

CHAPTER III

CALCULATION PROCEDURES AND PROPOSED WORKS

3.1 Calculation Procedures

3.1.1 The Newton-Raphson Method

When only real roots are required, which is always the case with equations of state, the Newton-Raphson method is convenient. Figure 3.1 depicts the graphical Newton-Raphson method. If the initial guess at root

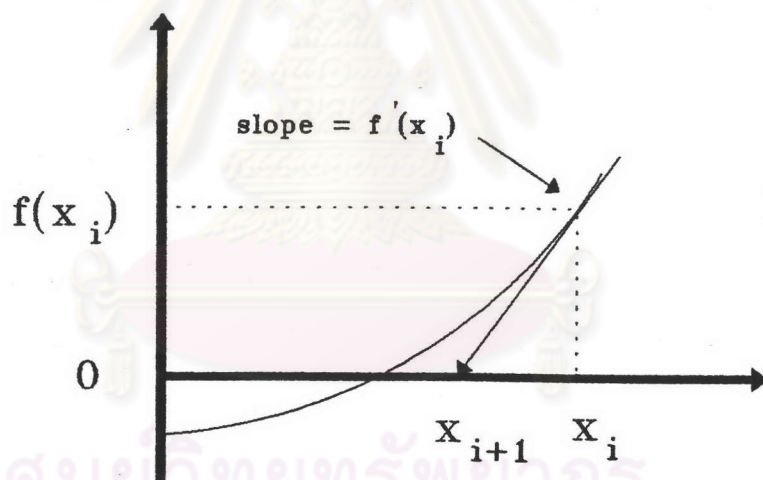


Figure 3.1 Graphical depiction of the Newton-Raphson method.

is x_i , a tangent can be extended from the point $[x_i, f(x_i)]$. The point where this tangent crosses the x axis, x_{i+1} usually represents an improved estimate of the root. The Newton-Raphson method can be derived on the basis of this geometrical interpretation. As in Figure 3.1, the first derivative at x_i is equivalent to the slope :

$$f'(x_i) = \frac{f(x_i) - 0}{x_i - x_{i+1}} \quad (3.1)$$

which can be rearranged to yield

$$x_{i+1} = x_i - \frac{f(x_i)}{f'(x_i)} \quad (3.2)$$

which is called the Newton-Raphson formula.

When it is applied to equations of state calculation in this work, Eq. (3.2) can be

$$Z_{i+1} = Z_i - H_i \quad (3.3)$$

where

$$H_i = f(Z_i)/f'(Z_i) \quad (3.4)$$

For the case with vapor, the initial guess at root is $Z_i = 1$ and with liquid it is $Z_i = 0$. The true root can be obtained when Eq. (3.3) is iterated until absolute of H_i/Z_i approaches 0.0001.

3.1.2 Fibonacci Optimization Technique

The purpose of this technique is to find the minimum of a single variable $f(x)$, nonlinear function subject to constraints $a \leq x \leq d$. The upper and lower bounds, d and a are constants. In this work, it is applied for calculating the binary interaction parameters. The $f(x)$ is the objective function referred in Section 3.1.4. The a and d are initially guessed binary interaction parameters.

The procedure is the bracket reduction approach. It starts with a bracket $[a,d]$ for the minimum of the function f . The idea is to place two points $b < c$ symmetrically in this interval and then reduce the bracket to either $[a,c]$ or $[b,d]$ depending on whether $f(b) < f(c)$. If $f(b) > f(c)$, the new bracket is given by $[b,d]$. If not, the new bracket is given by $[a,c]$. The process is then repeated with this reduced bracket. There are $n-2$ steps in this process when n is the subscript of Fibonacci number F_n . At each stage i , the length of the bracket L_i

is reduced to

$$L_i = \frac{F_{n-(i-1)}}{F_n}(d-a) \quad (3.5)$$

The n is obtained when $F_n > (d-a)/\epsilon$. F_n is defined by

$$F_{n+1} = F_n + F_{n-1}; \quad F_0 = F_1 = 1 \quad (3.6)$$

As ϵ is the tolerance such as 0.01 in this work. It should be noted that when the step $n-2$ is taken the bracketing interval will approach its midpoint. The Fibonacci search is described as diagram in Figure 3.2.

3.1.3 The Bubble point Pressure Calculation

The bubble point pressure is the pressure at which a liquid of known composition first begins to boil in a given temperature. In this condition, the sum of this vapor composition occurring must be unity. At this equilibrium, the vapor composition y_i can be determined from liquid composition x_i as Eq. (2.34); thus,

$$\sum_i y_i = \sum_i \frac{x_i \hat{\phi}_i^L}{\hat{\phi}_i^V} \quad (3.7)$$

In other words, it can determine this pressure and vapor composition when a temperature and liquid composition are given. The key starting assumptions in this work are the first pressure which is equal to the experimental value and $\hat{\phi}_i^V = 1$. Then $\sum y_i$ can be determined. The method iterates at a given temperature until $\sum y_i = 1$. If $\sum y_i$ is not equal to unity, the pressure should be modified by multiplying with y_i and y_i should be normalized for the next series of iterations. Figure 3.3 shows the diagram for the bubble point pressure calculation.

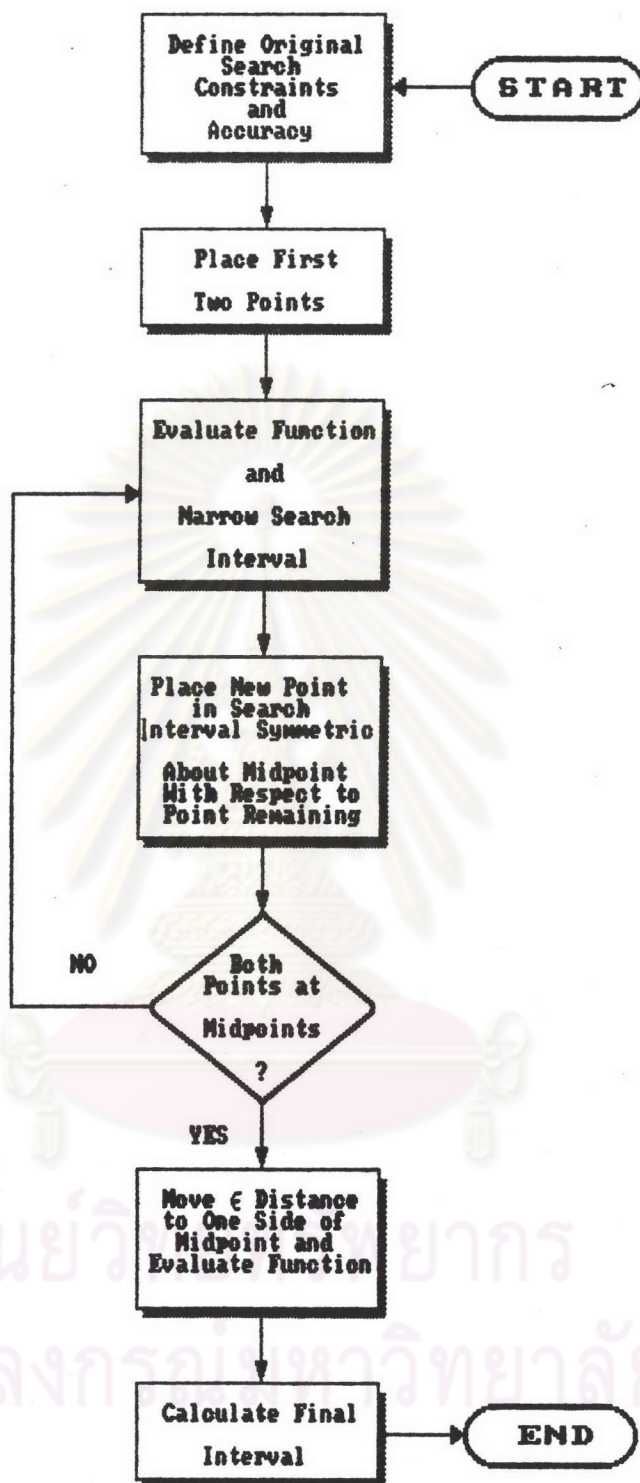


Figure 3.2 Fibonacci optimization technique diagram

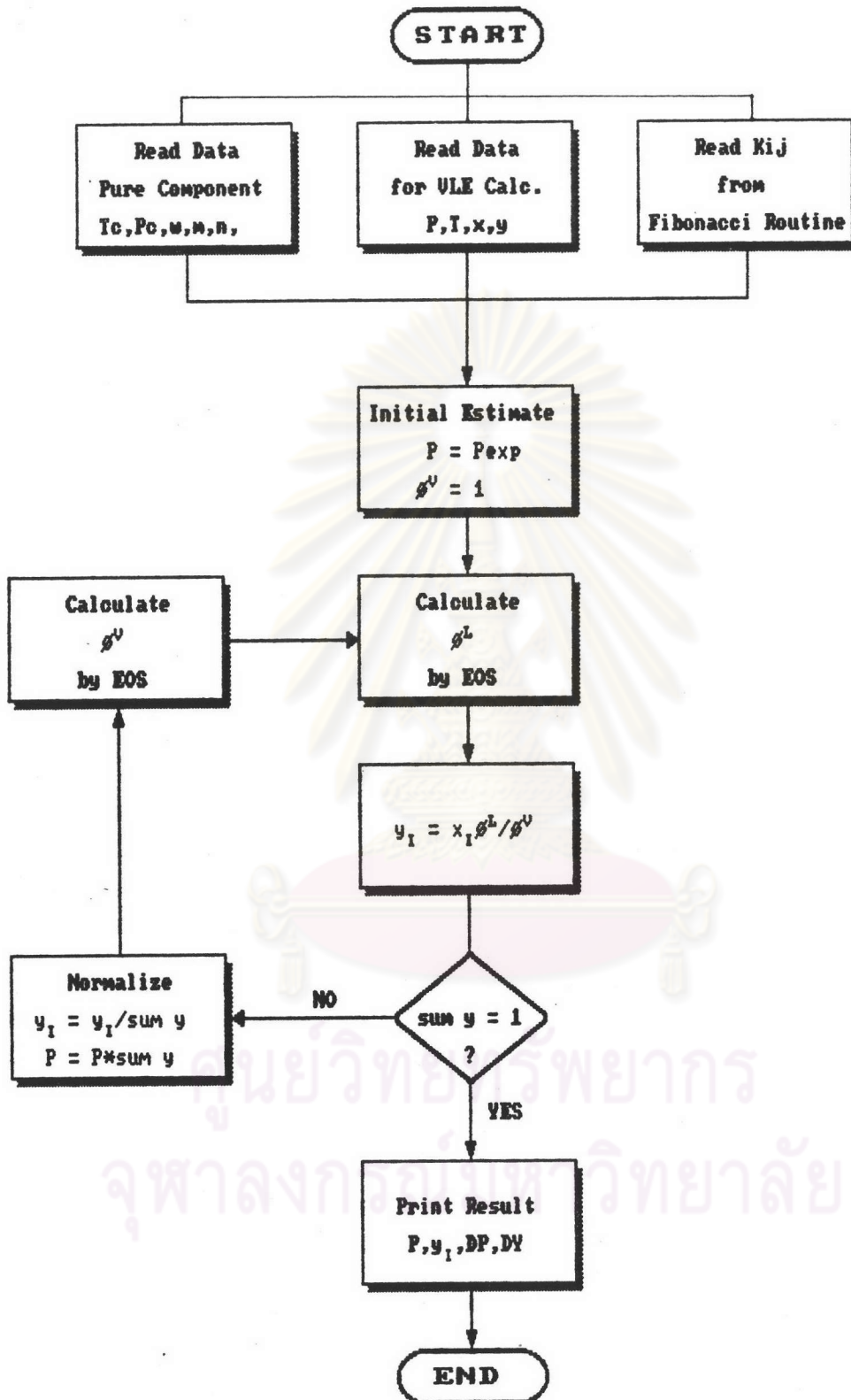


Figure 3.3 Diagram of the bubble point pressure calculation

3.1.4 Evaluation Procedures of the Optimal Binary Interaction Parameters

The optimal values of binary interaction parameters are determined from binary vapor-liquid equilibrium data by minimizing the difference between the calculated and experimental values of a selected equilibrium property. A number of criteria have been used for the evaluation as follows:

1. minimization of deviation in predicted K values [23]
2. minimization of deviation in predicted bubble point pressures [24,25,26]
3. minimization of deviation in predicted bubble point vapor composition [24]
4. minimization of the flash avolume variances [25]
5. minimazation of the sum of variances of the flash vapor and liquid compositions [27]
6. minimization of deviation between calculated vapor and liquid component fugacities [28]

However, there is no assurance that the binary interaction parameters obtained by different methods will be identical, presenting a problem of which method will yield the most desirable results. Mostly listed methods, method 1-5, for the determination of binary interaction parameters involves iterative calculations of either bubble point or flash type for each datum. Thus, these methods may be rather time-consuming, especially in cases where there is more than one binary interaction parameter in an equation of state, complicated state equation and/or large data set. However, the last one does not involve any iterative calculations. In this work, method 2 and 6 are selected for calculation work.

3.1.4.1 Minimization of Deviation in Predicted Bubble Point Pressures

The bubble point pressure criterion which seems to be the most widely used method is probably the most valuable. This statement is supported by Kato et al. [24] in 1976 and Graboski and Daubert [25] in 1978

who found the bubble point pressure criterion to be extremely sensitive to variations in the binary interaction parameters of the Redlich-Kwong equation of state if compared with the bubble point vapor composition and flash volume criteria. The objective function is

$$Q_p = \sum_{i=1}^N \left[\frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{P_i^{\text{exp}}} \right]^2 \quad (3.8)$$

where

- N = number of data points
 P_i^{exp} = experimental bubble point pressure
 P_i^{cal} = calculated bubble point pressure

3.1.4.2 Minimization of Deviation between Calculated Vapor and Liquid Component Fugacities

In 1981, Paunovicetal.[28] proposed a new objective function in terms of the differences between calculated vapor and liquid component fugacities for the determination of the binary interaction parameter of an equation of state from vapor-liquid equilibrium data. The proposed objective function is as follows:

$$Q_f = \sum_{i=1}^N \left[\left| \frac{f_1^L - f_1^V}{f_1^V} \right|_i + \left| \frac{f_2^L - f_2^V}{f_2^V} \right|_i \right] \quad (3.4)$$

where

- N = number of data points
 f_1^L = liquid phase fugacity of component 1
 f_1^V = vapor phase fugacity of component 1

The data used must be in the form of experimental values of the equilibrium vapor and liquid phase compositions for various temperatures and pressures. The new method saves considerably on computing time and effort because it avoids iterations in objective function calculations. In addition, it gives good estimates for binary interaction parameters which are reasonably consistent with those obtained by the bubble point pressure method.

3.2 Proposed Work

3.2.1 Selected Experimental Data

Eight systems containing methane, three systems containing ethane, two systems containing propane, three systems containing nitrogen and nine systems containing carbon dioxide are selected for this study. One thousand and ninety nine (1099) points included in 118 isotherms were considered in the analysis. Table 3.1 and 3.2 give details on the experimental data selected for this study. In those tables, N_i is the number of isotherms, N is the number of experiment points, "Range of P" is the minimum and maximum temperature of the data sets.



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Table 3.1 Details of the experimental data for systems containing methane, systems containing ethane and systems containing propane used in this study

SYSTEM	Ni	N	Range of T (K)	Range of P (atm)	Ref.
Methane – Ethane	12	100	130.370–280.000	1.8577–55.1800	30, 31
Methane – Propane	7	62	144.260–213.710	1.7011–44.2299	32
Methane – n-Butane	9	76	166.493–283.160	1.3600–108.6600	33, 34
Methane – Isobutane	2	31	310.938–344.271	5.4437–108.8736	35
Methane – n-Pentane	8	56	176.221–377.604	1.3677–136.0920	36, 37
Methane – Isopentane	2	15	344.271–377.604	33.9550–149.0888	37
Methane – Neopentane	2	14	344.271–377.604	20.9582–118.9444	37
Methane – n-Hexane	7	64	190.510–273.170	1.3541–108.8736	38
Ethane – Propane	7	123	185.000–270.000	0.2981–14.1683	39
Ethane – n-Butane	2	10	338.716–366.493	34.6354–47.7002	40
Ethane – Isobutane	1	14	311.271–344.493	10.5471–39.8069	41
Propane – Propylene	12	108	230.000–340.000	0.9968–28.2556	42
Propane – Isopentane	4	50	273.160–423.160	0.5000–35.0000	43

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Table 3.2 Details of the experimental data for systems containing nitrogen and systems containing CO₂ used in this study

SYSTEM	Ni	N	Range of T (K)	Range of P (atm)	Ref.
Nitrogen – Methane	7	54	113.716–172.049	2.7559–57.4800	44
Nitrogen – Ethane	6	54	138.716–280.000	3.4023–96.2851	31, 45
Nitrogen – Carbon dioxide	3	40	220.000–270.000	14.8927–142.5275	46, 47
Carbon dioxide – Methane	5	43	219.260–270.000	13.7952–77.0000	46, 48
Carbon dioxide – Ethane	1	13	250.000	14.2300–18.5100	48
Carbon dioxide – Propane	2	21	244.271–266.493	4.9674–25.7894	49
Carbon dioxide – n-Butane	2	13	368.160–393.160	15.1098–70.0913	50
Carbon dioxide – i-Butane	2	14	310.938–344.271	7.1448–61.7858	51
Carbon dioxide – n-Pentane	6	54	277.660–438.160	2.2455–88.4548	52, 53
Carbon dioxide – i-Pentane	1	9	408.160	15.9191–71.7197	53
Carbon dioxide – n-Heptane	4	45	310.660–477.216	4.1848–130.6483	54
Carbon dioxide – n-Decane	4	16	462.560–583.660	14.2500–51.0000	55

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3.2.2 Calculation Work

In this work, a computer program was written and compiled with a Turbo Pascal (version 5.5) compiler for convenience of calculations. The program was used to calculate and vapor-liquid equilibria of any binary system. In the program, the Newton-Raphson method was used to determine the compressibility Z of vapor and liquid phases. The Fibonacci method was used to minimize an objective function and evaluate the binary interaction parameters. The details of the computer program are given in Appendix A. The computational procedures are as follows:

3.2.2.1 Input Data

Input data are physical properties of each substance: critical temperature (T_c), critical pressure (P_c) and Pitcher's acentric factor (ω) [29]. The parameters m and n for the MSRK equation of state were summarized by Sandaruci et al. [15]. The parameter η and new acentric factor for the PR equation of state were proposed by Moshfeghian et al. [17]. The experimental vapor-liquid equilibrium data from various papers [30 - 55] are also required.

3.2.2.2 Minimization for K_{ij} Evaluation

The technique used is the Fibonacci optimization technique. First, the equation of state, objective function (the bubble point pressure method or the fugacity method) and temperature were chosen, then the initial K_{ij} interval was defined. Finally, the optimal K_{ij} for each binary system was obtained. Figure 3.4 shows the diagram of the binary interaction parameter evaluation procedure. The binary interaction parameter obtained is the value for the chosen temperature. The procedure was repeated for the calculation of K_{ij} at the other temperatures.

3.2.2.3 Vapor-liquid Equilibrium Calculation

In this work, the binary interaction parameter obtained from Section 3.2.2.2 was used to calculate the vapor-liquid equilibria of binary systems of Section 3.2.1.

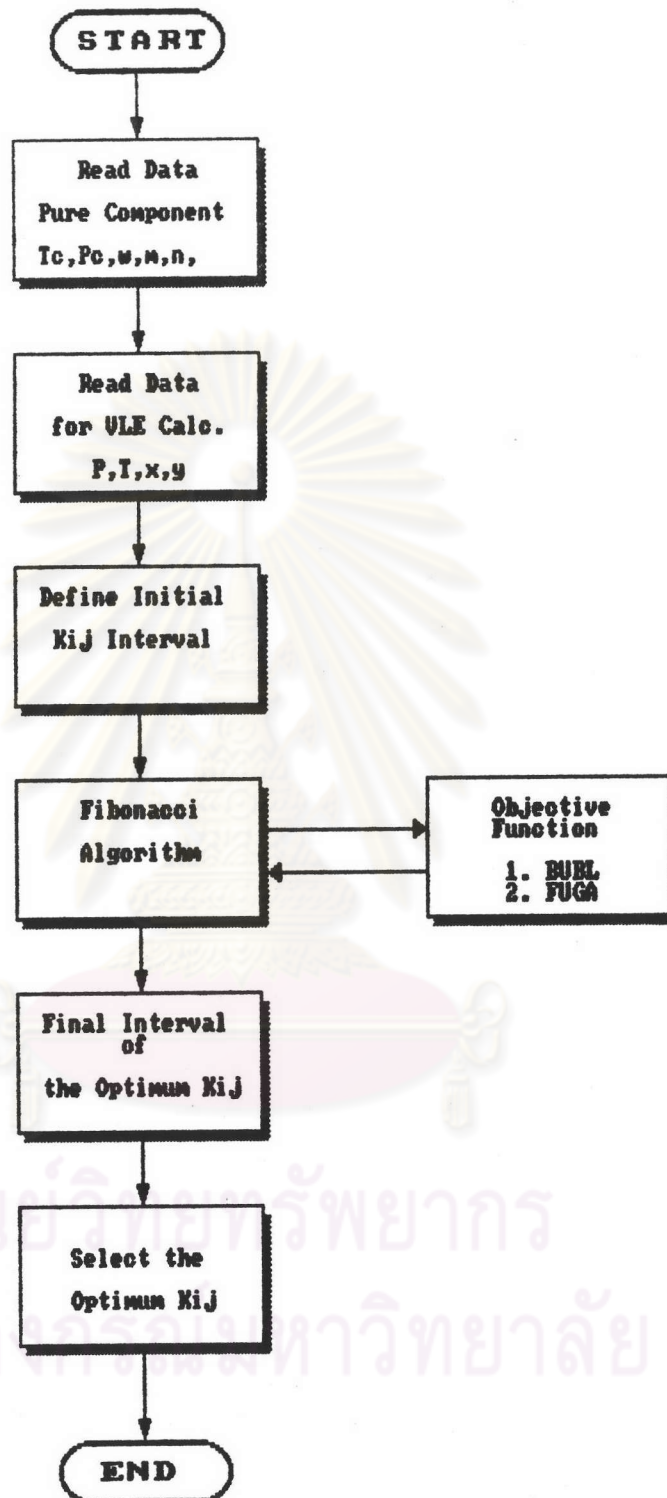


Figure 3.4 Diagram of the K_{ij} evaluation procedure