Chapter Three

Proposed Procedures and Calculation Works

3.1 Selected Objective Functions

The objective functions selected for the determination of the binary interaction coefficients in this work are :

3.1.1 Minimization of Deviation in Predicted Bubble Point Pressure

This criterion is the most accepted one and according to Graboski and Daubert (16) and Kato et al. (17), it is probably the best criterion for searching the optimum K_{ij}. In their work, they also stated that this method seemed to be extremely sensitive to variations in the K_{ij} values used in the equation if compared with the bubble point vapor composition and flash volume criteria. The objective function has the following form :

$$Q_p = \sum_{m=1}^{N} \frac{(P_m^{exp} - P_m^{calc})}{P_m^{exp}} \qquad (3.1)$$

where

N = number of data points

P_m^{exp} = experimental bubble point pressure

P_m^{cal} = calculated bubble point pressure.

3.1.2 Minimization of Deviation between Calculated Component Vapor and Liquid Fugacities

This fugacity criterion of Paunovic et al. (22) defined the objective function as

$$Q_f = \sum_{m=1}^{N} \frac{|f_1^L - f_1^V|}{f_1^V} + \frac{|f_2^L - f_2^V|}{f_2^V} \qquad (3.2)$$

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 value of the function Q_f can be calculated at any specified value of the incorporated binary coefficient, provided a relation exists for the component fugacity

corresponding to a selected equation of state and appropriate data. However, the data base must be in the form of experimental values of the equilibrium vapor and liquid phase composition for various temperatures and pressures. It is obvious that the evaluation of this objective function does not involve any iterative calculations which is the major advantage of this method.

3.2 Fibonacci Optimization Technique

The purpose of this algorithm is to find the optimum K_{ij} for each system that yields the minimum value of those previously selected objective functions to be used in the VLE calculations for all equations of state presented. The procedure is an interval elimination search method as presented by Kuester and Mize (23). Thus, starting with the original boundaries on the independent variable, K_{ij} in this case, the interval in which the minimum value of the objective function occurs is reduced to some final value, the magnitude of which depends on the desired accuracy. The location of points for function evaluations is based on the used of positive integer known as Fibonacci numbers. No derivatives are required. A specification of the desired accuracy will determine the number of function evaluations. Finally, a unimodal function is assumed. The algorithm process is shown in Figure 3.1.

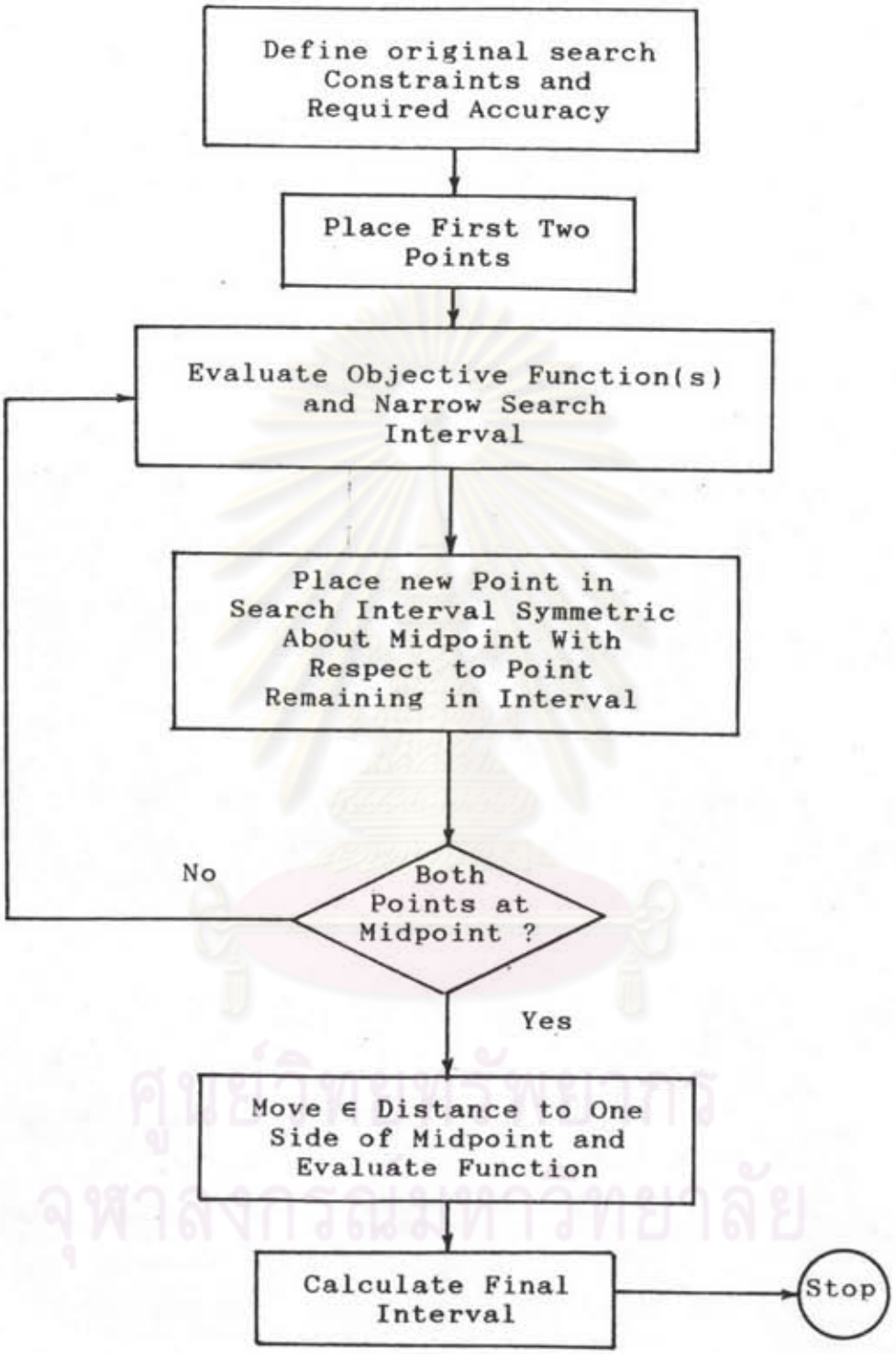

FIGURE 3.1 Fibonacci (FIBON ALGORITHM) optimization technique diagram (23)

Binary PVTx data were used for the calculation of the bubble point pressure through the bubble point routine for the first objective function and the calculation of the fugacities of both phases through the fugacity routine for the second one. The flow chart illustrating integrated evaluation procedure is given in Figure 3.2 with the complete computer program for all equations in the Appendix A.

3.3 Prediction of Vapor-liquid Equilibrium : Selected Experimental Data and Bubble Point Pressure Calculations

Six CO_2-hydrocarbon mixtures, five methane-heavier hydrocarbon mixtures, and three ethane-hydrocarbon mixtures were selected for this study. Six hundred and seventy-five (675) points included in 72 isotherms were considered in the analysis. Table 3.1, 3.2, and 3.3 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 T" is the minimum and maximum temperature of the data sets, and "range of P" is the minimum and maximum pressure of data sets.

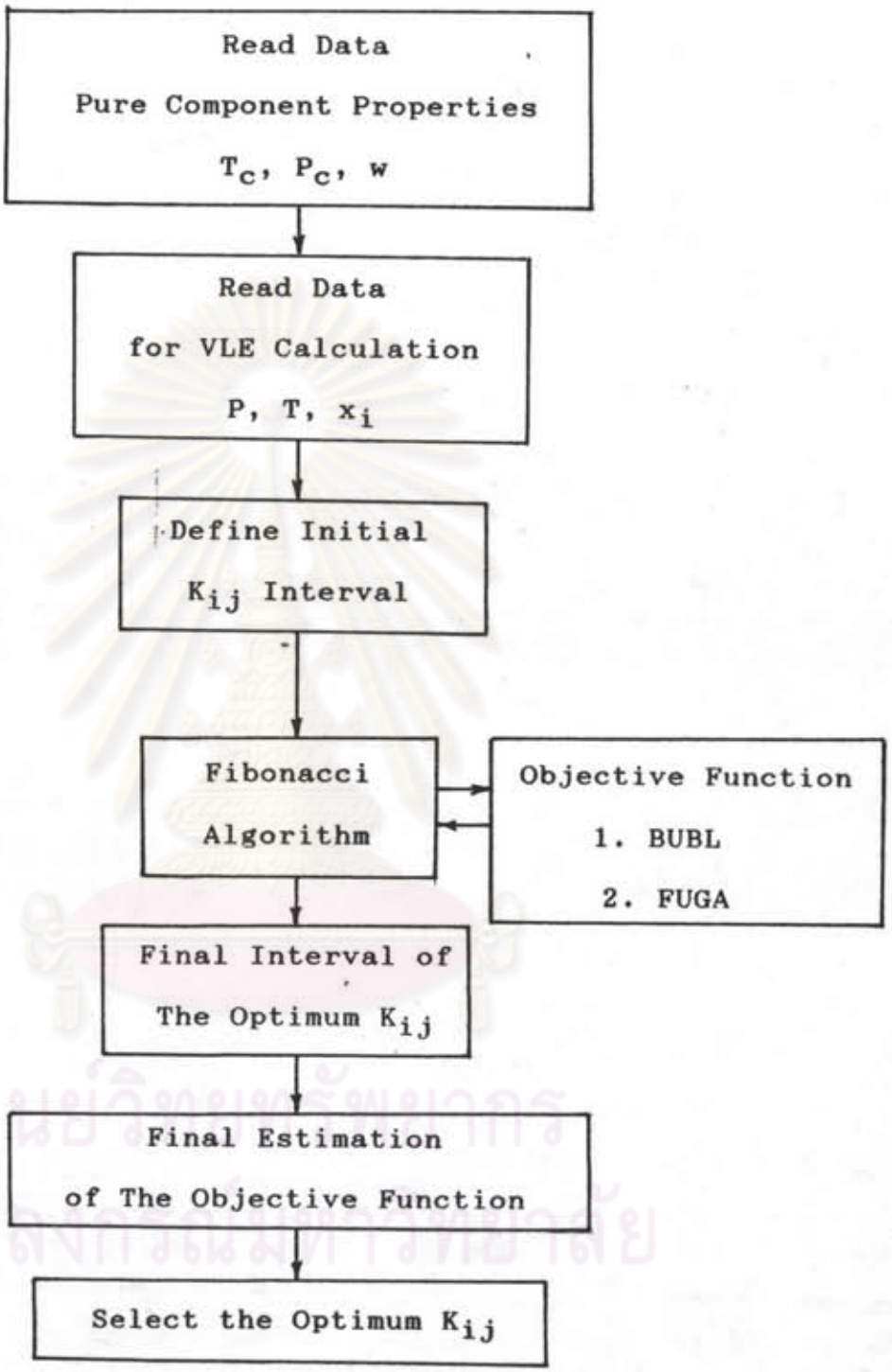

FIGURE 3.2 Flow chart of the integrated K_{ij} evaluation procedure.

TABLE 3.1 Details of the experimental data for CO_2-hydrocarbon mixtures used in this study

System	N_i	N	Range of T (K)	Range of P (atm)	Ref.
CO_2 - Ethane	1	13	250.00	14.23-18.51	24
CO_2 - n-Propane	2	21	244.27-266.49	4.97-25.79	25
CO_2 - i-Butane	4	29	310.94-394.27	7.14-70.90	26
CO_2 -n-Pentane	4	48	277.66-377.61	2.25-95.05	27
CO_2 - n-Heptane	4	63	310.66-477.22	1.84-313.38	28
CO_2 - n-Decane	4	16	462.56-583.66	14.25-51.00	29

TABLE 3.2 Details of the experimental data for methane-heavier hydrocarbon mixtures used in this study

System	N_i	N	Range of T (K)	Range of P (atm)	Ref.
Methane-Ethane	12	105	130.38-250.00	1.76-65.18	30,31
Methane-n-Propane	12	112	130.38-273.16	1.70-95.26	32,33
Methane-n-Butane	8	70	166.46-283.16	1.36-108.66	34
Methane-n-Pentane	7	46	176.22-273.17	1.37-136.09	35
Methane-n-Hexane	10	119	198.06-423.16	1.35-423.16	36,37

TABLE 3.3 Details of the experimental data for ethane-heavier hydrocarbon mixtures used in this study

System	N_i	N	Range of T (K)	Range of P (atm)	Ref.
Ethane-n-Propane	2	9	310.94-333.16	13.61-44.23	38
Ethane-i-Butane	2	10	311.27-344.49	10.55-45.18	39
Ethane-n-Pentane	4	22	277.60-410.94	6.80-47.63	40

The optimum binary interaction coefficients evaluated by both objective functions from previous procedure were used to calculate the bubble point pressures and vapor compositions by each equation of state for all systems. Figure 3.3 shows the flow chart for the bubble point pressure calculations. The convergence method used for the calculations is that of Chueh and Praunitz (41) while the solution method used for the polynomial equations of Z is that of Gundersen (42). The algorithm is shown in Figure 3.4.

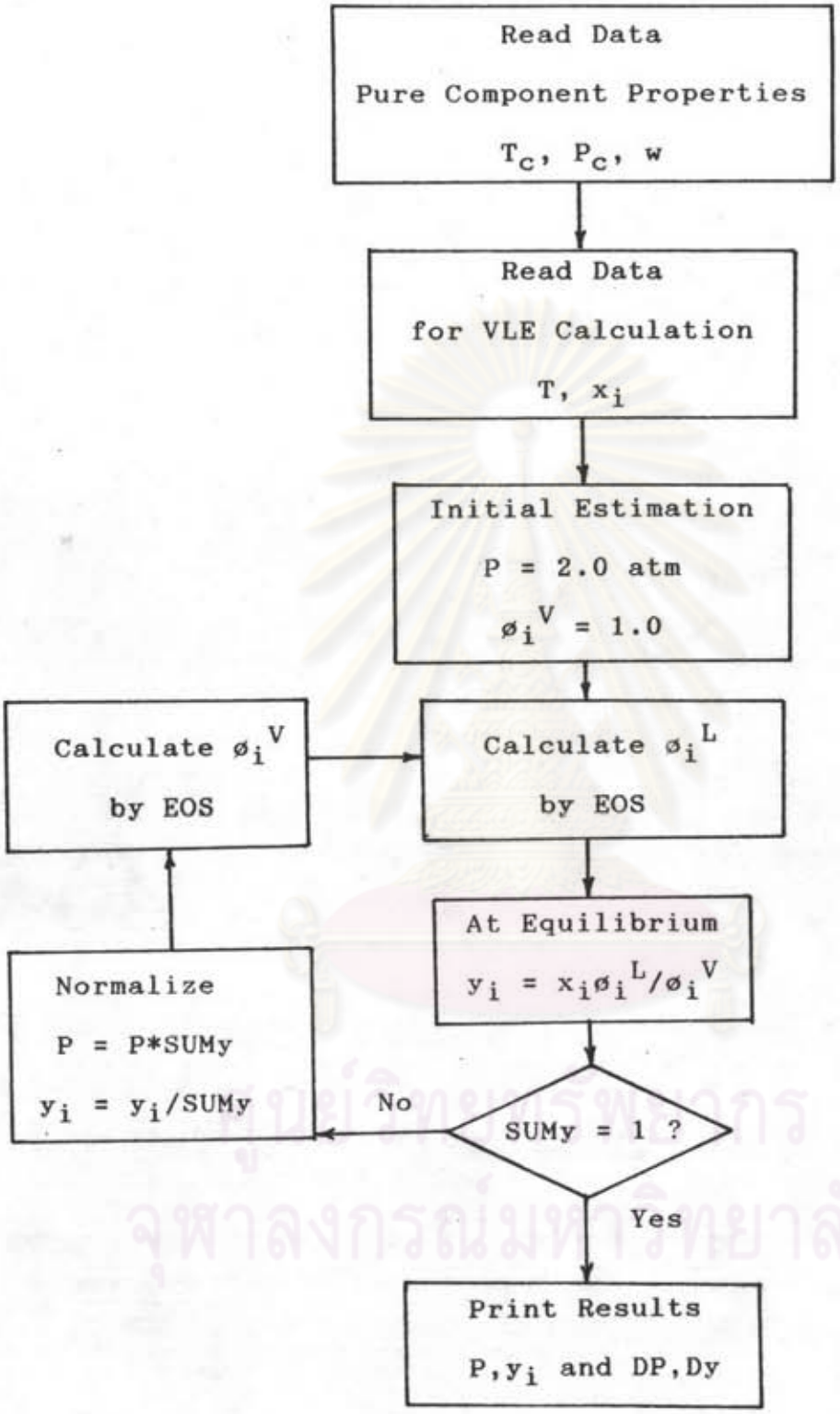

FIGURE 3.3 Flow chart for the bubble pressure calculation (BUBL ROUTINE)

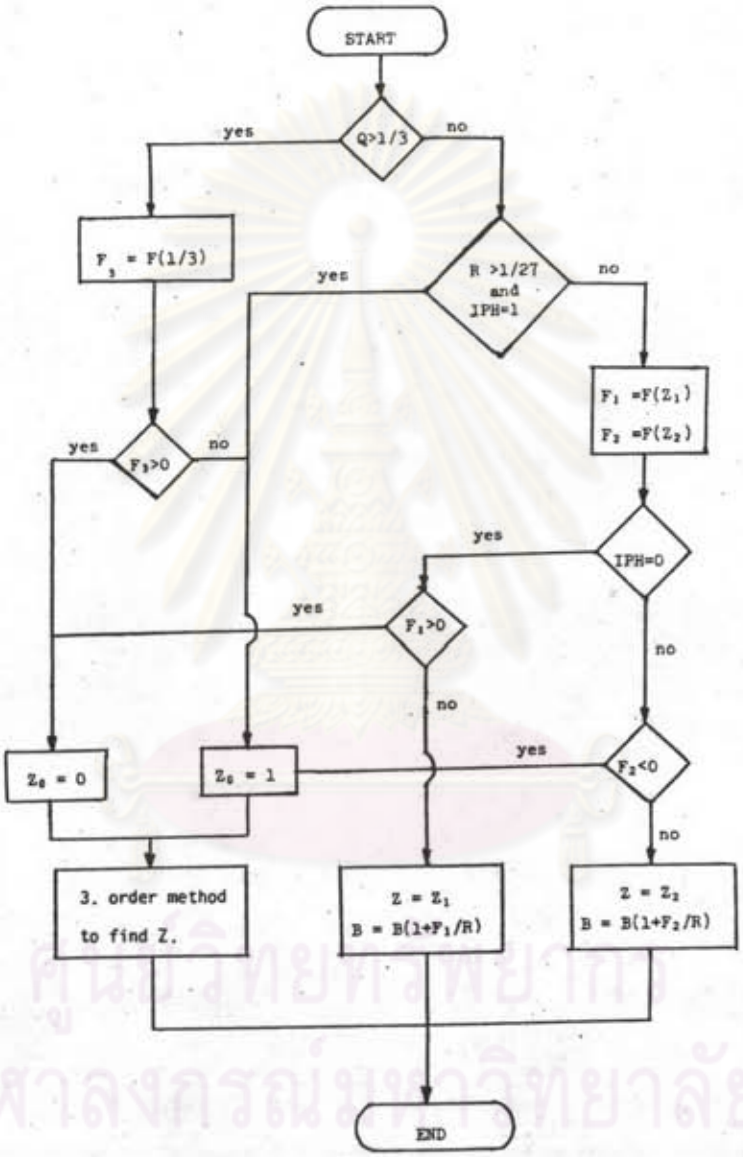

FIGURE 3.4 Gundersen Algorithm for the solution of the cubic SRK equation of state (42).