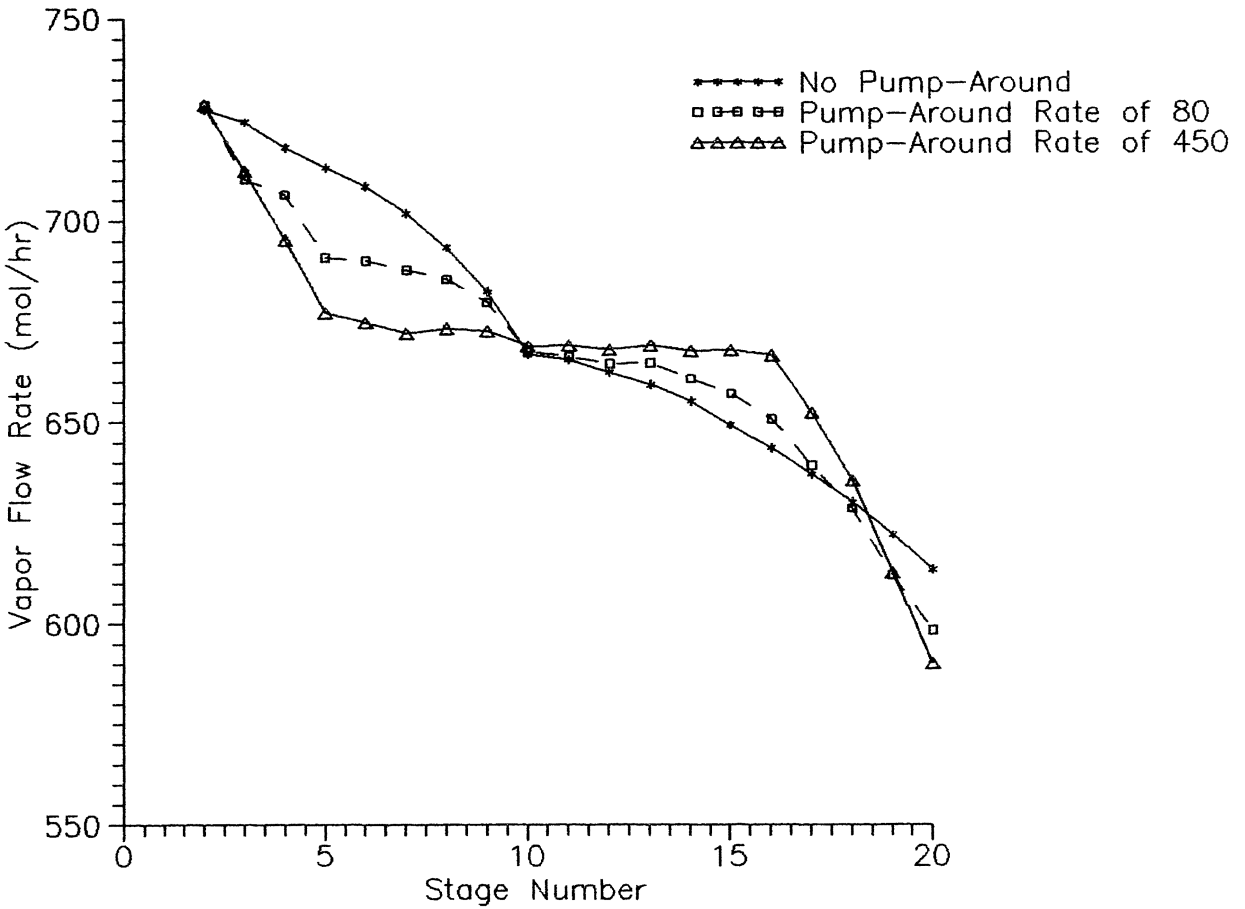
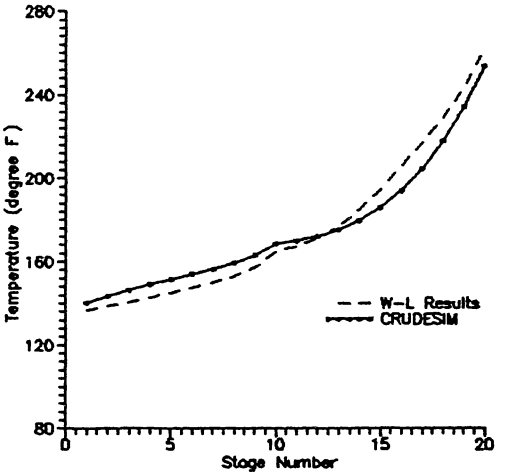


Figure 14: Vapor Flow Profiles

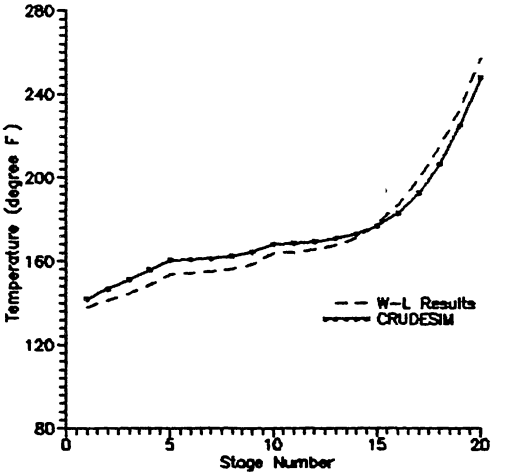
The temperature profiles are presented in Figure 15. As can be noticed, the tendencies are exactly the same, however, there are small deviations as a result of the different thermodynamic models used to calculate the thermophysical properties. These differences will also be reflected in the concentrations as it is shown next.

The product compositions are presented in Table VII for all three cases. The use of the more accurate equation of state models resulted in slightly lower propane concentrations in the overhead product. If purity is a concern in this particular problem, then a higher reflux ratio will be required.

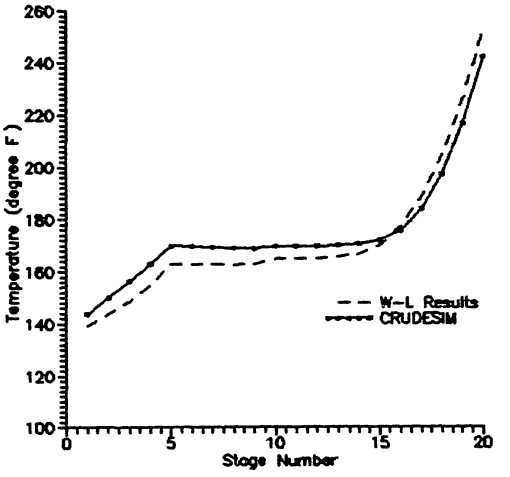
Although all the cases were solved in three iterations of the outer loop, more inner loop iterations were required as the initial guesses for the temperatures were further apart from the final answers. Finally, it should be noticed that the program can deal directly with a total condenser. Other algorithms have to imitate the total condenser by specifying a tiny amount of vapor product, i.e., 0.1% (Shah and Bishnoi, 1978). Additionally, the modifications needed to deal with the pump-around are completely transparent to the user. The only modification needed is the installation of the pump-around when defining the tower configuration.



(a) Profile with no Pump-Around



(b) Profile with a Pump-Around Rate of 80



(c) Profile with a Pump-Around Rate of 450

Figure 15: Temperature Profiles

TABLE VII

COMPARISON OF PRODUCT COMPOSITION

Component	Overhead Product					
	Pump-Around Rate					
	0(mol/nr)		80(mol/hr)		450(mol/hr)	
	W-L	This Work	W-L	This Work	W-L	This Work
C3	0.9764	0.9411	0.9590	0.9172	0.9430	0.8953
i-C_d	0.0207	0.0423	0.0330	0.0548	0.0428	0.0652
n-C4	0.0027	0.0165	0.0078	0.0269	0.0138	0.0364
n-C5	0.0000	0.0001	0.0000	0.0011	0.0002	0.0030
	Bottom Product					
C3	0.0275	0.0965	0.0606	0.1399	0.0912	0.1811
i-C_d	0.2510	0.2097	0.2276	0.1863	0.2089	0.1665
n-C4	0.2853	0.2587	0.2757	0.2395	0.2643	0.2214
n-C5	0.4360	0.4351	0.4359	0.4343	0.4355	0.4309

Test Problem 3: Absorption

This absorption problem was described by Boston (1970). It consists of an 8 stage tower operating at 300 psia. The lean oil is characterized as n-C8; and it is introduced in Stage 1. The rich gas enters the tower in the last stage. The feed compositions for both streams are described in Table VIII. Note that for this tower there are no additional specifications needed. The initial estimates of Boston are also used to initialize our problem. These are: The temperatures in stage 1 and 8 are 104 and 129.2°F respectively; the vapor product rate out of the absorber is 85 mol/hr. The thermodynamic properties (k-values and molar entholpies) were considered dependent only on temperature by Boston in his simulation.

Russell (1983) has suggested that damping of the local model parameters helps convergence. This test problem was used to evaluate the effect of damping on rate of convergence for our algorithm. Table IX presents the iteration summary for several degrees of damping. A damping factor of one means no damping and it is the default value for any simulation, unless changed by the user when defining the input.

The solution of the problem without any damping took the higher number of iterations: 6 outer loop iterations and a total of 13 inner loop iterations. On the other hand, the use of some moderate damping increases significantly the rate of convergence. With a damping factor of

TABLE VIII

TEST PROBLEM 3: ABSORTION FEED COMPOSITIONS

Component	Feed #1	Feed #2
C1	0.0	0.70
C2	0.0	0.15
C3	0.0	0.10
N-C4	0.0	0.04
N-C5	0.0	0.01
N-C8	1.0	0.0
Rate (mol/hr)	20.0	100.0
Feed Conditions:		
Location	Stage 1	Stage 8
Temperature (°F)	90.0	68.47

TABLE IX

EFFECT OF DAMPING

a.) Damping Factor 1.0

Iteration	Heat and Spec Errors	Local Mod. Errors
1	.8238E-02 in 1 iter	.1883E-01
2	.3271E-03 in 2 iter	.1662E-01
3*	.1835E-02 in 3 iter	.2410E-02
4	.2390E-04 in 2 iter	.4211E-02
5	.4155E-03 in 4 iter	.1377E-02
6	.3187E-03 in 1 iter	.3199E-03

b.) Damping Factor 0.8

Iteration	Heat and Spec Errors	Local Mod. Errors
1	.6442E-02 in 1 iter	.1945E-01
2	.2772E-03 in 2 iter	.1193E-01
3	.4182E-03 in 1 iter	.2656E-02
4	.7444E-04 in 1 iter	.4784E-03

c.) Damping Factor 0.6

Iteration	Heat and Spec Errors	Local Mod. Errors
1	.7150E-02 in 1 iter	.1750E-01
2	.1157E-03 in 2 iter	.1020E-01
3	.2173E-03 in 1 iter	.4179E-02
4	.1010E-03 in 1 iter	.1581E-02
5	.3842E-04 in 1 iter	.5383E-03
6	.1177E-04 in 1 iter	.1648E-03

*Numerical Jacobian needed to be reevaluated

0.8, it took only 4 iterations of the outer loop and a total of 5 inner loop interations to reach the answer. It is important to point-out that no Jacobian reevaluations were required in this case. This process takes a lot of computing time since all the derivatives are calculated numerically. Further damping makes convergence slower, although it provides a very stable approach to the answer.

The temperature profile is shown in Figure 16 along with the results of Friday and Smith (1964), and Boston (1970). A direct comparison of the simulation results is always clouded by differences in the thermodynamic prediction methods. It can be seen that our results are intermediate between those of the two references. Boston used the original inside-out algorithm to generate these results and Friday and Smith used the sum of rates method. It is interesting to note that CRUDESIM was able to generate the curved temperature profile starting from a linear profile.

The vapor and liquid profiles are shown in Figure 17. In general, the agreement of the results is reasonably good. The numerical results are included in Appendix I for reference.

Test Problem 4: Reboiled - Absortion

This problem was presented by Holland (1981). It describes an 11 stage tower at a working pressure of 300 psia. The absortion oil is introduced in stage 1 at 100°F. Holland indicates that the rich gas is introduced on stage

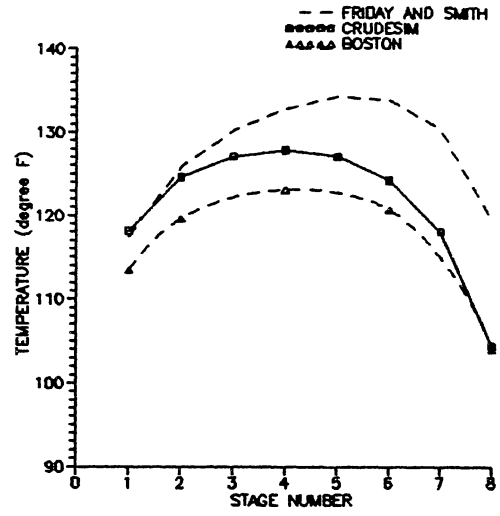


Figure 16: Temperature Profiles

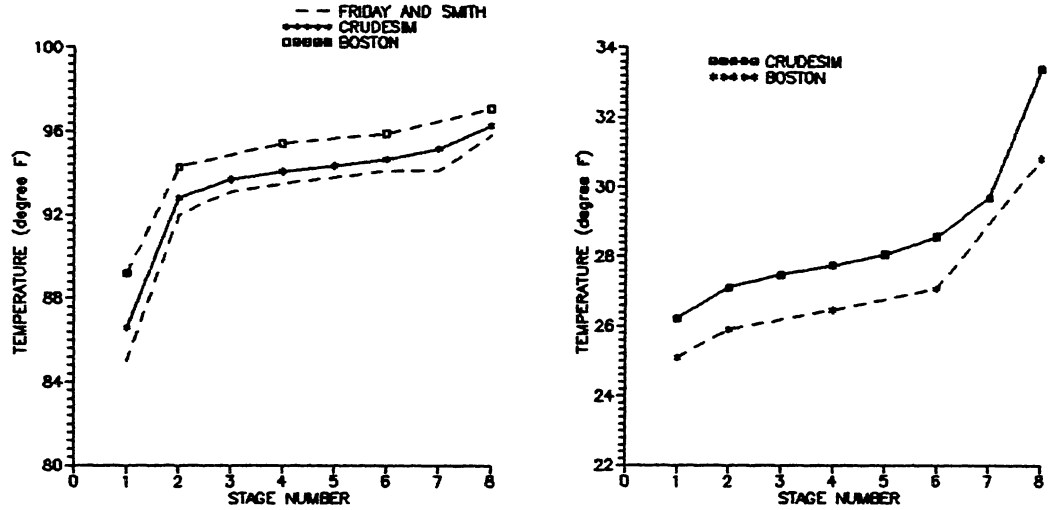


Figure 17: Flow Rate Profiles

5, however, the tower profiles clearly indicate that the feed stage is #6. The feed compositions and tower specifications are presented in Table X. CRUDESIM calculates the dew point of the rich gas at 169.18°F, Holland does not report this value.

In general convergence was difficult for this tower. Therefore, the problem was first solved for an easier specification: the vapor product rate was specified equal to Holland's answer. The reboiler duty was calculated as $2.77*10^6$ Btu/hr. Then, these results were taken as initial guesses to solve the original problem by using the "RERUN" option of the output menu. Both answers are included for reference in Appendix J.

The temperature profiles are shown in Figure 18. As can be seen, Holland's profile presents a discontinuity in Stage 4 which seems strange, since the feed is introduced in Stage 6. Both cases run with CRUDESIM present the discontinuity at the feed stage. The case with higher heat duty has higher temperatures in the stripping section.

The vapor and liquid rates are shown in Figure 19. The two CRUDESIM cases are very similar. The difference appear on the stripping section, where the simulation with higher reboiler duty shows higher liquid and vapor traffics as expected. Holland's profiles present sharp spikes around the feed area which seems unlikely, and may indicate some VLE failure in that section of the tower. Product compositions are presented in Table XI. Overall, the

TABLE X

TEST PROBLEM 4: REBOILED - ABSORTION
FEED COMPOSITIONS

Component	Rich Gas	Absortion Oil
C1	65	0
C2	13	0
C3	1	0
i-C4	1	0
n-C5	20	0
n-C8	0	100
Feed Conditions:		
Location	6	1
Pressure (psia)	300	300
Temperature (°F)	dew point	100

Tower Specifications:

1. Reboiler duty: $3.0*10^6$ Btu/hr

Temperature Estimates:

T1 = 100=°F T10 = 300°F T11 = 450°F

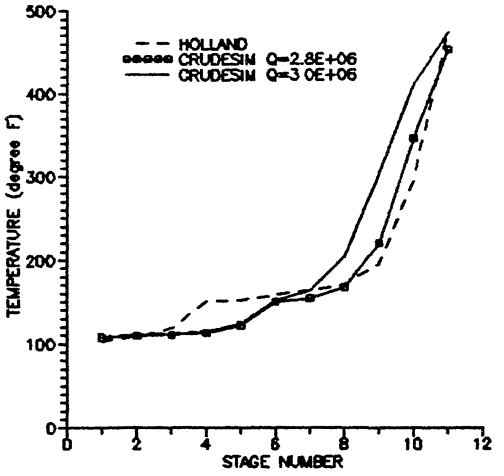
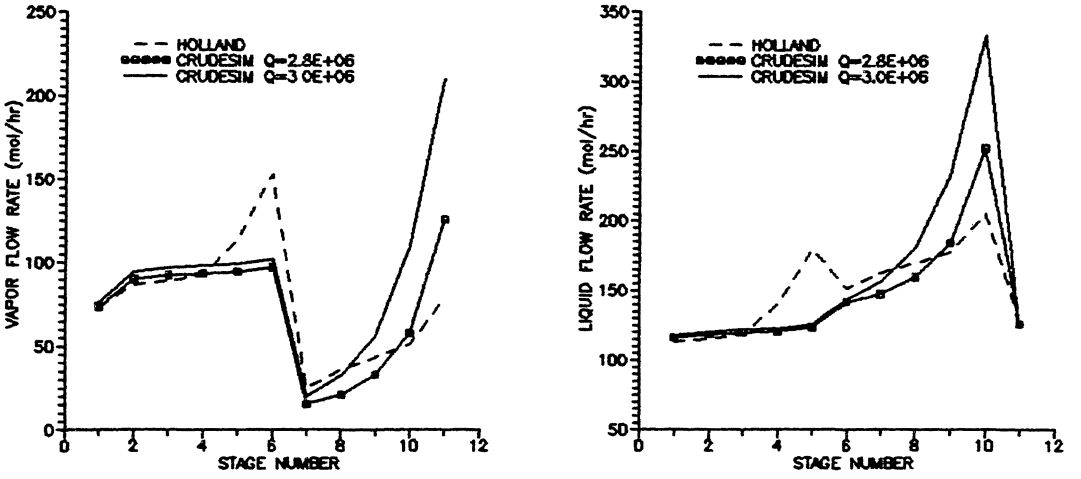


Figure 18: Temperature Profile



(a) Vapor Rate Profiles

(b) Liquid Rate Profiles

Figure 19: Flow Profiles

TABLE XI

PRODUCT FLOW RATES

Component	Holland (1981)	CRUDESIM	
		Q = 2.77*106	Q = 3.0*106
	a.) Overhead Product		
C1	64.995	64.830	64.950
C2	8.4004	8.422	10.928
C3	0.0728	0.026	0.040
i-C4	0.0046	0.000	0.001
N-C5	0.0004	0.000	0.000
N-C8	0.15292	0.262	0.281
	b.) Bottom Product		
C1	0.00447	0.170	0.050
C2	4.59966	4.578	2.072
C3	0.92729	0.974	0.060
C-C4	0.99538	1.000	0.999
N-C5	19.999	20.000	20.000
N-C8	99.847	99.738	99.719

simulation with the product specification produced results closer to those reported by Holland.

The domain of convergence for reboiled absorbers was not as good as in the other type of problems. In order to reach the answer, accurate estimates were needed for the temperature in stages 1, 10 and 11; the others were generated by linear interpolation. It seems that better initial vapor and liquid profiles are needed in order to provide a more robust behavior. The constant molar overflow guesses used here deviate considerably of the sharp curvatures shown by the final answer in the stripping section. This was partially verified by improving the guess value for V_{10} and V_{11}. This small change increased the domain of convergence for the temperature by 20 °F.

Therefore, it is strongly recommended that the user improves the vapor and liquid profiles when simulating reboiled absorbers. This can be easily done in CRUDESIM. After the initial guess has been generated, a screen is presented with the initial profiles. At this point the user can confirm or "improve" any value by typing over. It is important to remember that there is no substitute for a good initial guess.

Test Problem 5: Crude Distillation Tower

This problem is presented in the Manual for Hysim (1987) and it is shown in Figure 20. It consists of a 65,000 barrels/day (3465 lb-mol/hr) crude tower with three

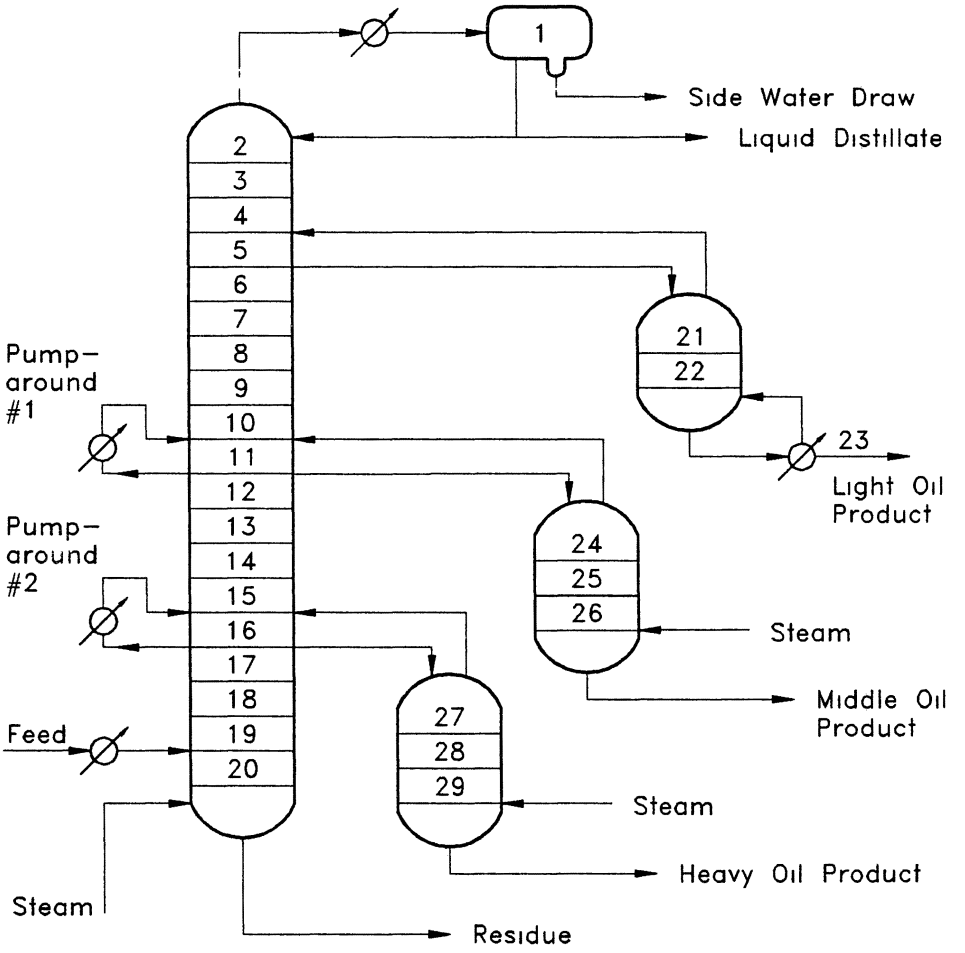


Figure 20: Atmospheric Crude Tower for Test Problem 5

side strippers. The top one has a reboiler and the other two use stripping steam at a rate of 1000 lb/hr. Steam is also used for additional stripping in the main column. The tower has a total condenser, two pump-arounds with cooling and a prefeed heater.

The crude oil characterization without the light ends is presented in Figure 21. The numerical values are included for reference in Appendix K. The feed conditions and tower specifications are shown in Table XII, where the specification set given is equivalent to those in the Hysim manual. A side water draw is installed in Stage 1. Therefore, the program will take as a fact that three phases are always present on this stage, no stability checking is done. Note that a water side draw does not introduce an extra specification.

The feed compositions and other details of the characterization are given in Appendix K. The C6+ fraction was divided into 24 pseudo-component which are the same as those in the Hysim simulation except for 13 and 14, that were combined into a single component.

This simulation is obviously more complex then the previous ones, and therefore more difficult to converge. However, with the appropriate damping factor, the simulation usually converges in less than 10 iterations of the outer loop. For this example, a damping factor of 0.4 provided a very stable approach to the answer. Some problems were experience with damping factors bigger than 0.7.

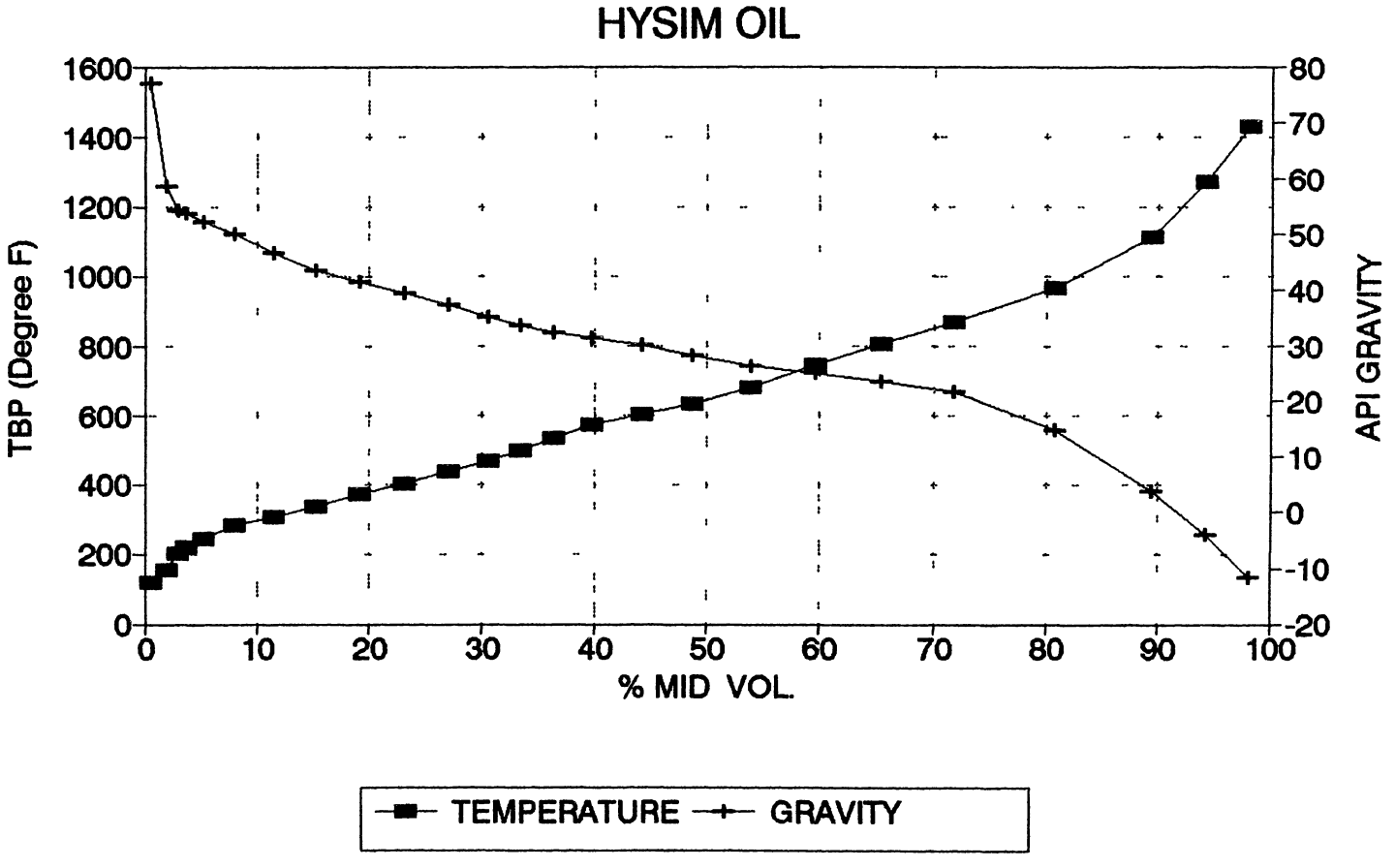


Figure 21: Crude Oil Characterization

TABLE XII

FEEDS AND SPECIFICATIONS

Feed Conditions				
Feed	1	2	3	4
Stage	19	20	26	29
Temperature (°F)	637	375	375	375
Pressure (psia)	29.7	164.7	164.7	164.7
Flow Rate (lb-mol/hr)	3465.104	194.228	55.494	55.494

Specifications

1. Overhead product flow rate: 1062.5 lb-mol/hr
2. Exchanger duty in stage 10: - 40.0 $*10^6$ Btu/hr
3. Exchanger duty in stage 15: - 40.0 $*10^6$ Btu/hr
4. Exchanger duty in stage 23: 2.5 $*10^6$ Btu/hr
5. Flow rate in pump-around #1: 1764.9 lb-mol/hr
6. Flow rate in pump-around #2: 1340.5 lb-mol/hr
7. Product flow rate outof the top side stripper: 690.4 lb-mol/hr
8. Product flow rate out of the middle side stripper: 430.3 lb-mol/hr
9. Product flow rate out of the bottom side stripper: 412.9 lb-mol/hr
10. Overflash of 2000 barrels/day @ 73.1 lb-mol/hr

Additionally a side water draw is installed on stage 1.

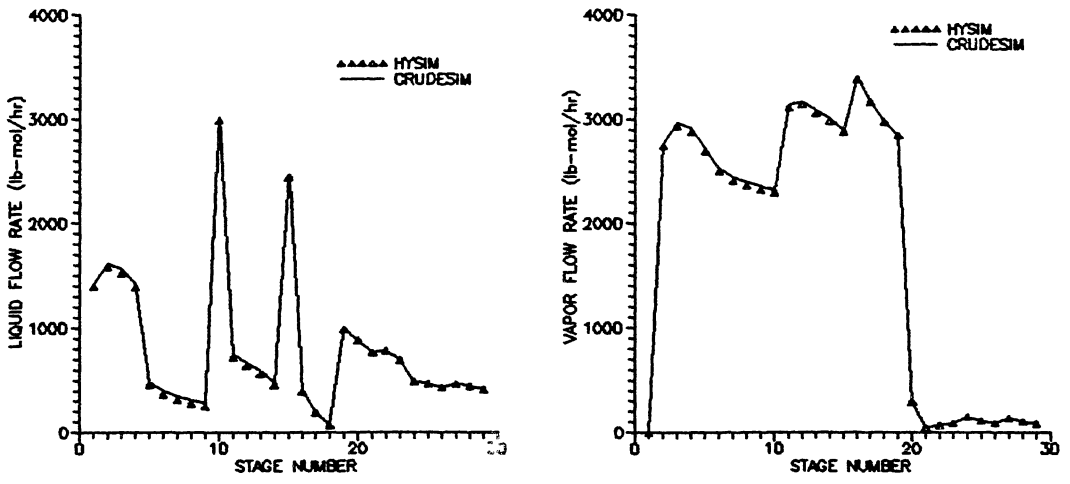
Temperature Estimates: T_1 = 200°F T_2 = 300°F t_{20} = 600°F

The results are shown in Figures 22 and 23. As can be seen, the profiles obtained with CRUDESIM are practically the same as those reported for the Hysim simulation. A similar agreement is found with respect to the product compositions. The complete numerical values of the results are included for reference in Appendix K.

Next, the effect of the number of pseudo-components in the oil characterization was investigated. The simulation was run with a reduced characterization with only 10 pseudo-components. The partial TBP on which this characterization was based is given in Appendix K. The results are shown in Figures 24 and 25. The numerical results are included in the same appendix.

As can be noticed, the results are surprisingly close. The biggest temperature difference is 10°F, and it takes place in the condenser. However, the main characteristics of the answer are retained in this simulation, which runs in a fraction of the time needed for the one with the complete characterization. On the negative side, it was found that the answer is less sensitive to changes in the operation parameters. The other difficulty is that fewer points are obtained from the product compositions to draw the ASTM curves. Since product specifications are sometimes given in terms of these curves, the accuracy of the results is affected.

One more simulation was done with this example in order to test the performance of the program in the three



(A) Liquid Rate Profiles

(B) Vapor Rate Profiles

Figure 22: Flow Profiles

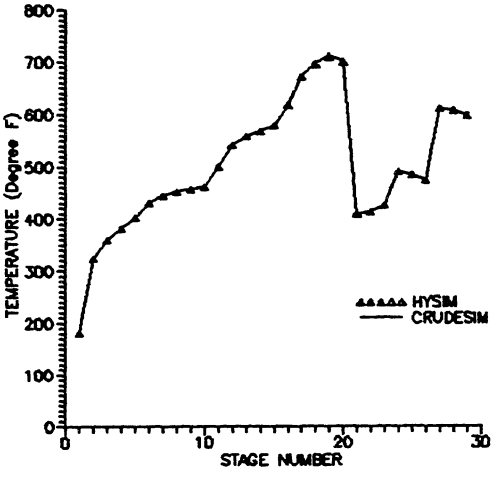
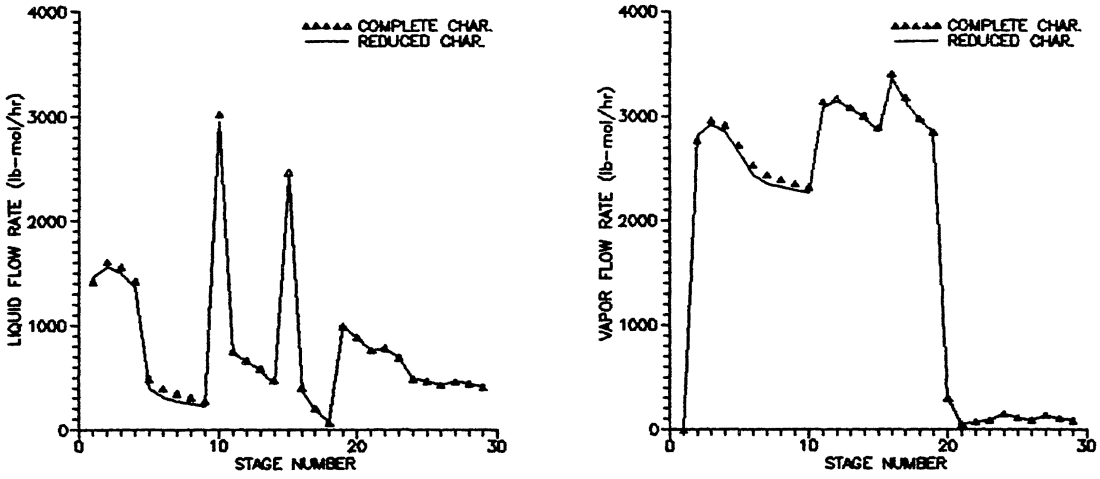


Figure 23: Temperature Profiles



(a) Liquid Rate Profiles

(b) Vapor Rate Profiles

Figure 24: Effect of Characterization on Flow Profiles

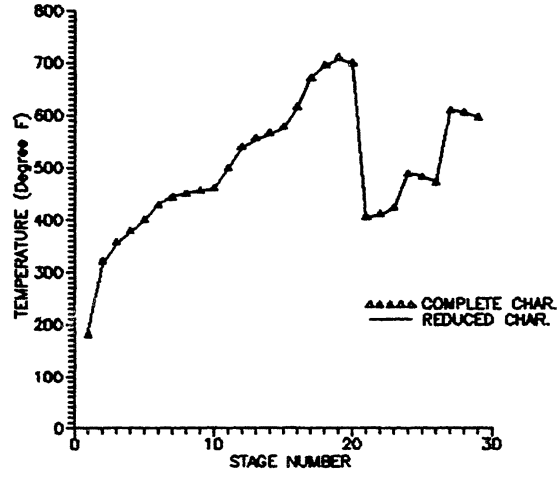


Figure 25: Effect of Characterization on Temperature Profile

phase mode. In general, a three phase simulation is much more difficult to solve than a two-phase one. For instance, Ross and Seider (1981) mentioned that it took 30 iterations of the outer loop, to solve a three component problem with their algorithm. The difficulty comes from the fact that split calculations are done in both the inner and outer loop. This introduces excessive variations in the liquid compositions (noise) that affect significantly the rate of covergence.

Table XIII shows the iteration summaries for two simulations of this test problem run with the reduced characterization. As can be seen the full three phase model has a harder time in reaching the answer. The numerical results are included also in Appendix K, and are essentially the same for both runs. However, it was necessary to introduce two changes in the three phase model:

1. The first change was already suggested by Ross and Seider (1981), and consists of damping the overall liquid concentration, $\bar{X}_{ij}$, before updating the local models. This helps getting convergence of the inner loop in subsequent iterations.
2. It was noticed that the excessive noise in the outer loop was linked to oscillations in the temperature. This pattern was well established after 4 or 5 iterations. Therefore, after the

TABLE XIII

ITERATION SUMMARY

Case A: Waterside Draw Installed In Stage 1

Iteration	Heat And Spec Errors	Local Mod. Errors
1	.3512E-01 in 2 iter	.1640E-01
2	.5399E-02 in 6 iter	.2212E-01
3	.2356E-03 in 4 iter	.1259E-01
4	.2459E-03 in 4 iter	.9316E-02
5	.3839E-03 in 1 iter	.5735E-02
6	.9255E-04 in 1 iter	.3309E-02
7	.1147E-03 in 1 iter	.1840E-02
8	.3476E-04 in 1 iter	.1074E-02
9	.2767E-04 in 1 iter	.6659E-03
10	.1124E-04 in 1 iter	.4020E-03

Case B: Full Three Phase Mode

Iteration	Heat And Spec Errors	Local Mod. Errors
1	.3553E-01 in 2 iter	.1398E-01
2	.5859E-03 in 7 iter	.2102E-01
3	.9407E-03 in 10 iter	.1024E+00
4	.4687E-02 in 2 iter	.2686E-01
5	.5778E-02 in 2 iter	.9704E-02
6	.6226E-02 in 2 iter	.3321E-02
7	.5423E-02 in 2 iter	.3186E-02
8	.4425E-03 in 2 iter	.4932E-02
9	.4466E-03 in 2 iter	.2128E-02
10	.2666E-03 in 2 iter	.1171E-02
11	.5406E-04 in 1 iter	.6788E-03
12	.6582E-04 in 1 iter	.3861E-03

fifth iteration, the oscillations are damped by averging the last two outer loop temperatures.

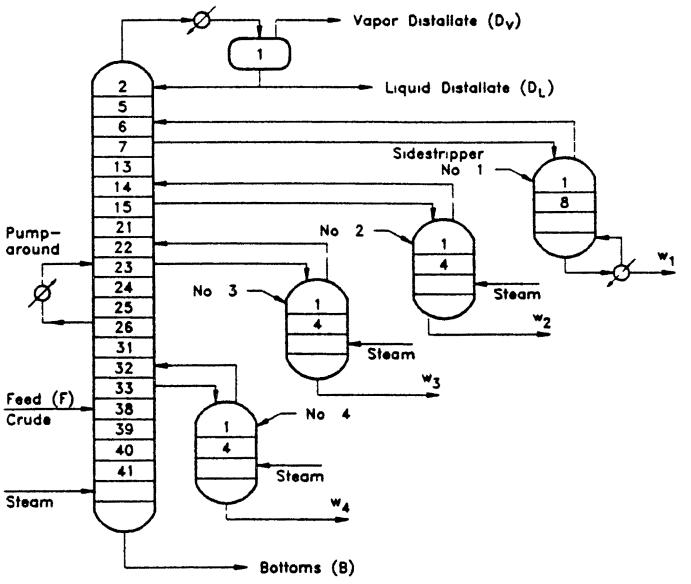
Once these two changes were implemented, the three phase algorithm was able to converge consistently from different guesses. All these procedures are completely transparent to the user, the built-in "intelligence" takes care of the variations.

Test Problem 6: Exxon's Tower

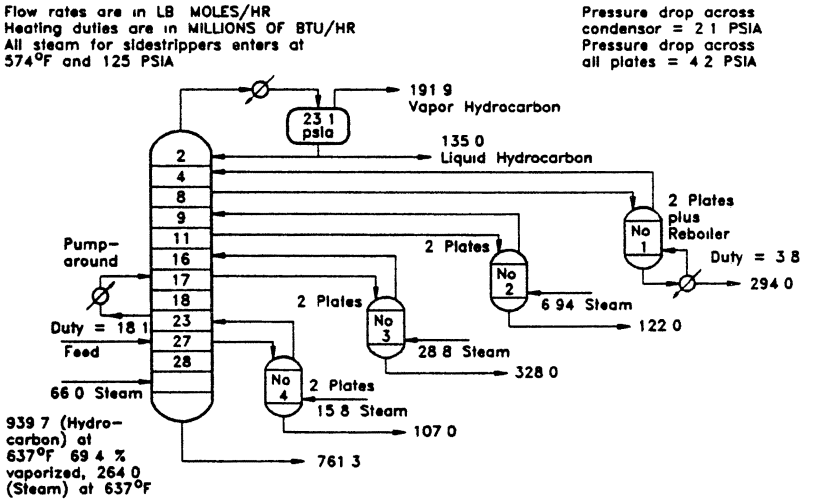
More difficult than reproducing a computer simulation, is to simulate a real crude distillation unit. In this test problem, we study the simulation of a commercial Exxon crude tower originally presented by Cecchettiet al. (1963).

The tower configuration is shown in Figure 26(a). It consists of a 36,700 barrels/day crude unit with four side strippers and one pump-around. The feed enters the flash zone at 637°F. The pressure in the partial condenser is 23.1 psia, and its pressure drop is 2.1 psia. The pressure drop across the rest of the tower is taken as 4.2 psia. Other conditions are as indicated in Figure 26(b).

In order to obtain a reasonable match between calculated results and actual tower conditions, the concept of "theoretical analogue" was presented by Cecchetti et al.(1963). These authors defined the theoretical analogue column as the one which has the required number of equilibrium stages between each product withdrawal position so that the product streams possess the same characteristics



(a) Actual Crude Tower



(b) Theoretical Analogue

Figure 26: Exxon's Crude Tower

as those withdrawn from the actual tower. The analogue for this case is presented in Figure 26(b).

Cecchetti et al. solved this problem by the "theta" method. However, Hess et al. (1977) pointed out that this method in general fails for this type of tower and proposed the multi "theta" method. In their solution, these authors changed the original tower specifications, and selected the feed enthalpy as a fixed specification. This choice is really odd and the authors offer no reason for it. They also fail to mention whether or not this enthalpy is consistent with the feed conditions. Temperature dependant k-values and enthalpies were used in both simulations. Russell (1983) said in his paper that he simulated this tower but offers no details at all. He list neither the complete set of specifications used nor does he discuss the quality of the solution.

Hsie (1989) also solved this problem by means of a relaxation method. Although he had subroutines to calculate the thermodynamic properties better, this author preferred to use the empirical expressions by Hess et al. (1977) for k-values and enthalpies. He also used the same specifications as Hess et al. One problem with his solution is that it does not completely close the overall material balance.

For this work, the original specifications by Cecchetti et al. (1963) were used. These, along with the feed conditions are presented in Table XIV. The crude oil

TABLE XIV

FEEDS AND SPECIFICATIONS

EXXON TOWER

Feed Conditions					
Feed	1	2	3	4	5
Stage	27	33	35	37	28
Temperature(F)	637	574	574	574	574
Pressure (psia)	29.4	125	125	125	125
Flow-Rate (lb-mol/hr)	2203.2*	6.94	26.8	15.8	66.0

Specifications

1. Overhead vapor product: 206.03 lb-mol/hr*
2. Overhead liquid product: 135 lb-mol/hr
3. Exchanger duty in stage 31: $0.65*10^6$ Btu/hr
4. Exchanger duty in stage 18: $-18.1*10^6$ Btu/hr
5. Flow rate in Pump-Around: 823 lb-mol/hr
6. Product flow rate out of stripper #1: 294.0 mol/hr
7. Product flow rate out of stripper #2: 122.0 lb-mol/hr
8. Product flow rate out of stripper #3: 328.0 lb-mol/hr
9. Product flow rate out of stripper #4: 107.0 lb-mol/hr

Additionally, a side water draw was installed in stage 1

Other estimates:

T_1 = 110 °F T_2 = 160 °F T_{28} = 630 °F Reflux ratio: 6.464

* includes the steam with the hydrocarbon

characterization is shown in Figure 27. A total of 30 components were used for this simulation as opposed to 35 used by Hess et al. (1977). The details of the characterization are included for reference in Appendix L.

When one tries to solve the problem with this specifications, the program never converges. There is not enough energy in the flash zone; consequently, a lot of the oil comes out at the bottom of the tower. This physical constraint makes it impossible to satisfy the product specifications at the top of the tower. This is probably the reason why Hess et al. (1977) changed the problem to specify the amount of energy entering the flash zone. In this way, they made sure there was sufficient energy to vaporize enough oil to satisfy the product specifications. Nevertheless, the feed enthalpy still has to be consistent with the feed conditions, and these authors do not explain if that is the case in their problem.

The simulation fails because there is a bias in the crude oil characterization and tuning is required. In the simulation by Hess et al. (1977), this tuning was provided by using functions to calculate the k-values and component enthalpies that were specific for that crude oil. This is probably the reason why Hsie (1989) used these same expressions despite the fact that his software had better property prediction methods.

The need to tune crude oil characterizations is a well recognized one, especially when very heavy fractions are

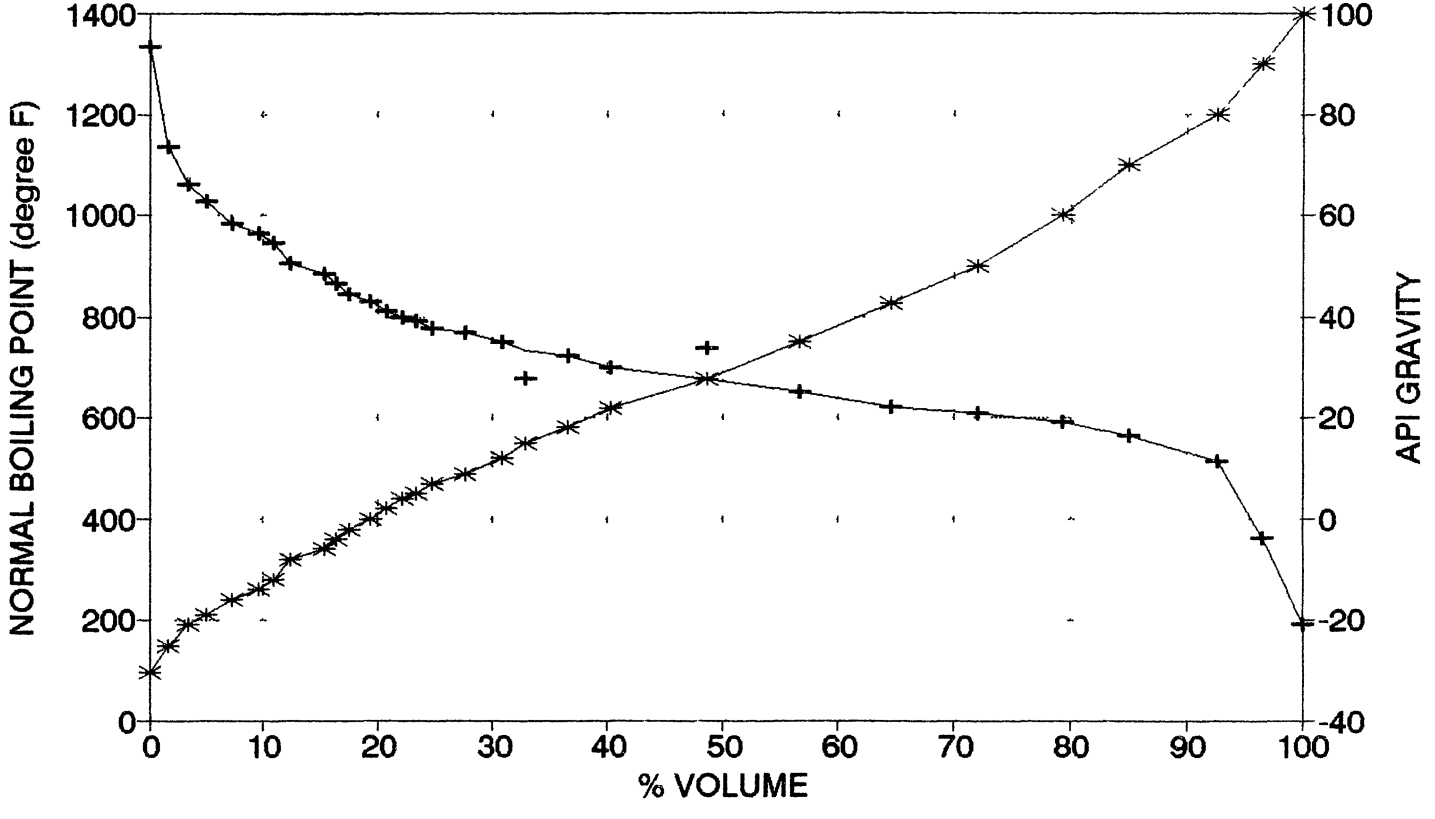


Figure 27: Crude Oil Characterization

involved. Some pioneering work was done by Wilson et al. (1978). Maddox and Erbar (1982) give some more details of these tuning methods. More recently, Gani and Fredenslund (1987) have described criteria and programs for this tuning, although they are too complex to be included in a general simulator at this time.

In any case, the information needed to apply these procedures was not available for this problem. However, it is important to point out the need for simple and efficient tuning methods that could be used in general simulators like the one presented in this work.

Going back to our problem, the "analogue" was modified in order to provide the "missing" energy to the flash zone. A heat exchanger was installed in the feed tray, and the duty adjusted in order to obtain a bottom product rate equal to the actual problem. This rate was 660 lb-mol/hr in Cecchetti's version, 778.86 lb-mol/hr in Hess' paper and 768.1 lb-mol/hr in Hsie's version. A value of 770 lb-mol/hr was chosen in this work.

It was easy to obtain a good solution once this modification was done. Figure 28 compares the actual product TBP's with those obtained from the simulation results. The temperature profiles are shown in Figure 29. As can be seen, the product curves match very well the actual product curves. However, the temperatures are higher in the bottom of the tower due to the heat exchanger. For the same reason, the internal vapor and

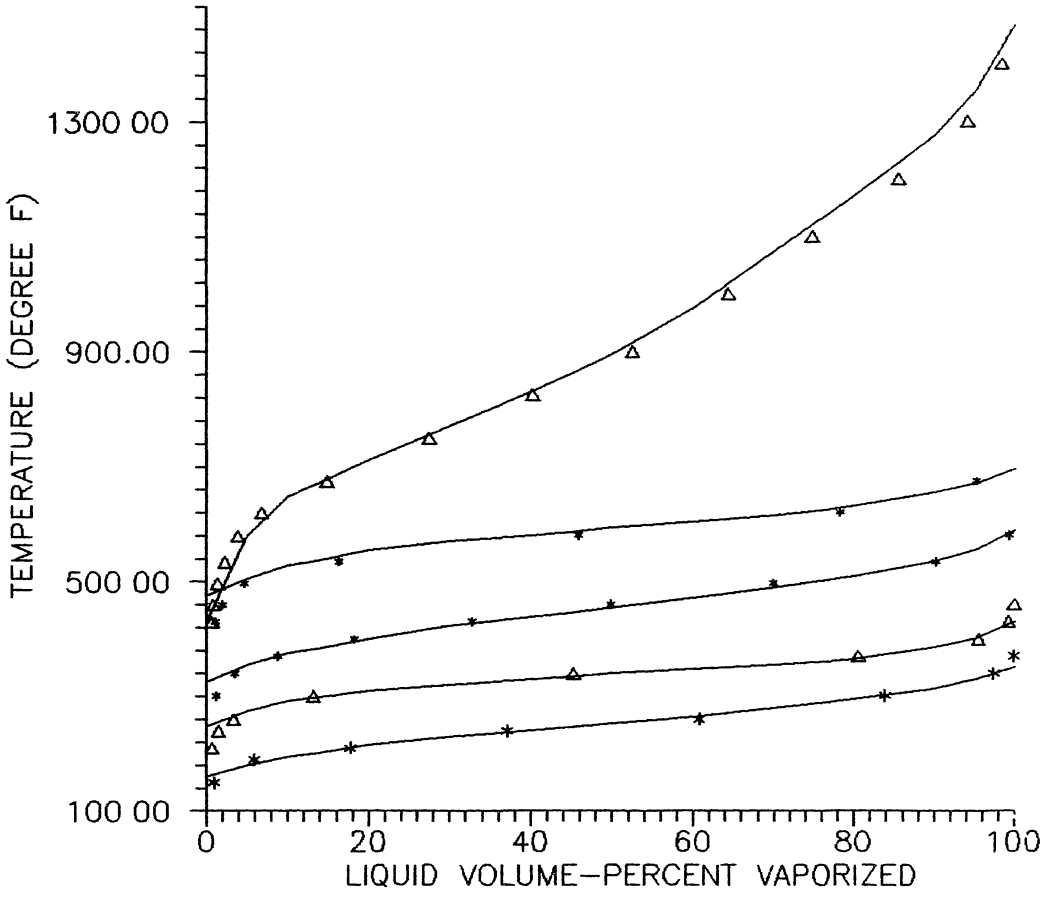


Figure 28: Product Compositions

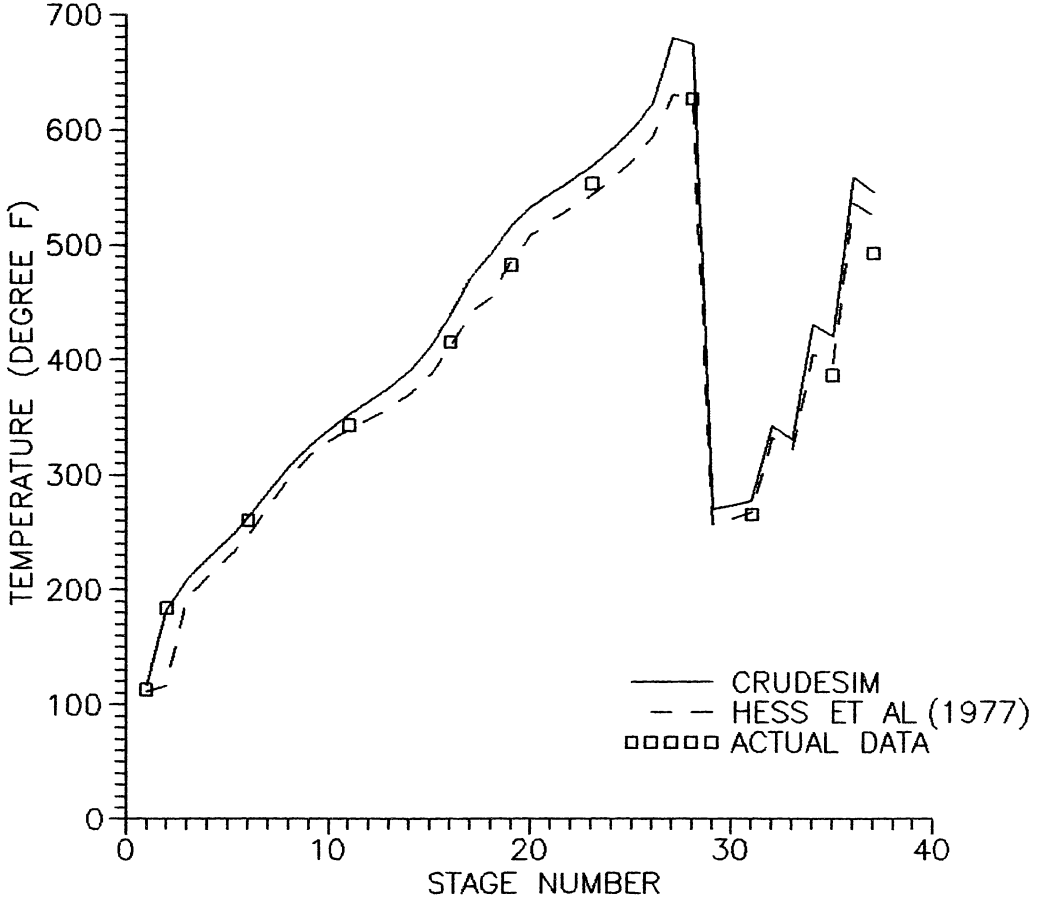


Figure 29: Temperature Profile

liquid rates are higher than those reported by Hess et al. (1977). The numerical results are included for reference in Appendix L. It should be noticed that Hess reports a temperature of 116.8°F for stage 2. If this is indeed his answer, then there is something very wrong in his simulation. Normally, there is a jump of more than 50°F between the temperature in the condenser and that in stage 2 for this type of tower.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

In process simulation, a considerable amount of time is spent in thermodynamic property calculations. Local models can be used to substantially reduce the total number of property evaluations, and thus produce very efficient programs. This approach has successfully being used to develop a group of algorithms that can efficiently simulate a wide range of separation problems in microcomputers.

Important advantages of this program are its capability to deal with a wide variety of tower specifications and its internal procedure to generate the initial guess from a few estimates provided by the user.

The algorithms were further extended to the three phase case by using the tangent plane stability analysis of Michelsen (1982). In the three phase mode, the simulator can detect water condensation in any of the trays of a crude unit, and modify the model equations to produce the correct result.

A powerful user interface with graphical capabilities was developed in order to integrate all the procedures in a coherent highly interactive simulator. In addition to the

fractionation module, a series of options are available to the user which increase significantly the power of the simulator: 7 types of VLE calculations, a component library of 61 components, capabilities to optimize EOS parameters based on experimental equilibrium data, 4 different procedures to characterize petroleum fractions, on-screen plotting capabilities.

The procedures included in the simulator were successfully validated by solving a series of test problems. The model validation included absorbers, distillation towers, simple and complex towers, towers with pump-arounds and systems of interlinked towers like crude distillation units.

The author realizes that no project is ever finished, and that is specially true in a field as vast as this one. The following recommendations represent some of the areas in which the author feels this research effort could be extended:

a) Test the three phase algorithm with more conventional three phase distillation units (Table I). Three major modifications will be required: extend the thermodynamic package, include acceleration methods in the stability analysis, and modify the model equations to allow the second liquid phase to flow between stages.

b) Extend the algorithms to deal with other interlinked systems like distillation tower-reboiled absorbers and many others. Wayburn and Seader (1984)

provide an excellent review of the work done on interlinked system of towers. Major modifications will be required on the initialization procedures and scaling subprograms.

c) Develop efficient procedures for tuning crude oil characterizations. Although some methods are available in the open literature, none of them can presently be used in a general purpose simulator like the one developed in this work.

d) Extend this work to separation processes with chemical reaction. Several changes will be needed here: extension of the thermodynamic package, modification of the modelling equations to include the generation term, incorporation of constitutive equations for reaction rates.

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APPENDIXES

APPENDIX A

MODEL EQUATIONS

Single Stage

With the notation illustrated in Figure 30, the component material balance is

$$v_{ij} + W_j\, y_{ij} + l_{ij} + U_j\, X_{ij} - l_{i,j-1} - v_{i,j+1} + l''_{ij} = f_{ij}$$

$$v_{ij}\left[1 + \frac{W_j}{V_j}\right] + l_{ij}\left[1 + \frac{U_j}{L_j}\right] - l_{i,j-1} -$$

$$v_{i,j+1} + l''_{ij} = f_{ij} \qquad (1)$$

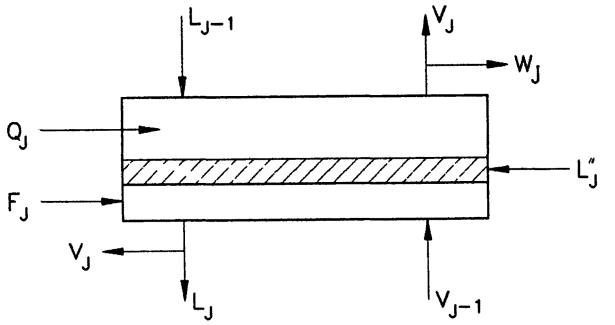


Figure 30: Single-Stage

Introducing the expression for the liquid-liquid equilibrium.

$$X_{ij} \, K'_{ij} = X''_{ij} \, K''_{ij}$$

$$\frac{l_{ij}}{L_j} \, K'_{ij} = \frac{l''_{ij}}{L''_j} \, K''_{ij}$$

$$l''_{ij} = l_{ij} \times \left(\frac{L''_j}{L_j}\right) \times \left(\frac{K''_{ij}}{K''_{ij}}\right)$$

$$l''_{ij} = l_{ij} \, \beta_j \, K^D_{ij} \qquad (2)$$

where $K^D_{ij} = k'_{ij}/k''_{ij}$ and $\beta_j = L''_j/L_j$

Substituting equation (2) into equation (1)

$$v_{ij} \left[1 + \frac{W_j}{V_j}\right] + l_{ij} \left[1 + \frac{U_j}{L_j}\right] - l_{i,j-1} -$$

$$v_{i,j+1} + l_{ij} \, \beta_j \, K^D_{ij} = f_{ij} \qquad (3)$$

the vapor-liquid equilibrium or efficiency relation is given by

$$y_{ij} = E_j \, K'_{ij} \, X_{ij}$$

$$\frac{v_{ij}}{V_j} = E_j \, \alpha_{ij} \, K_{bj} \, \frac{l_{ij}}{L_j}$$

$$v_{ij} = E_j \alpha_{ij} \left(\frac{K_{bj} V_j}{L_j}\right) l_{ij} = E_j \alpha_{ij} S_j l_{ij} \qquad (4)$$

where $S_j = \frac{K_{bj} V_j}{L_j}$ is the stripping factor. Let's further define the relative stripping factors as

$$S_{rj} = \frac{S_j}{S_b} \qquad (5)$$

Substituting (5) into (4).

$$v_{ij} = E_j \alpha_{ij} S_b S_{rj} l_{ij} \qquad (6)$$

Substituting (6) into (3).

$$RV_j E_j \alpha_{ij} S_b S_{rj} l_{ij} + l_{ij} RL_j - l_{i,j-1} -$$

$$E_{j+1} \alpha_{i,j+1} S_b S_{rj+1} l_{i,j+1} + l_{ij} \beta_j \overset{D}{K}_{ij} = f_{ij}$$

$$-l_{i,j-1} + \{RL_j + E_j \alpha_{ij} S_b S_{rj} RV_j + \beta_j \overset{D}{K}_{ij}\} l_{ij}$$

$$- \{E_{j+1} \alpha_{i,j+1} S_b S_{rj+1}\} l_{i,j+1} = f_{ij} \qquad (7)$$

where:

$RL_j = 1 + \frac{U_j}{L_j}$ = liquid withdrawal factor

$RV_j = 1 + \frac{W_j}{V_j}$ = vapor withdrawal factor

On the other hand, the energy balance is given by

$$L_{j-1}\, h_{j-1} + V_{j+1}\, H_{j+1} - (V_j + W_j)\, H_j - (L'_j + U_j) h_j + F_j\, J_{Fj} + Q_j - L''_j\, h_w = 0 \qquad (8)$$

where:

$$L_j = \sum_{i=1}^{c} l_{ij}$$

$$V_j = \sum_{i=1}^{c} v_{ij} = \sum_{i=1}^{c} \{E_j\, \alpha_{ij}\, S_b\, S_{rj}\}\, l_{ij}$$

$$W_j = V_j\, (RV_j - 1)$$

$$U_j = L_j\, (RL_j - 1)$$

$$L''_j = \sum_{i=1}^{c} l''_{ij} = \sum_{i=1}^{c} \{\beta_j\, K_{ij}^{D}\} l_{ij}$$

If the stage is the REBOILER, then:

$$V_{j+1} = V_{N+1} = 0$$

$$U_j = 0$$

If the stage is a CONDENSER, then:

$$L_{j-1} = L_o = 0$$

$$W_j = 0$$

If the condenser is a total condenser then $V_j = V_1 = 0$ and $Sr_1 = 0$. If the condenser is a partial condenser, then the stripping factor has a finite value different from zero.

Pump-Around Stages

As shown in Figure 31, the occurrence of a pump-around in the tower affects two stages in the configuration; the sending stage and the receiving stage. The heat exchanger if present, is installed in the receiving tray.

Receiving Stage

The component material balance is given first:

$$v_{ij}\left(1 + \frac{W_j}{V_j}\right) + l_{ij}\left(1 + \frac{U_j}{L_j}\right) - l_{i,j-1} - v_{i,j+1}$$

$$+ l''_{ij} = f_{ij} + G_s X_{is}$$

Using the same procedure as described in the previous section, the following expression is obtained

$$-l_{i,j-1} + [RL_j + E_j \alpha_{ij} S_b S_{rj} RV_j + \beta_j K^D_{ij}]l_{ij}$$

$$-[E_{j+1} \alpha_{i,j+1} S_b Sr_{j+1}] l_{i,j+1} - \left(\frac{G_s}{L_s}\right) l_{is} = f_{ij} \qquad (9)$$

The energy balance is given by the following expression

$$L_{j-1} h_{j-1} + V_{j+1} H_{j+1} + F_j H_{Fj} + G_s h_s -$$

$$(V_j + W_j) H_j - (L_j + U_j) h_j - L''_j h_w + Q_p = 0 \qquad (10)$$

Sending Tray

Following the same procedure as above, the component material balance is:

$$v_{ij}\left(1 + \frac{W_j}{V_j}\right) + l_{ij}\left(1 + \frac{U_j}{L_j}\right) - l_{i,j-1} - v_{i,j+1}$$

$$+ l''_{ij} = f_{ij} - G_j \frac{l_{ij}}{L_j}$$

where $j = s$

$$-l_{i,j-1} + \{RL_j + E_j \alpha_{ij} S_b S_{rj} RV_j + \beta_j K^D_{ij}$$

$$+ \frac{G_j}{L_j}\}l_{ij} - \{E_{j+1} \alpha_{i,j+1} S_b S_{rj+1}\}l_{i,j+1} = f_{ij} \qquad (11)$$

And the energy balance by

$$L_{j-1} h_{j-1} + V_{j+1} H_{j+1} + F_j HF_j - (V_j + W_j)H_j$$

$$- (L_j + U_j + G_j)h_j - L''_j h_w + Q_j = 0 \qquad (12)$$

Side-Strippers

As illustrated in Figure 32, the occurrence of a side stripper in a column modify the energy and material balances of three trays in the tower: the sending tray in the main fractionator, the receiving tower in the main column and the top tray of the side stripper. The rest of the stages are described by the equation presented previously.

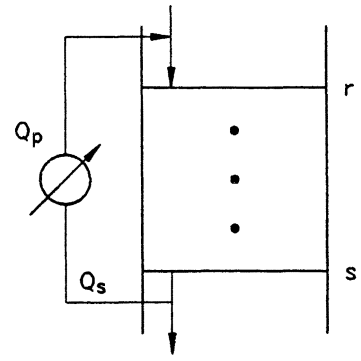
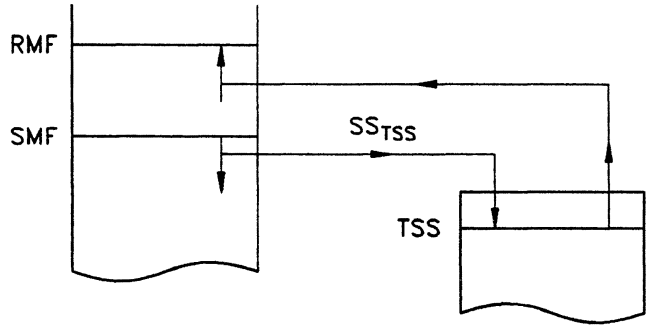


Figure 31: Pump-around Stages



TSS = Top tray in Side Stripper
RMF = Receiving tray in Main Fractionator
SMF = Sending tray in Main Fractionator

Figure 32: Side-Strippers Stages

Sending Tray (SMF)

Using the nomenclature of Figure 32.

$$v_{ij}\left(1+\frac{W_j}{V_j}\right)+l_{ij}\left(1+\frac{U_j}{L_j}\right)+SS_j\,X_{ij}$$

$$-l_{i,j-1}-v_{i,j+1}+\beta_j\,K_{ij}^{D}\,l_{ij}=f_{ij}$$

Following the same procedure as before with j = SMF

$$-l_{i,j-1}+\left[RL_j+E_j\,\alpha_{ij}\,S_b\,S_{rj}\,RV_j+\beta_j\,K_{ij}^{D}\right.$$

$$\left.+\frac{SS_j}{L_j}\right]l_{ij}-\left[E_{j+1}\,\alpha_{i,j+1}\,S_b\,S_{rj+1}\right]l_{i,j+1}=f_{ij} \qquad (13)$$

The energy balance is given by

$$L_{j-1}\,h_{j-1}+V_{j+1}\,H_{j+1}-(V_j+W_j)H_j$$

$$-(L_j+U_j+SS_j)h_j+F_j\,HF_j+Q_j-\overset{"}{L}_j\,h_w=0 \qquad (14)$$

Top Tray in Side Stripper (TSS)

$$v_{ij}\left(1+\frac{W_j}{V_j}\right)+l_{ij}\left(1+\frac{U_j}{L_j}\right)-l_{i,j-1}$$

$$-v_{i,j+1}+\overset{"}{l}_{ij}=f_{ij}$$

where j = TSS. For this case however

$$l_{i,j-1}=SS_{SMF}\,X_{i,SMF}=SS_{SMF}\,\frac{l_{i,SMF}}{L_{SMF}}$$

Substituting this expression in the previous one, and proceeding as before, the following expression is obtained

$$[RL_j + E_j \alpha_{ij} S_b S_{rj} RV_j + \beta_j \overset{D}{K}_{ij}]l_{ij} - [E_{j+1} \alpha_{i,j+1} S_b S_{rj+1}]l_{i,j+1} - \left(\frac{SS_{SMF}}{L_{SMF}}\right) x\ l_{i,SMF} = f_{ij} \quad (15)$$

the energy balance is given by

$$SS_{SMF}\ h_{SMF} + V_{j+1}\ H_{j+1} - (V_j + W_j)H_j - (L_j + U_j)h_j + F_j\ HF_j + Q_j - \overset{''}{L}_j\ h_w = 0 \quad (16)$$

where j = TSS.

Receiving Tray in Main Fractionator (RMF)

$$v_{ij}\left(1 + \frac{W_j}{V_j}\right) + l_{ij}\left(1 + \frac{U_j}{L_j}\right) - l_{i,j-1} - v_{i,j+1} + \overset{''}{l}_{ij} = f_{ij} + v_{i,TSS}$$

Proceeding as before

$$- l_{i,j-1} + [RL_j + E_j \alpha_{ij} S_b S_{rj} RV_j + \beta_j \overset{D}{K}_{ij}]l_{ij} [E_{j+1} \alpha_{i,j+1} S_b S_{rj+1}]\ l_{i,j+1} - [E_{TSS} \alpha_{i,TSS} S_b S_{rTSS}]l_{i,TSS} = f_{ij} \quad (17)$$

and the energy balance is given by

$$L_{j-1}\ h_{j-1} + V_{j+1}\ H_{j+1} + V_{TSS}\ H_{TSS} - (V_j + W_j)H_j - (L_j + U_j)\ h_j + F_j\ HF_j + Q_j - \overset{''}{L}_j\ h_w = 0 \quad (18)$$

where j = RMF.

APPENDIX B

INITIAL PROFILES

It is necessary to somehow generate initial profiles for the compositions, flow rates and temperatures in order to calculate the initial value of the outer loop variables, (local model parameters) and inner loop variables (stripping factors). The procedure used consists of two parts, the first which results in preliminary estimates, and a second one which generates more refined estimates.

Preliminary Estimates

It is assumed that the pressure profile is known. In this work, a linear pressure profile is calculated based on the user supplied information. An initial temperature profile is obtained by linear interpolation between the two estimates supplied by the user, the top and bottom temperatures. These temperatures become the reference temperatures, T^*, in which to base the relations for the enthalpy departure functions.

A composite feed is formed by adding together all the feed streams. A single stage flash calculation of this composite feed is performed at the median temperature and pressure. Preliminary estimates of the equilibrium ratios

are obtained using the vapor and liquid compositions from the flash calculation, the linear temperature profile and the known pressure profile. These equilibrium ratios are taken as the initial estimates of the volatility parameters, and the initial Kb's are all taken as unity.

The liquid flow rates are calculated from a constant molar overflow liquid balance around each stage, and the vapor rates are calculated from similar vapor phase balances. Finally, the stripping factors and withdrawal factors are calculated from the following expressions:

$$S_j = K_{bj}\ V_j/L_j \tag{1}$$

$$S_b = \left(\Pi\ S_j\right)^{1/n} \tag{2}$$

$$S_{rj} = \frac{S_j}{S_b} \tag{3}$$

$$RL_j = 1 + U_j/L_j \tag{4}$$

$$RV_j = 1 + W_j/V_j \tag{5}$$

Refined Estimates

Using the preliminary estimates for the volatility parameters, stripping and withdrawal factors, the component mol balances are solved to obtain the component molar flow rates. Then, liquid and vapor compositions are calculated.

Based on these compositions, and the current temperatures and pressures, the equilibrium ratios and enthalpy departure functions are evaluated. The coefficients A_j and B_j of the K_b-models are then

calculated, and the K_b's evaluated from the next expression.

$$K_{bj} = \exp \{A_j - B_j/T_j\} \qquad (6)$$

Using these K_b values, and the constant molar overflow estimate of the vapor and liquid flow rates, refined estimates of the stripping factors are obtained from equations (1) to (3).

The parameters of the enthalpy departure functions are evaluated with the current value of the variables as indicated in Chapter II.

APPENDIX C

LIQUID-LIQUID EQUILIBRIUM IN A TRAY WITH A WATER SIDE DRAW

The overall liquid compositions for a tray with a side draw are described by the following expressions:

$$\bar{L}\,\bar{X}_{ij} = (L_j' + U_j)\,x_{ij} + L_j''\,X_{ij}'' \tag{1}$$

$$\bar{L} = L_j' + U_j' + L_j'' \tag{2}$$

Combining equation (1) and (2):

$$\left(1 + \frac{U_j}{L_j''} + \frac{L_j''}{L_j'}\right)\bar{X}_{ij} = \left(1 + \frac{U_j''}{L_j'}\right)x_{ij} + \frac{L_j''}{L_j'}\,X_{ij}'' \tag{3}$$

Defining:

$$\beta_j = \frac{L_j''}{L_j'} \tag{4}$$

$$RL_j = 1 + \frac{U_j'}{L_j'} \tag{5}$$

And using the L-L equilibrium relationship:

$$X''_{ij} = \left(\frac{K'_{ij}}{K''_{ij}}\right) X_{ij} = K^{D}_{ij}\, X_{ij} \qquad (6)$$

Substituting (4), (5), and (6) in equation (3), an expression for the liquid composition in the HC phase is obtained:

$$X_{ij} = \frac{(RL_j + \beta_j)\ \bar{X}_{ij}}{(RL_j + \beta_j\ K^{D}_{ij})} \qquad (7)$$

Similarly, the liquid composition in the water-rich phase is given by:

$$X''_{ij} = \frac{K^{D}_{ij}\ (RL_j + \beta_j)\ \bar{X}_{ij}}{(RL_j + \beta_j\ K^{D}_{ij})} \qquad (8)$$

The "flash" equation is obtained from:

$$\sum_i X_{ij} - \sum_i X''_{ij} = 0 \qquad (9)$$

Substituting (7) and (8).

$$\sum_{i=1}^{NC} \frac{(RL_j + \beta_j)\ (1 - K^{D}_{ij})\ \bar{X}_{ij}}{(RL_j + \beta_j\ K^{D}_{ij})} = 0 \qquad (10)$$

Once equation (10) is solved for β_j, the other variables are calculated from the following expressions:

$$L_j' = \frac{\bar{L}_j}{RL_j + \beta_j} \tag{11}$$

$$L_j'' = \beta_j \, L_j' \tag{12}$$

$$U_j' = \bar{L} - L_j' - L_j'' \tag{13}$$

Besides, the liquid compositions are obtained from equations (7) and (8).

APPENDIX D

SCALING PROCEDURES

In this appendix, the particular procedures to do the scaling of the stripping factors are presented. The specific procedure depends upon the type of tower.

Distillation Towers

The procedure described by Boston and Sullivan (1974) is chosen for this type of towers.

The component liquid flow rates resulting from the solution of the component mass balances, depend on the value of the scaling parameters Sb. However, these results always satisfy the overall total balance regardless of the value of Sb.

$$\overset{c}{U_1} + \overset{c}{L_N} = \sum_{k=1}^{NF} F_k \tag{1}$$

where

$$\overset{c}{L_N} = \sum_{j=1}^{c} l_{iN} \tag{2}$$

$$\overset{c}{U_1} + \overset{c}{L_1} \; (RL_1 - 1) \tag{3}$$

here L_N and U_1 are the calculated values. The standard specifications usually provide the values L_1, U_1 and L_N. Thus, the overall balance equation

$$U_1 + L_N = \sum_{k=1}^{NF} F_k \tag{4}$$

is also satisfied. However, no restraint has been imposed which requires either $U_1^c = U_1$ or $L_N^c = L_N$. The S_b value could be determined to force the last condition to be satisfied.

Boston warns that numerical difficulties arise because the sensitivity of L_N^c to changes in S_b is rather small. He proposed the following modification to the previous procedure.

The components of the feeds are first ordered according to the relative volatilities and all the least volatile components for which the combined feed rates equals precisely the bottom product rate L_N are designated as "heavy" components. The remaining components are the "light" components:

$$U_1^{hc} + L_N^{hc} = \sum_{k=1}^{N} F_k^h \tag{5}$$

The criterion $L_N^c = L_N$ for the determination of S_b is now written in terms of light and heavy components

$$L_N^{lc} = L_N + L_N^{hc} \tag{6}$$

Solving equation (5) for L_N^{hc}, substituting the result in (6) and using the definition of heavies, the final result is:

$$L_N^{lc} = U_1^{hc} \tag{7}$$

For the general case with liquid and vapor withdrawals, the final working equation is

$$L_N^{lc} + W_N^{lc} + \sum_{k=N+1}^{n=1} (U_k^{lc} + W_k^{lc}) = U_1^{hc} + V_1^{hc}$$

$$+ \sum_{k=2}^{\bar{N}} (U_k^{hc} + W_k^{hc}) \tag{8}$$

where N is the number of stage and $\bar{N}$ was selected to divide the column in two equal segments.

Equation (8) is implemented by defining the error as:

$$e = \frac{\text{(LEFT SIDE) - (RIGHT SIDE)}}{\text{(RIGHT SIDE)}} = 0 \tag{9}$$

The secant method is used in this work to iterate in the value of S_b until equation (9) is satisfied within a certain tolerance, that for this work is 10^{-6}.

For the case of partial condensers, Boston recommends the use of two scaling factors S_b and S_{b1}. They are chosen as two satisfy simultaneously two criteria consistent of equation (9) and the next one

$$e1 = \frac{V_1^c/L_1^c - V_1/L_1}{V_1/L_1} = 0 \qquad (10)$$

A nested secant method is used in this work for this purpose.

Reboiled-Absorbers

For this type of towers, the value of S_b is determined to satisfy the criterion

$$e = \frac{(V_1^c - V_1)}{V} = 0 \qquad (11)$$

as originally suggested by Boston (1970). Again, the procedure is converged with the secant method.

Absorbers

Boston (1970) proposed the use of the overall energy balance to determine the value of S_b. However his equations are found to be a little cumbersome. Instead, the straight form of the overall energy balance is used here:

$$\sum_{j=1}^{N} Q_j + \sum_{k=1}^{NF} F_k \, HF_k = V_1 \, H_1 + L_N \, H_N$$

$$+ \sum_{j=1}^{N} U_j \, h_j + \sum_{j=1}^{N} W_j \, H_j \qquad (12)$$

The local models of Chapter II are used to calculate the molar enthalpies of the streams.

Again, the secant method is used to iterate on S_b until the criterion below is satisfied within a tolerance

$$e = \frac{\text{(Left side of 12) - (RIGHT SIDE)}}{\text{(Left Side)}} = 0 \qquad (13)$$

Refluxed-Absorbers

After experimenting with several criteria, the following one seems to do a good job.

$$e = \frac{(L_1^c - L_1^{specs})}{L_1^{specs}} = 0 \qquad (14)$$

If specifications are such that the value of L_1 is completely specified, the criteria above is used directly.

Very often however, the specifications for this type of towers (crude towers in particular) are such that L_1 is not specified. In such a case, on independent estimate of L_1 is obtained from the iteration variables.

$$L_1^{specs} = \frac{U_1}{\{RL_1 - 1\}} \qquad (15)$$

Where RL_1 is an inner loop variable and U_1 can be a tower specification. If not, the current value of U_1 is taken for the purpose of using (15).

Like before, the secant method is used to iterate in S_b until (14) is satisfied. If the condenser is a partial condenser, a second scaling factor for stage 1 is introduced, and the criteria given for equation (10) added to the problem.

APPENDIX E

VALIDATION OF THERMODYNAMIC PACKAGE

The thermodynamic package of CRUDESIM was extensively checked against the one in MAXISIM, a process flowsheet simulator developed at Oklahoma State University, for a period of time.

In this Appendix, some typical comparisons are done. The first case is a mixture of defined components. Table E-1 shows the results of a FLASH calculation with MAXISIM. Table E-2 shows the same results as obtained in CRUDESIM. As can be seen the agreement is excellent. Table E-3 presents some comparisons with regard to enthalpy calculations. Again, the agreement is very good.

The second case is a mixture of pseudo-component obtained from characterizing a given petroleum fraction. Table E-4 shows the results of a Flash calculation with MAXISIM. Table E-5 presents the same calculation as done by CRUDESIM, and Table E-6 shows a comparison of the enthalpies. As can be seen again, the agreement is excellent.

TABLE E-1

FLASH CALCULATION WITH MAXISIM
(Case 1)

SCI MAXISIM JOB ID:2
VERSION #2.2 DATE: 30-MAY-1991
PAGE 1 USER: ELA

ENTHALPY DIFFERENCES

SK METHOD USED TO PREDICT THERMO PROPS
FLASH: VARY L/F; FIX T1;P1

TEMPERATURE = 47.25 DEG F, PRESSURE = 14.70 PSIA

FEED/PRODUCT RATES ARE LB-MOLS

Component Name	Feed Mols	Feed Mol Fr	Liquid Mols	Liquid Mol Fr	Vapor Mols	Vapor Mol Fr	K Value
CH_4	12.23	0.1701	0.03	0.0016	12.20	0.2404	152.14857
C_2H_6	10.60	0.1474	0.19	0.0091	10.40	0.2051	22.51781
C_3H_8	8.15	0.1133	0.57	0.0269	7.58	0.1494	5.55019
IC_4H_{10}	8.39	0.1166	1.42	0.0672	6.96	0.1372	2.04094
NC_4H_{10}	7.66	0.1065	1.79	0.0844	5.88	0.1158	1.37253
IC_5H_{12}	6.92	0.0963	3.17	0.1500	3.75	0.0739	0.49257
NC_5H_{12}	5.96	0.0829	3.21	0.1518	2.75	0.0541	0.35664
NC_6H_{14}	5.00	0.0695	4.06	0.1918	0.94	0.0184	0.09607
NC_7H_{16}	4.00	0.0556	3.76	0.1778	0.24	0.0046	0.02615
NC_8H_{18}	3.00	0.0417	2.95	0.1393	0.05	0.0010	0.00719
Total	71.91	1.0000	21.17	1.0000	50.74	1.0000	
H;KBTU	242.80	3.377	-63.35	-2.993	306.15	6.024	
S;KBTU/R	4.78	0.067	1.47	0.069	3.32	0.065	
MOL WT	54.382		82.335		42.721		
D;LB/FT3			41.307		0.117		
MASS;LB	3910.5		1742.70		2167.70		

MOL % VAP= 70.56; WT 70.56; WT % VAP= 55.43;
VOL % LIQ = 0.23

TABLE E-2

FLASH CALCULATION WITH CRUDESIM
(Case 1)

Component Name	Feed Mols	Feed Mol Fr	Liquid Mols	Liquid Mol Fr	Vapor Mols	Vapor Mol Fr	K Value
CH_4	12.23	0.1701	0.03	0.0016	12.20	0.2405	154.51461
C_2H_6	10.60	0.1471	0.19	0.0091	10.40	0.2051	22.46712
C_3H_8	8.15	0.1133	0.57	0.0268	7.58	0.1494	5.57562
IC_4H_{10}	8.39	0.1166	1.41	0.0667	6.97	0.1375	2.06122
NC_4H_{10}	7.66	0.1065	1.77	0.0838	5.89	0.1160	1.38447
IC_5H_{12}	6.92	0.0963	3.19	0.1509	3.73	0.0735	0.48726
NC_5H_{12}	5.96	0.0829	3.23	0.1524	2.73	0.0539	0.35363
NC_6H_{14}	5.00	0.0695	4.05	0.1915	0.94	0.0186	0.09695
NC_7H_{16}	4.00	0.0556	3.77	0.1780	0.23	0.0046	0.02574
NC_8H_{18}	3.00	0.0417	2.95	0.1393	0.05	0.0010	0.00720

TABLE E-3

ENTHALPY COMPARISON
(Case 1)

CASE	MAXISIM (btu/lb-mol)	CRUDESIM (btu/lb-mol)	DIFFERENCES (%)
$\Delta H \Big\vert_{48.0}^{14.7}$	4.676	4.668	-0.17
$\Delta H \Big\vert_{70.0}^{47.2}$	1.637	1.629	0.5

Note: The first case involves the calculation of ΔH for a mixture at constant T from 14.7 psia to 480 psia. The second case involves the calculation of ΔH for a mixture at constant P from 47.2 °F to 70 °F. The mixture is the same one described in Table E-1.

TABLE E-4

FLASH CALCULATION WITH MAXISIM
(Case 2)

Component Name	Feed Mols	Feed Mol Fr	Liquid Mols	Liquid Mol Fr	Vapor Mols	Vapor Mol Fr	K Value
FRAC 1	0.10	0.1000	0.00	0.0076	0.10	0.1566	20.57554
FRAC 2	0.10	0.1000	0.00	0.0112	0.10	0.1544	13.78982
FRAC 3	0.10	0.1000	0.01	0.0159	0.09	0.1515	9.54795
FRAC 4	0.10	0.1000	0.01	0.0229	0.09	0.1472	6.43099
FRAC 5	0.10	0.1000	0.01	0.0362	0.09	0.1391	3.83689
FRAC 6	0.10	0.1000	0.02	0.0633	0.08	0.1225	1.93661
FRAC 7	0.10	0.1000	0.05	0.1224	0.05	0.0863	0.7052
FRAC 8	0.10	0.1000	0.08	0.2069	0.02	0.0345	0.16694
FRAC 9	0.10	0.1000	0.10	0.2518	0.00	0.0070	0.02770
FRAC 10	0.10	0.1000	0.10	0.2619	0.00	0.0008	0.00314
Total	1.00	1.0000	0.38	1.0000	0.62	1.0000	

H;KBTU	54.3554.354	23.5261.906	30.8449.727
S;KBTU/R	0.12 0.121	0.06 0.161	0.06 0.097
MOL WT	203.786	297.883	146.134
D;LB/FT3		45.386	0.214
MASS;LB	203.8	113.2	90.6

MOL % VAP= 62.01;WT % VAP= 44.47;VOL % LIQ = 0.59

TABLE E-5

FLASH CALCULATION WITH CRUDESIM
(Case 2)

Component Name	Feed Mols	Feed Mol Fr	Liquid Mols	Liquid Mol Fr	Vapor Mols	Vapor Mol Fr	K Value
FRAC 1	0.10	0.1000	0.00	0.0076	0.10	0.1566	20.56764
FRAC 2	0.10	0.1000	0.00	0.0112	0.10	0.1544	13.79267
FRAC 3	0.10	0.1000	0.01	0.0159	0.09	0.1515	9.54403
FRAC 4	0.10	0.1000	0.01	0.0229	0.09	0.1472	6.43103
FRAC 5	0.10	0.1000	0.01	0.0362	0.09	0.1391	3.83774
FRAC 6	0.10	0.1000	0.02	0.0633	0.08	0.1225	1.93604
FRAC 7	0.10	0.1000	0.05	0.1224	0.05	0.0863	0.70481
FRAC 8	0.10	0.1000	0.08	0.2068	0.02	0.0345	0.16694
FRAC 9	0.10	0.1000	0.10	0.2518	0.00	0.0070	0.02767
FRAC 10	0.10	0.1000	0.10	0.2618	0.00	0.0008	0.00313
Total	1.00	1.0000	0.38	1.0000	0.62	1.0000	

TABLE E-3

ENTHALPY COMPARISON
(Case 1)

CASE	MAXISIM (btu/lb-mol)	CRUDESIM (btu/lb-mol)	DIFFERENCES (%)
$\Delta H \Big\vert_{14.7}^{50}$	5.224	5.230	0.115
$\Delta H \Big\vert_{600}^{600}$	17.782	17.870	0.495

Note: The mixture is the same one described in Table E-4. The first case involves the calculation of ΔH when taking the mixture from 14.7 psia to 50 psia at constant temperature. The second case involves the calculation of ΔH when taking the mixture from 500 °F to 600 °F at constant pressure.

APPENDIX F

SAMPLE OUTPUT FOR VLE OPTION IN PERFORMANCE MODE

SUMMARY OF RESULTS

	%RMSE	AAD	APD	BIAS
X(1) :	2.93173	.00523	2.17058	-.00135
X(2) :	2.96915	.00523	1.59247	.00135
Y(1) :	.17184	.00121	.12583	.00088
Y(2) :	5.16333	.00121	3.59984	-.00088
K(1) :	3.04504	.14969	2.21347	.14541
K(2) :	3.25670	0.00255	2.80573	-.00231
D.LIQ :	.00000	.00000	.00000	.00000
D.VAP :	.00000	.00000	.00000	.00000

PRESS ANY KEY TO CONTINUE

Figure 33: Output Sample 1

S-R-K EQUATION OF STATE
PREDICTIONS DEMO #3

DATA	TEMP	PRESS	YEXP(I)	YCAL(I)	DEVE	%DEV
1	280.00	49.99	.8903	.8888	-.0015	-.17
2	280.00	100.00	.9403	.9408	.0005	.05
3	280.00	149.99	.9571	.9579	.0008	.08
4	280.00	199.99	.9654	.9663	.0009	.09
5	280.00	299.99	.9737	.9742	.0005	.05
6	280.00	400.00	.9766	.9776	.0010	.10
7	280.00	599.99	.9770	.9787	.0017	.17
8	280.00	800.00	.9671	.9712	.0041	.42
9	280.00	872.99	.9283	.9283	.0000	.00

KIJ = .0000

KIJ = .0000

%RMSE = .1718 AAD = .0012 %AAD = .13
BIAS = .0009 NPTS = 9

PRESS ANY KEY TO CONTINUE

Figure 34: Output Sample 2

APPENDIX G

TEST PROBLEM 1: DISTILLATION

TABLE G-1

TEST PROBLEM 1: DISTILLATION RESULTS

Stage	Temp. degree F.	Molar Flow Rates Liquid	Vapor
1	25.94	30.6	30.6
2	66.98	31.1	61.1
3	81.71	30.0	61.7
4	92.78	28.3	60.6
5	104.86	25.0	58.9
6	126.64	104.8	55.6
7	169.33	121.1	63.4
8	187.07	126.8	79.8
9	198.68	129.0	85.5
10	210.14	128.6	87.7
11	225.57	123.0	87.2
12	256.43	41.3	81.6

TABLE G-2

ITERATION SUMMARY

Iteration	Heat and Spec Errors	Local Mod. Errors
1	.8393E-02 in 1 iter	.1872E-01
2	.6459E-03 in 2 iter	.7571E-02
3	.1910E-03 in 3 iter	.4884E-02
4	.2877E-03 in 2 iter	.1339E-02
5	.1109E-03 in 1 iter	.5825E-03
6	.4778E-04 in 1 iter	.1669E-03

TABLE G-3

SIMPLE DISTILLATION UNIT

Global Variables

Stage	Press Psia	Temp. Degree F	Molar Flow Rates Liquid	Vapor	Feed	Heat Duty BTU/HR
1	200.00	25.77	30.58	30.58	.00	-.2257E+06
2	200.45	66.88	31.18	61.16	.00	.0000E+00
3	200.91	81.82	30.06	61.76	.00	.0000E+00
4	201.36	92.92	28.41	60.65	.00	.0000E+00
5	201.82	104.89	25.09	59.00	.00	.0000E+00
6	202.27	126.46	105.65	55.67	71.91	.0000E+00
7	202.73	168.80	122.17	64.33	.00	.0000E+00
8	203.18	186.18	127.95	80.84	.00	.0000E+00
9	203.64	197.84	130.13	86.62	.00	.0000E+00
10	204.09	209.05	129.61	88.81	.00	.0000E+00
11	204.55	224.51	123.74	88.29	.00	.0000E+00
12	205.00	255.71	41.32	82.42	.00	.7284E+06

Products Report

	Vapor From Stage 1 Lbmol/hr	Mol fraction	Liquid From Stage 12 Lbmol/hr	Mol fraction
CH4	12.233	.4000E+00	.000	.8434E-07
C2H6	10.594	.34643+00	.004	.1017E-03
C3H8	7.322	.2394E+00	.826	.1999E-01
I-C4H10	.385	.1257E-01	8.000	.1936E+00
N-C4H10	.049	.1603E-02	7.612	.1842E+00
I-C5H12	.000	.6966E-05	6.924	.1676E+00
N-C5H12	.000	.1353E-05	5.961	.1443E+00
N-C6H14	.000	.2170E-08	4.996	.1209E+00
N-C7H16	.000	.3149E-11	4.000	.9680E-01
N-C8H18	.000	.5313E-14	3.000	.7260E-01

APPENDIX H

TEST PROBLEM 2: DISTILLATION WITH A PUMP-AROUND

TABLE H-1

ITERATION SUMMARY NO PUMP-AROUND

Iteration	Heat and Spec Errors	Local Mod. Errors
1	.3649E-03 in 1 iter	.7942E-02
2	.1403E-03 in 1 iter	.7496E-03
3	.1997E-03 in 1 iter	.5497E-04

TABLE H-2

Products Report

	Liquid From Stage 1		Liquid From Stage 20	
	Lbmol/hr	Mol fraction	Lbmol/hr	Mol fraction
C3H8	308.379	.9411E+00	16.621	.9646E-01
I-C4H10	13.860	.4230E-01	36.140	.20973+00
N-C4H10	5.420	.1654E-01	44.580	.2587E+00
N-C5H12	.031	.9359E-04	74.969	.4351E+00

TABLE H-3

SIMULATION WITH NO PUMP-AROUND

Stage	Press Psia	Temp. Degree F	Molar Flow Rates Liquid	Vapor	Feed	Heat Duty BTU/HR
1	300.00	140.35	399.78	.00	.00	-.3684E+07
2	300.00	143.50	396.72	727.47	.00	.0000E+00
3	300.00	146.48	390.86	724.41	.00	.0000E+00
4	300.00	149.20	385.35	718.55	.00	.0000E+00
5	300.00	151.67	380.71	713.04	.00	.0000E+00
6	300.00	154.01	373.97	708.40	.00	.0000E+00
7	300.00	156.44	365.56	701.66	.00	.0000E+00
8	300.00	159.34	354.57	693.25	.00	.0000E+00
9	300.00	163.24	339.00	682.26	.00	.0000E+00
10	300.00	168.58	837.67	666.69	500.00	.0000E+00
11	300.00	169.96	834.53	665.36	.00	.0000E+00
12	300.00	172.03	831.51	662.22	.00	.0000E+00
13	300.00	175.12	827.40	659.20	.00	.0000E+00
14	300.00	179.57	821.48	655.09	.00	.0000E+00
15	300.00	185.72	815.87	649.17	.00	.0000E+00
16	300.00	193.90	809.32	643.56	.00	.0000E+00
17	300.00	204.38	802.32	637.01	.00	.0000E+00
18	300.00	217.55	794.33	630.01	.00	.0000E+00
19	300.00	233.89	785.66	622.02	.00	.00003+00
20	300.00	253.49	172.31	613.35	.00	.4042E+07

TABLE H-4

ITERATION SUMMARY PUMP-AROUND:
80 LB-MOL/HR

Iteration	Heat and Spec Errors	Local Mod. Errors
1	.2369E-02 in 1 iter	.6952E-02
2	.3617E-04 in 1 iter	.4571E-02
3	.3883E-03 in 1 iter	.1151E-03

TABLE H-5

PRODUCTS REPORT

	Liquid From Stage 1		Liquid From Stage 20	
	Lbmol/hr	Mol fraction	Lbmol/hr	Mol fraction
C3H8	300.958	.9172E+00	24.042	.13993+00
I-C4H10	17.976	.5478E-01	32.024	.1863E+00
N-C4H10	8.834	.2692E-01	41.166	.2395E+00
N-C5H12	.364	.1111E-02	74.636	.4343E+00

TABLE H-6

SIMULATION WITH PUMP-AROUND

Stage	Press Psia	Temp. Degree F	Molar Flow Rates Liquid	Vapor	Feed	Heat Duty BTU/HR
1	300.00	142.08	400.32	.00	.00	-.3726E+07
2	300.00	146.77	382.16	728.45	.00	.0000E+00
3	300.00	151.31	378.23	710.30	.00	.0000E+00
4	300.00	155.89	362.71	706.36	.00	.0000E+00
5	300.00	160.59	442.13	690.84	.00	.0000E+00
					80.24 PP	
6	300.00	160.90	439.77	690.03	.00	.0000E+00
7	300.00	161.46	437.42	687.66	.00	.0000E+00
8	300.00	162.54	431.70	685.32	.00	.0000E+00
9	300.00	164.57	419.51	679.60	.00	.0000E+00
10	300.00	168.21	918.38	667.40	500.00	.0000E+00
11	300.00	168.69	916.43	666.28	.00	.0000E+00
12	300.00	169.47	916.68	664.32	.00	.0000E+00
13	300.00	170.84	912.82	664.58	.00	.0000E+00
14	300.00	173.10	909.02	660.72	.00	.0000E+00
15	300.00	176.86	902.76	656.92	.00	.0000E+00
16	300.00	182.98	811.12	650.66	.00	.0000E+00
					-80.24 PP	
17	300.00	192.67	800.40	639.25	.00	.0000E+00
18	300.00	206.37	783.86	628.53	.00	.0000E+00
19	300.00	224.81	770.11	611.99	.00	.0000E+00
20	300.00	247.83	171.87	598.25	.00	.4021E+07

TABLE H-7

ITERATION SUMMARY PUMP-AROUND:
450 LB-MOL/HR

Iteration	Heat and Spec Errors	Local Mod. Errors
1	.4219E-02 in 1 iter	.1039E-01
2	.6610E-03 in 4 iter	.1839E-02
3	.2391E-03 in 4 iter	.1146E-03

TABLE H-8

PRODUCTS REPORT

	Liquid From Stage 1		Liquid From Stage 20	
	Lbmol/hr	Mol fraction	Lbmol/hr	Mol fraction
C3H8	293.887	.8953E+00	31.113	.1811E+00
I-C4H10	21.397	.6519E-01	28.603	.1665E+00
N-C4H10	11.975	.3648E-01	38.025	.2214E+00
N-C5H12	.986	.3005E-02	74.014	.4309E+00

TABLE H-9

SIMULATION WITH PUMP-AROUND OF
450 LB-MOL/HR

Stage	Press Psia	Temp. Degree F	Molar Flow Rates Liquid	Vapor	Feed	Heat Duty BTU/HR	
1	300.00	143.74	400.46	.00	.00	-.3776E+07	
2	300.00	150.01	384.03	728.70	.00	.0000E+00	
3	300.00		3	300.00	156.34	367.00	712.28
4	300.00	162.83	348.79	695.24	.00	.0000E+00	
5	300.00	169.75	796.41	677.03	.00	.0000E+00	
					449.88 PP		
6	300.00	169.59	793.59	674.77	.00	.0000E+00	
7	300.00	169.28	794.84	671.96	.00	.0000E+00	
8	300.00	168.98	794.13	673.21	.00	.0000E+00	
9	300.00	168.58	790.41	672.50	.00	.0000E+00	
10	300.00	169.62	1290.60	668.78	500.00	.0000E+00	
11	300.00	169.67	1289.52	668.97	.00	.0000E+00	
12	300.00	169.74	1290.53	667.89	.00	.0000E+00	
13	300.00	169.99	1289.21	668.90	.00	.0000E+00	
14	300.00	170.52	1289.42	667.58	.00	.0000E+00	
15	300.00	171.69	1288.12	667.79	.00	.0000E+00	
16	300.00	175.49	824.05	666.49	.00	.0000E+00	
					-449.88 PP		
17	300.00	184.01	807.18	652.30	.00	.0000E+00	
18	300.00	197.22	784.37	635.42	.00	.0000E+00	
19	300.00	216.62	761.97	612.62	.00	.0000E+00	
20	300.00	242.20	171.76	590.21	.00	.4018E+07	

APPENDIX I

TEST PROBLEM 2: ABSORTIONS

TABLE I-1

GLOBAL VARIABLES

Stage	Press Psia	Temp. Degree F	Molar Flow Rates Liquid	Vapor	Feed	Heat Duty BTU/HR
1	300.00	118.13	26.22	86.60	20.00	.0000E+00
2	300.00	124.60	27.10	92.81	.00	.0000E+00
3	300.00	127.15	27.47	93.69	.00	.0000E+00
4	300.00	127.87	27.74	94.07	.00	.0000E+00
5	300.00	127.06	28.06	94.34	.00	.0000E+00
6	300.00	124.22	28.57	94.66	.00	.0000E+00
7	300.00	118.06	29.69	95.17	.00	.0000E+00
8	300.00	104.49	33.40	96.28	100.00	.0000E+00

TABLE I-2

PRODUCTS REPORT

	Liquid From Stage 1 Lbmol/hr	Mol fraction	Liquid From Stage 20 Lbmol/hr	Mol fraction
CH4	67.472	.7792E+00	2.528	.7568E-01
C2H6	12.647	.1460E+00	2.353	.7044E-01
C3H8	5.725	.6612E-01	4.275	.1280E+00
I-C4H10	.369	.4258E-02	3.631	.1087E+00
N-C5H12	.000	.2358E-05	1.000	.2993E-01
N-C8H18	.383	.4424E-02	19.617	.5873E+00

APPENDIX J

TEST PROBLEM 4: REBOILED-ABSORTION

Two cases were simulated for this reboiled-absorber, the difference being the tower specification given:

Case 1: V_1 = 73.537 mol/hr

Case 2: $Q_r = 3.0 \times 10^{-6}$ btu/hr

TABLE J-1

ITERATION SUMMARY: CASE 1

Iteration	Heat and Spec Errors	Local Mod. Errors
1	.2293E+00 in 1 iter	.2242E+00
2	.1105E+00 in 3 iter	.5025E-01
3	.2924E-02 in 6 iter	.1634E+00
4	.1784E-03 in 9 iter	.1474E-01
5	.1128E-03 in 6 iter	.1711E-02
6	.7918E-04 in 5 iter	.2222E-03

TABLE J-2

PRODUCTS REPORT: CASE 1

	Liquid From Stage 1		Liquid From Stage 11	
	Lbmol/hr	Mol fraction	Lbmol/hr	Mol fraction
CH4	64.830	.8816E+00	.170	.1341E-02
C2H6	8.422	.1145E+00	4.578	.3620E-01
C3H8	.026	.3516E-03	.974	.7703E-02
I-C4H10	.000	.5701E-05	1.000	.7904E-02
N-C5H12	.000	.4786E-07	20.000	.1582E+00
N-C8H18	.262	.3564E-02	99.738	.7887E+00

TABLE J-3

GLOBAL VARIABLES: CASE 1

Stage	Press	Temp.	Molar Flow Rates			Heat Duty
	Psia	Degree F	Liquid	Vapor	Feed	BTU/HR
1	300.00	107.57	116.47	73.54	100.00	.0000E+00
2	300.00	109.63	118.71	90.01	.00	.0000E+00
3	300.00	111.04	119.95	92.25	.00	.0000E+00
4	300.00	113.55	120.89	93.49	.00	.0000E+00
5	300.00	122.75	123.63	94.43	.00	.0000E+00
6	300.00	151.05	141.93	97.17	100.00	.0000E+00
7	300.00	155.14	147.52	15.47	.00	.0000E+00
8	300.00	168.11	159.70	21.06	.00	.0000E+00
9	300.00	221.07	184.32	33.24	.00	.0000E+00
10	300.00	347.16	252.31	57.86	.00	.0000E+00
11	300.00	454.29	126.46	125.85	.00	.2776E+07

TABLE J-4

ITERATION SUMMARY: CASE 2

Iteration	Heat and Spec Errors	Local Mod. Errors
1	.3317E-02 in 1 iter	.1274E-01
2	.5419E-02 in 1 iter	.9073E-02
3	.3405E-02 in 3 iter	.2367E-01
4	.5038E-04 in 2 iter	.7214E-02
5	.1806E-03 in 1 iter	.2434E-02
6	.1947E-03 in 1 iter	.5094E-03
7	.2046E-03 in 1 iter	.3889E-03

TABLE J-5

PRODUCTS REPORT: CASE 2

	Liquid From Stage 1		Liquid From Stage 11	
	Lbmol/hr	Mol fraction	Lbmol/hr	Mol fraction
CH4	64.950	.8524E+00	.050	.4037E-03
C2H6	10.928	.1434E+00	2.072	.1674E-01
C3H8	.040	.5210E-03	.960	.7757E-02
I-C4H10	.001	.7892E-05	.999	.8073E-02
N-C5H12	.000	.6819E-07	20.000	.1615E+00
N-C8H18	.281	.3685E-02	99.719	.8055E+00

TABLE J-6

GLOBAL VARIABLES: CASE 2

Stage	Press Psia	Temp. Degree F	Molar Flow Rates Liquid	Vapor	Feed	Heat Duty BTU/HR
1	300.00	108.80	117.83	76.20	100.00	.0000E+00
2	300.00	111.11	120.45	94.03	.00	.0000E+00
3	300.00	112.69	121.82	96.65	.00	.0000E+00
4	300.00	115.46	122.81	98.02	.00	.0000E+00
5	300.00	125.06	125.65	99.01	.00	.0000E+00
6	300.00	152.92	143.84	101.85	100.00	.0000E+00
7	300.00	164.71	156.39	20.03	.00	.0000E+00
8	300.00	205.30	180.25	32.59	.00	.0000E+00
9	300.00	305.29	233.40	56.45	.00	.0000E+00
10	300.00	411.63	333.88	109.60	.00	.0000E+00
11	300.00	475.09	123.80	210.08	.00	.3000E+02

APPENDIX K

TEST PROBLEM 5: ATMOSPHERIC CRUDE TOWER FROM HYSIM

TABLE K-1

CHARACTERISTICS OF C6-PLUS FRACTION (HYSIM OIL)

#	% Mid.Vol	TBP	API
1	0.6476	117.20	77.03
2	1.8935	156.25	58.60
3	2.9505	203.44	54.43
4	3.6639	221.23	53.83
5	5.2415	246.73	52.51
6	8.0767	282.13	50.06
7	11.4527	306.87	46.84
8	15.2806	339.57	43.58
9	19.2414	371.83	41.44
10	23.2070	403.93	39.65
11	27.0721	436.54	37.48
12	30.4819	468.72	35.36
13	33.3934	501.20	33.69
14	36.3053	533.77	32.43
15	39.7998	570.56	31.37
16	44.1585	601.08	30.17
17	48.7081	632.09	28.36
18	53.7998	682.11	26.35
19	59.5014	746.43	25.07
20	65.4367	806.53	23.76
21	71.8170	866.95	21.71
22	80.7546	965.15	14.88
23	89.4199	1115.78	3.91
24	94.2210	1270.97	-4.11
25	98.0341	1429.54	-11.51

Molecular weights are calcuated based on this information by the program.

TABLE K-2

LIGHT ENDS ANALYSIS

Component	Volume %
Propane	0.010
i-Butane	0.015
n-Butane	0.060
i-Pentane	0.120
n-Pentane	0.250

TABLE K-3

FEED COMPOSITION

Component	Mol Fraction (10^2)
H_2O	0.000
C_3	0.031
$i\text{-}C_4$	0.039
$N\text{-}C_4$	0.164
$i\text{-}C_5$	0.282
$N\text{-}C_5$	0.594
FRAC 1	3.127
FRAC 2	2.844
FRAC 3	1.931
FRAC 4	1.012
FRAC 5	4.883
FRAC 6	5.148
FRAC 7	6.082
FRAC 8	6.021
FRAC 9	5.750
FRAC 10	5.300
FRAC 11	4.794
FRAC 12	3.614
FRAC 13	6.308
FRAC 14	3.865
FRAC 15	4.392
FRAC 16	3.813
FRAC 17	4.716
FRAC 18	3.999
FRAC 19	4.107
FRAC 20	3.855
FRAC 21	6.326
FRAC 22	3.095
FRAC 23	1.865
FRAC 24	2.002

TABLE K-4

TOWER PROFILES

Stage	Press Psia	Temp. (F)	Molar Flow Rates Liquid	Vapor	Feed		Heat Duty BTU/HR
1	19.70	182.73	1423.87	.00	.00		-.6034E+08
2	24.70	323.39	1613.89	2775.22	.00		.0000E+00
3	24.98	359.59	1560.52	2965.24	.00		.0000E+00
4	25.26	381.15	1424.17	2911.87	.00		.0000E+00
					49.91	SS	
5	25.52	402.72	489.02	2725.62	.00		.0000E+00
					-740.48	SS	
6	25.81	430.85	397.95	2530.94	.00		.0000E+00
7	26.09	444.99	350.45	2439.87	.00		.0000E+00
8	26.37	452.53	312.79	2392.38	.00		.0000E+00
9	26.64	457.86	277.49	2354.71	.00		.0000E+00
10	26.92	462.71	3017.54	2319.41	.00		-.4000E+08
					1766.18	PP	
					152.47	SS	
11	27.20	501.51	750.65	3140.81	.00		.0000E+00
					-1766.18	PP	
					-527.70	SS	
12	27.48	541.90	667.74	3167.80	.00		.0000E+00
13	27.76	558.44	588.50	3084.89	.00		.0000E+00
14	28.03	568.70	478.00	3005.65	.00		.0000E+00
15	28.31	580.07	2466.76	2895.16	.00		-.4000E+08
					1340.86	PP	
					138.43	SS	
16	28.59	618.33	404.89	3404.62	.00		.0000E+00
					-1340.86	PP	
					-495.86	SS	
17	28.87	672.70	205.93	3179.48	.00		.0000E+00
18	29.14	697.37	72.97	2980.51	.00		.0000E+00
19	29.42	712.55	989.50	2847.55	3465.10		.4592E+08
20	29.70	701.23	884.75	298.99	194.23		.0000E+00
21	25.00	408.36	764.52	49.91	.00		.0000E+00
22	25.25	413.57	7782.01	73.95	.00		.0000E+00
23	25.50	424.43	690.57	91.44	.00		.2500E+07
24	27.00	491.14	488.26	152.47	.00		.0000E+00
25	27.50	484.30	466.03	113.03	.00		.0000E+00
26	28.00	474.53	430.72	90.80	55.49		.0000E+00
27	28.50	610.79	464.01	138.43	.00		.0000E+00
28	29.00	607.40	444.31	106.58	.00		.0000E+00
29	29.50	598.17	412.92	86.89	55.49		.0000E+00

TABLE K-5

PRODUCT COMPOSITION

	Liquid From Stage 1		Liquid From Stage 20	
	Lbmol/hr	Mol fraction	Lbmol/hr	Mol fraction
H_2O	4.931	.4646E-02	5.197	.5874E-02
C_3H_8	1.083	.1021E-02	.000	.2565E-06
i-C_4H_{10}	1.366	.1287E-02	.000	.5079E-06
N-C_4H_{10}	5.666	.5339E-02	.002	.2472E-05
i-C_5H_{12}	9.754	.9190E-02	.006	.6694E-05
N-C_5H_{12}	20.499	.1931E-01	.014	.1536E-04
FRAC 1	107.718	.1015E+00	.091	.1032E-03
FRAC 2	98.564	.9286E-01	.124	.1402E-03
FRAC 3	64.715	.6097E-01	.130	.1474E-03
FRAC 4	33.522	.3158E-01	.081	.9152E-04
FRAC 5	157.773	.1486E+00	.500	.5648E-03
FRAC 6	156.727	.1477E+00	.750	.8477E-03
FRAC 7	170.870	.1610E+00	1.157	.1307E-02
FRAC 8	133.886	.1261E+00	1.626	.1838E-02
FRAC 9	70.979	.6687E-01	2.197	.2483E-02
FRAC 10	19.871	.1872E-01	2.870	.3244E-02
FRAC 11	3.139	.2958E-02	3.729	.4215E-02
FRAC 12	.304	.2868E-03	4.031	.4556E-02
FRAC 13	.012	.1121E-04	12.140	.1372E-01
FRAC 14	.000	.2012E-07	12.993	.1469E-01
FRAC 15	.000	.2317E-09	20.259	.2290E-01
FRAC 16	.000	.9074E-12	24.109	.2725E-01
FRAC 17	.000	.2934E-16	47.422	.5360E-01
FRAC 18	.000	.2055E-23	66.567	.7524E-01
FRAC 19	.000	.6910E-31	99.133	.1120E+00
FRAC 20	.000	.2102E-39	119.818	.1354E+00
FRAC 21	.000	.1449E-54	218.556	.2470E+00
FRAC 22	.000	.2574E-80	107.246	.1212E+00
FRAC 23	.000	.1679-115	64.618	.7304E-01
FRAC 24	.00	.7157-152	69.379	.7842E-01

TABLE K-6

PRODUCT COMPOSITION

	Liquid From Stage 23		Liquid From Stage 26	
	Lbmol/hr	Mol fraction	Lbmol/hr	Mol fraction
H_2O	.001	.1088E-05	2.5224	.5860E-02
C_3H_8	.000	.9559E-07	.000	.3319E-08
$I\text{-}C_4H_{10}$	.000	.5399E-06	.000	.1616E-07
$N\text{-}C_4H_{10}$	.003	.3873E-05	.000	.1096E-06
$I\text{-}C_5H_{12}$	.019	.2721E-04	.000	.7315E-06
$N\text{-}C_5H_{12}$	.054	.7892E-04	.001	.2095E-05
FRAC 1	.519	.7512E-03	.009	.2114E-04
FRAC 2	1.190	.1723E-02	.025	.5731E-04
FRAC 3	1.991	.2883E-02	.060	.1382E-03
FRAC 4	1.418	.2053E-02	.050	.1162E-03
FRAC 5	10.386	.1504E-01	.470	.1090E-02
FRAC 6	19.535	.2829E-01	1.204	.2795E-02
FRAC 7	35.826	.5188E-01	2.582	.5995E-02
FRAC 8	67.187	.9729E-01	5.302	.1231E-01
FRAC 9	115.137	.1667E+00	9.791	.2273E-01
FRAC 10	142.368	.2062E+00	16.526	.3837E-01
FRAC 11	129.446	.1874E+00	26.399	.6129E-01
FRAC 12	83.112	.1204E+00	33.237	.7717E-01
FRAC 13	76.282	.1105E+00	112.236	.2606E+00
FRAC 14	5.448	.7890E-02	89.770	.2084E+00
FRAC 15	.623	.9016E-03	82.693	.1920E+00
FRAC 16	.028	.3993E-04	41.084	.9538E-01
FRAC 17	.000	.8772E-07	6.665	.1547E-01
FRAC 18	.000	.2649E-11	.097	.2247E-03
FRAC 19	.000	.4802E-16	.001	.2433E-05
FRAC 20	.000	.1536E-21	.000	.9317E-08
FRAC 21	.000	.1567E-31	.000	.2049E-12
FRAC 22	.000	.5509E-49	.000	.2941E-21
FRAC 23	.000	.1062E-72	.000	.3899E-33
FRAC 24	.000	.2615E-97	.000	.1789E-45

TABLE K-7

PRODUCT COMPOSITION

	Liquid From Stage 29		Liquid From Stage 1	
	Lbmol/hr	Mol fraction	Lbmol/hr	Mol fraction
H_2O	2.682	.6495E-02	289.964	.1000E+01
C_3H_8	.000	.2148E-08	.000	.2970E-06
$I\text{-}C_4H_{10}$	.000	.7849E-08	.000	.1793E-06
$N\text{-}C_4H_{10}$	.000	.4696E-07	.000	.5882E-06
$I\text{-}C_5H_{12}$	.000	.2347E-06	.000	.4747E-06
$N\text{-}C_5H_{12}$	.000	.6148E-06	.000	.7104E-06
FRAC 1	.002	.5507E-05	.000	.1533E-05
FRAC 2	.005	.11848-04	.002	.8344E-05
FRAC 3	.009	.2249E-04	.001	.3881E-05
FRAC 4	.007	.1749E-04	.000	.1451E-05
FRAC 5	.061	.1489E-03	.001	.4280E-05
FRAC 6	.143	.3470E-03	.001	.2487E-05
FRAC 7	.297	.7197E-03	.001	.3131E-05
FRAC 8	.607	.1469E-02	.001	.2276E-05
FRAC 9	1.149	.2783E-02	.000	.8846E-06
FRAC 10	2.023	.4898E-02	.000	.1712E-06
FRAC 11	3.395	.8222E-02	.000	.2292E-07
FRAC 12	4.528	.1097E-01	.000	.2074E-08
FRAC 13	17.907	.4337E-01	.000	.5527E-10
FRAC 14	25.719	.6229E-01	.000	.4287E-13
FRAC 15	48.621	.1177E+00	.000	.3659E-15
FRAC 16	66.916	.1621E+00	.000	.1940E-17
FRAC 17	109.330	.2648E+00	.000	.5274E-22
FRAC 18	71.917	.1742E+00	.000	.5413E-30
FRAC 19	43.176	.1046E+00	.000	.1573E-38
FRAC 20	13.770	.3335E-01	.000	.1421E-47
FRAC 21	.656	.1588E-02	.000	.3408E-59
FRAC 22	.000	.6058E-06	.000	.5958E-81
FRAC 23	.000	.2076E-06	.000	.6072-120
FRAC 24	.000	.5986E-15	.000	.8063-160

TABLE K-8

NON-STANDARD TBP FOR REDUCED CHARACTERIZATION

Liquid Vol. %	TBP (°F)
0	104.0
2	161.2
5	243.7
10	297.2
15	337.1
20	377.9
30	463.9
40	572.2
50	643.9
60	751.7
70	849.6
80	955.3
90	1131.9
95	1300.8
98	1428.0
100	1523.5

Bulk Properties:

Oil specific gravity: 0.900

Oil molecular weights: 246.294

TABLE K-9

TOWER PROFILES WITH REDUCED CHARATERIZATION (CASE A)

Stage	Press Psia	Temp. (°F)	Molar Flow Rates Liquid	Vapor	Feed		Heat Duty BTU/HR
1	19.70	191.22	1464.48	.00	.00		-.5822E+08
2	24.70	315.11	1565.38	2816.20	.00		.0000E+00
3	24.98	353.60	1498.24	2917.11	.00		.0000E+00
4	25.26	376.72	1359.96	2849.97	.00		.0000E+00
					50.74	SS	
5	25.52	399.60	394.44	2660.94	.00		.0000E+00
					-741.13	SS	
6	25.81	431.96	309.07	2436.54	.00		.0000E+00
7	26.09	445.80	275.02	2351.18	.00		.0000E+00
8	26.37	445.80	275.02	2351.18	.00		.0000E+00
9	26.64	451.70	248.72	2317.13	.00		.0000E+00
10	26.92	455.65	225.09	2290.83	.00		.0000E+00
					1764.83	PP	
					150.02	SS	
11	27.20	498.98	731.18	3079.93	.00		.0000E+00
					-1764.83	PP	
					-524.81	SS	
12	27.48	537.46	659.41	3148.08	.00		.0000E+00
13	27.76	552.80	566.95	3076.31	.00		.0000E+00
14	28.03	563.81	442.55	2983.85	.00		.0000E+00
15	28.31	576.58	2420.66	2859.45	.00		-.4000E+08
					1340.51	PP	
					136.96	SS	
16	28.59	616.28	370.14	3360.09	.00		.0000E+00
					-1340.51	PP	
					-494.37	SS	
17	28.87	671.52	192.55	3144.45	.00		.0000E+00
18	29.14	694.27	73.11	2966.86	.00		.0000E+00
19	29.42	708.02	992.30	2847.42	3465.10		.4271E+08
20	29.70	698.48	885.02	301.50	194.2		.0000E+00
21	25.00	404.44	762.94	50.74	.00		.0000E+00
22	25.25	409.03	776.72	72.56	.00		.0000E+00
23	25.50	422.16	690.38	86.33	.00		.2500E+07
24	27.00	27.00	489.45	485.98	150.02		.0000E+00
25	27.50	483.14	463.61	111.19	.00		.0000E+00
26	28.00	472.30	430.28	88.82	55.49		.0000E+00
27	28.50	609.75	461.78	136.96	.00		.0000E+00
28	29.00	605.37	443.30	104.37	.00		.0000E+00
29	29.50	596.25	412.90	85.89	55.49		.0000E+00

TABLE K-10

TOWER PROFILES WITH REDUCED CHARATERIZATION

Case b: Full Three Phase Model

Stage	Press Psia	Temp. (°F)	Molar Flow Rates Liquid	Vapor	Feed		Heat Duty BTU/HR
1	19.70	191.04	1467.49	.00	.00		-.5829E+08
2	24.70	314.95	1568.46	2819.28	.00		.0000E+00
3	24.98	353.41	1502.77	2920.03	.00		.0000E+00
4	25.26	376.41	1364.11	2854.33	.00		.0000E+00
					50.61	SS	
5	25.53	399.13	397.21	2665.07	.00		.0000E+00
					-741.04	SS	
6	25.81	431.53	311.54	2439.21	.00		.0000E+00
7	26.09	445.42	277.01	2353.54	.00		.0000E+00
8	26.37	451.34	250.69	2319.01	.00		.0000E+00
9	26.64	455.32	226.43	2292.69	.00		.0000E+00
10	26.92	458.87	2954.88	2268.43	.00		-.4000E+00
					1765.14	PP	
					149.03	SS	
11	27.20	498.65	733.85	3082.71	.00		.0000E+00
					-1765.14	PP	
					-523.87	SS	
12	27.48	537.10	662.39	3150.69	.00		.0000E+00
13	27.76	552.37	569.75	3079.22	.00		.0000E+00
14	28.03	563.35	444.25	2986.59	.00		.0000E+00
15	28.31	576.23	2423.34	2861.08	.00		-.4000E+08
					1340.52	PP	
					136.68	SS	
16	28.59	615.78	370.05	3362.98	.00		.000E+00
					-1340.52	PP	
					-494.08	SS	
17	28.87	671.33	192.44	3144.28	.00		.0000E+00
18	29.14	694.20	73.10	2966.66	.00		.0000E+00
19	29.42	708.02	991.59	2847.33	3465.10		.4272E+08
20	29.70	698.75	885.10	300.72	194.23		.0000E+00
21	25.00	403.92	761.47	50.61	.00		.0000E+00
22	25.25	408.51	776.97	71.04	.00		.0000E+00
23	25.50	421.70	690.43	86.54	.00		.2500E+07
24	27.00	489.42	485.72	149.03	.00		.0000E+00
25	27.50	483.40	463.62	110.88	.00		.0000E+00
26	28.00	472.53	430.33	88.78	55.49		.0000E+00
27	28.50	610.39	461.01	136.68	.00		.0000E+00
28	29.00	605.15	442.95	103.61	.00		.0000E+00
29	29.50	596.19	412.89	85.86	55.49		.0000E+00

APPENDIX L

EXXON CRUDE TOWER

TABLE L-1

CRUDE OIL CHARACTERIZATION

Component	Avg. Boiling Point (F)	API Gravity	Mol Wt.**	Composition
H_2O*	--	--	--	1.198E-01
C_1	--	--	--	3.3101E-03
C_2	--	--	--	1.1660E-02
C_3	--	--	--	1.7250E-02
$N-C_4$	--	--	--	1.9880E-02
$N-C_5$	--	--	--	4.3441E-02
FRAC 1	150.00	73.67	86.37	3.3082E-02
FRAC 2	190.00	66.11	97.86	2.88743-02
FRAC 3	210.00	62.85	103.70	2.8700E-02
FRAC 4	240.00	58.74	112.60	3.4376E-02
FRAC 5	260.00	56.35	118.88	3.4266E-02
FRAC 6	300.73	52.61	132.15	3.9227E-02
FRAC 7	340.00	48.34	145.05	3.8553E-02
FRAC 8	370.17	45.50	155.58	2.6136E-02
FRAC 9	400.00	43.01	166.58	2.2619E-02
FRAC 10	430.18	40.60	178.25	3.0082E-02
FRAC 11	460.18	38.50	190.53	2.7086E-02
FRAC 12	497.20	36.40	206.79	3.8728E-02
FRAC 13	534.63	34.30	224.10	3.8118E-02
FRAC 14	580.00	32.12	246.54	3.1498E-02
FRAC 15	620.00	30.11	267.22	2.9926E-02
FRAC 16	675.00	27.50	297.18	5.9281E-02
FRAC 17	750.00	25.17	342.14	5.1383E-02
FRAC 18	825.00	22.31	388.62	4.4650E-02
FRAC 19	900.00	20.72	439.79	3.8016E-02
FRAC 20	1000.00	19.17	512.94	3.2345E-02
FRAC 21	1100.00	16.52	584.92	2.2772E-02
FRAC 22	1200.00	11.32	643.45	2.7978E-02
FRAC 23	1300.00	-3.69	740.00	1.3775E-02
FRAC 24	1400.00	-20.94	800.00	1.3171E-02

* Water is introduced with the crude oil in the feed stream.
** MW is calculated by the program, except for the last two fractions. Their value is adjusted to match the molecular weight distribution shown in the next page.

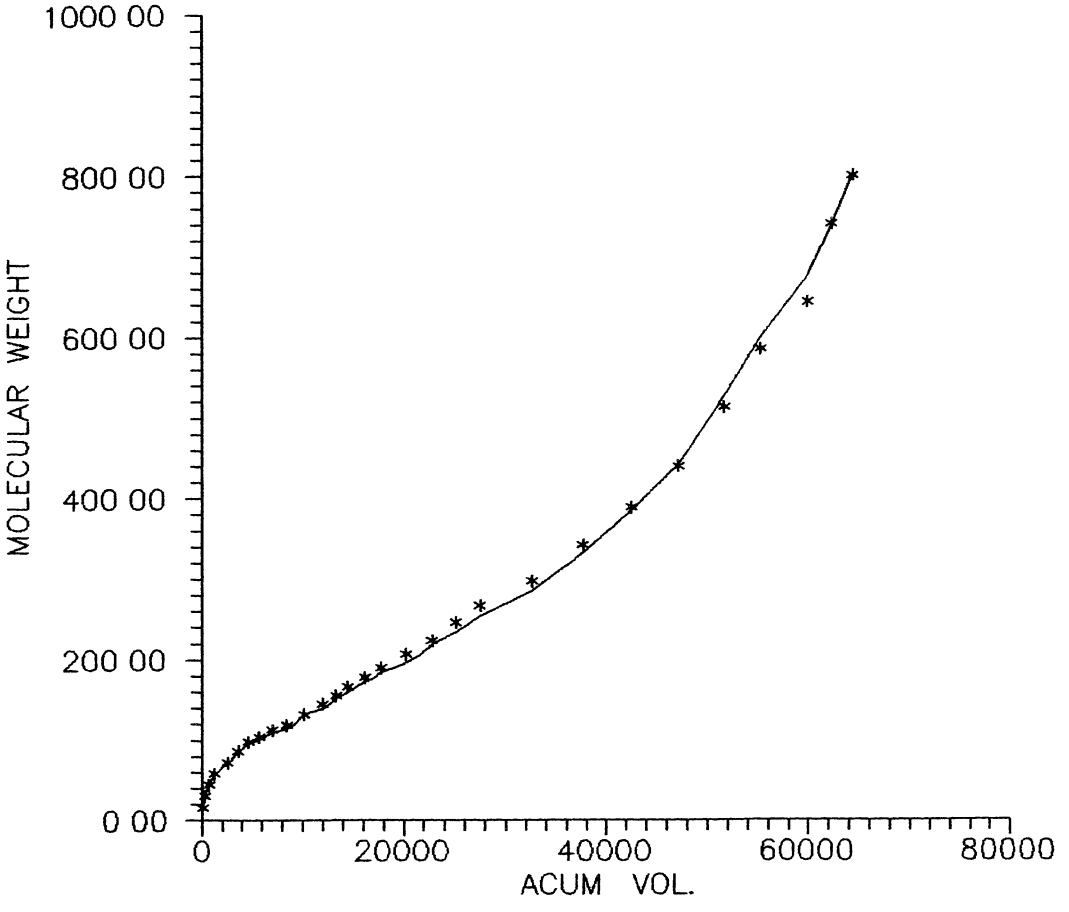


Figure 33: Molecular Weight Distribution

TABLE L-2

GLOBAL VARIABLES

Stage	Press Psia	Temp. (°F)	Molar Flow Rates Liquid	Vapor	Feed		Heat Duty BTU/HR
1	23.10	117.23	3211.72	203.83	.00		-.5107E+08
2	25.20	181.69	3330.64	3909.45	.00		.0000E+00
3	25.36	208.65	3289.73	4028.38	.00		.0000E+00
4	25.52	226.82	3191.75	3987.46	.00		.0000E+00
5	25.68	243.56	3042.80	3889.48	.00		.0000E+00
					25.69	SS	
6	25.85	262.59	2544.12	3714.85	.00		.0000E+00
					-319.69	SS	
7	26.01	285.23	2399.25	3535.86	.00		.0000E+00
8	26.17	306.76	2306.06	3390.99	.00		.0000E+00
9	26.33	324.92	2245.32	3297.79	.00		.0000E+00
10	26.49	339.55	2194.09	3237.06	.00		.0000E+00
					23.34	SS	
11	26.65	351.90	1998.89	3162.49	.00		.0000E+00
					-138.40	SS	
12	26.82	363.50	1925.46	3105.69	.00		.0000E+00
13	26.98	375.53	1822.38	3032.26	.00		.0000E+00
14	27.14	390.21	1672.22	2929.18	.00		.0000E+00
15	27.30	410.54	1476.43	2779.02	.00		.0000E+00
					74.65	SS	
16	27.46	438.86	923.97	2508.58	.00		.0000E+00
					-375.85	SS	
17	27.62	471.38	846.27	2331.96	.00		.0000E+00
18	27.78	492.30	2190.02	2254.27	.00		-.1810E+08
					823.00	PP	
19	27.95	516.19	1446.43	2775.02	.00		.0000E+00
					-823.00	PP	
20	28.11	532.55	1414.79	2854.43	.00		.0000E+00
21	28.27	544.28	1352.69	2822.78	.00		.0000E+00
22	28.43	555.43	1271.39	2760.69	.00		.0000E+00
					37.31	SS	
23	28.59	567.87	1040.68	2642.08	.00		.0000E+00
					-128.51	SS	
24	28.75	582.96	922.57	2539.88	.00		.0000E+00
25	28.92	600.39	773.92	2421.77	.00		.0000E+00
26	29.08	622.88	434.72	2272.12	.00		.0000E+00
27	29.24	678.96	820.78	1933.92	2203.20		.2781E+08
28	29.40	674.42	770.00	116.78	66.00		.0000E+00
29	25.85	269.77	330.70	25.69	.00		.0000E+00
30	26.01	272.65	334.34	36.70	.00		.0000E+00
31	26.17	277.16	294.00	40.34	.00		.6500E+06
32	26.65	342.18	131.22	23.34	.00		.0000E+00
33	26.82	330.42	122.00	16.16	6.94		.0000E+00
34	27.46	430.49	355.14	74.65	.00		.0000E+00
35	27.62	419.66	328.00	53.94	26.80		.0000E+00
36	28.59	558.19	119.07	37.31	.00		.0000E+00
37	28.75	544.87	107.00	27.88	15.80		.0000E+00

TABLE L-3

PRODUCT COMPOSITION

	Liquid From Stage 1		Liquid From Stage 28	
	Lbmol/hr	Mol fraction	Lbmol/hr	Mol fraction
H_2O	13.138	.6445E-01	4.321	.5612E-02
CH_4	7.254	.3559E-01	.001	.1504E-05
C_2H_6	25.059	.1229E+00	.010	.1234E-04
C_3H_8	35.262	.1730E+00	.026	.3423E-04
$N\text{-}C_4H_{10}$	35.263	.1730E+00	.056	.7241E-04
$N\text{-}C_5H_{12}$	55.061	.2701E+00	.209	.2709E-03
FRAC 1	23.847	.1170E+00	.266	.3449E-03
FRAC 2	6.901	.3386E-01	.331	.4294E-03
FRAC 3	1.900	.9323E-02	.395	.5132E-03
FRAC 4	.151	.7418E-03	.629	.8172E-03
FRAC 5	.020	.9682E-04	.758	.9850E-03
FRAC 6	.000	.1099E-05	1.284	.1668E-02
FRAC 7	.000	.2737E-08	1.867	.2424E-02
FRAC 8	.000	.4326E-11	1.715	.2227E-02
FRAC 9	.000	.2818E-14	2.006	.2605E-02
FRAC 10	.000	.1079E-17	3.627	.4710E-02
FRAC 11	.000	.1685E-21	4.438	.5763E-02
FRAC 12	.000	.2696E-26	9.303	.1208E-01
FRAC 13	.000	.9814E-32	14.030	.1822E-01
FRAC 14	.000	.9497E-40	23.618	.3067E-01
FRAC 15	.000	.7062E-48	41.113	.5339E-01
FRAC 16	.000	.4524E-60	122.390	.1589E+00
FRAC 17	.000	.7576E-80	113.030	.1468E+00
FRAC 18	.000	.4565-102	98.373	.1278E+00
FRAC 19	.000	.4464-128	83.758	.1088E+00
FRAC 20	.000	.2953-168	71.264	.9255E-01
FRAC 21	.000	.2121-215	50.172	.6516E-01
FRAC 22	.000	.1341-269	61.642	.8005E-01
FRAC 23	.000	.7558-299	30.350	.3942E-01
FRAC 24	.000	.1931-304	29.019	.3769E-01

TABLE L-4

PRODUCT COMPOSITION

	Liquid From Stage 31		Liquid From Stage 33	
	Lbmol/hr	Mol fraction	Lbmol/hr	Mol fraction
H_2O	.001	.2533E-05	.587	.4813E-02
CH_4	.000	.4354E-08	.000	.3029E-07
C_2H_6	.000	.8532E-06	.000	.1401E-05
C_3H_8	.006	.2113E-04	.002	.1299E-04
$N\text{-}C_4H_{10}$	.082	.2801E-03	.010	.8319E-04
$N\text{-}C_5H_{12}$	1.067	.3631E-02	.096	.7850E-03
FRAC 1	4.736	.1611E-01	.233	.1912E-02
FRAC 2	28.529	.9704E-01	.456	.3740E-02
FRAC 3	48.625	.1654E+00	.701	.5742E-02
FRAC 4	70.418	.2395E+00	1.815	.1487E-01
FRAC 5	69.320	.2358E+00	3.495	.2865E-01
FRAC 6	58.794	.2000E+00	22.256	.1824E+00
FRAC 7	11.762	.4001E-01	57.001	.4672E+00
FRAC 8	.646	.2196E-02	27.144	.2225E+00
FRAC 9	.017	.5662E-04	6.677	.5473E-01
FRAC 10	.000	.1060E-05	1.364	.1118E-01
FRAC 11	.000	.9652E-08	.150	.1231E-02
FRAC 12	.000	.3213E-10	.013	.1063E-03
FRAC 13	.000	.3577E-13	.000	.3884E-05
FRAC 14	.000	.6101E-18	.000	.6235E-08
FRAC 15	.000	.5092E-23	.000	.3747E-11
FRAC 16	.000	.1122E-30	.000	.4766E-16
FRAC 17	.000	.2359E-43	.000	.1941E-24
FRAC 18	.000	.1191E-57	.000	.6296E-34
FRAC 19	.000	.2904E-74	.000	.6768E-45
FRAC 20	.000	.7621-100	.000	.9608E-82
FRAC 21	.000	.3707-130	.000	.7444E-82
FRAC 22	.000	.2963-165	.000	.3366-105
FRAC 23	.000	.3011-180	.000	.3388-116
FRAC 24	.000	.5060-177	.000	.6033-115

TABLE L-5

PRODUCT COMPOSITION

	Liquid From Stage 35		Liquid From Stage 37	
	Lbmol/hr	Mol fraction	Lbmol/hr	Mol fraction
H_2O	1.657	.5053E-02	.611	.5712E-02
CH_4	.000	.2501E-07	.000	.1430E-07
C_2H_6	.000	.7528E-06	.000	.2589E-06
C_3H_8	.002	.5281E-05	.000	.1289E-05
$N\text{-}C_4H_{10}$	.009	.2711E-04	.001	.4841E-05
$N\text{-}C_5H_{12}$	.073	.2230E-03	.003	.3072E-04
FRAC 1	.175	.5329E-03	.007	.6308E-04
FRAC 2	.335	.1021E-02	.012	.1111E-03
FRAC 3	.492	.1500E-02	.017	.1585E-03
FRAC 4	1.049	.3199E-02	.035	.3302E-03
FRAC 5	1.523	.4644E-02	.051	.4750E-03
FRAC 6	3.960	.1207E-01	.123	.1145E-02
FRAC 7	14.064	.4288E-01	.247	.2306E-02
FRAC 8	27.793	.9474E-01	.287	.2679E-02
FRAC 9	40.717	.1241E+00	.418	.3908E-02
FRAC 10	60.343	.1840E+00	.943	.8817E-02
FRAC 11	53.604	.1634E+00	1.485	.1388E-01
FRAC 12	70.738	.2157E+00	5.273	.4928E-01
FRAC 13	47.979	.1463E+00	21.974	.2054E+00
FRAC 14	3.413	.1041E-01	42.367	.3960E+00
FRAC 15	.073	.2221E-03	24.749	.2313E+00
FRAC 16	.000	.5681E-06	8.218	.7681E-01
FRAC 17	.000	.8277E-11	.177	.1657E-02
FRAC 18	.000	.2678E-16	.002	.1848E-04
FRAC 19	.000	.1308E-22	.000	.1048E-06
FRAC 20	.000	.2798E-32	.000	.3981E-10
FRAC 21	.000	.6401E-44	.000	.2617E-14
FRAC 22	.000	.2148E-57	.000	.5360E-19
FRAC 23	.000	.1876E-64	.000	.7473E-22
FRAC 24	.000	.2599E-64	.000	.5435E-22

TABLE L-6

PRODUCT COMPOSITION

	Liquid From Stage 1 Lbmol/hr	Mol fraction	Liquid From Stage 1 Lbmol/hr	Mol fraction
H_2O	359.037	.1000E+01	0.164	.1219E-02
CH_4	.000	.8489E-06	0.038	.2798E-03
C_2H_6	.001	.3007E-05	0.620	.4594E-02
C_3H_8	.001	.3431E-05	2.707	.2000E-01
$N\text{-}C_4H_{10}$	.001	.3352E-05	8.379	.6213E-01
$N\text{-}C_5H_{12}$	.002	.1096E-05	39.200	.2907E+00
FRAC 1	.000	.5101E-05	43.624	.3233E+00
FRAC 2	.000	.2178E-06	27.053	.2006E+00
FRAC 3	.000	.8745E-07	11.104	.8233E-01
FRAC 4	.000	.1800E-07	1.641	.1217E-01
FRAC 5	.000	.3105E-08	.329	.2440E-02
FRAC 6	.000	.5322E-10	.009	.6934E-04
FRAC 7	.000	.3883E-12	.000	.4392E-06
FRAC 8	.000	.1319E-14	.000	.1479E-08
FRAC 9	.000	.1801E-17	.000	.2112E-11
FRAC 10	.000	.1638E-20	.000	.1856E-14
FRAC 11	.000	.5935E-24	.000	.6916E-18
FRAC 12	.000	.2369E-28	.000	.3473E-22
FRAC 13	.000	.2749E-33	.000	.4309E-27
FRAC 14	.000	.1087E-40	.000	.2073E-34
FRAC 15	.000	.4146E-48	.000	.6949E-42
FRAC 16	.000	.3534E-59	.000	.4179E-53
FRAC 17	.000	.6827E-78	.000	.2353E-71
FRAC 18	.000	.2291E-98	.000	.7102E-92
FRAC 19	.000	.4507-124	.000	.7304-116
FRAC 20	.000	.6586-167	.000	.6617-153
FRAC 21	.000	.1524-212	.000	.1895-196
FRAC 22	.000	.2580-259	.000	.1420-246
FRAC 23	.000	.1355-264	.000	.6095-275
FRAC 24	.000	.8672-258	.000	.1011-281

VITA

Edgardo A. Lopez

Candidate for the Degree of

Doctor of Philosophy

Thesis: MODELING AND SIMULATION OF COMPLEX REFINERY DISTILLATIONS

Major Field: Chemical Engineering

Biographical:

Personal Data: Born in San Jose, Costa Rica, February 9, 1958, the son of Gonzalo and Hilda Lopez.

Education: Graduated in 1975 from High School in San Jose, Costa Rica. Received the "Lincenciado" degree in Chemical Engineering from the "Universidad de Costa Rica" in May, 1981. Received a Master of Science degree in Chemical Engineering from the University of Michigan in July, 1983. Completed the requirements for the Doctor of Philosophy degree at Oklahoma State University in December, 1991.

Professional Experience: Teaching Assistant, School of Chemistry, University of Costa Rica, 1978-1980. Planning Engineer, Costa Rican Petroleum Refinery, 1983-1984. Quality Assurance Representative, Coca Cola Inter-American Corporation, San Jose, Costa Rica, 1984-1987. Adjunct Assistant Professor, Department of Chemical Engineering, the University Costa Rica, 1983-1984, 1986-1987. Head, Department of Industrial Conversion, Costa Rican Petroleum Refinery, 1987-1988. Research Assistant, School of Chemical Engineering, Oklahoma State University, September 1988 to September 1991.