



## CHAPTER VII

### SIMULATION RESULTS AND DISCUSSION

Applications of present program, which is developed in the previous chapter, are shown in this chapter. In this chapter, the results are separate to 2 part. In first part, the simulation results of the present program are discussed and compared with steady state program, PRO II and real data from the Debutanizer column of The Bangchak Petroleum Public Company Limited in order to test the accuracy of the present program. In second part, the applications to and oil refinery are discussed on the effect of thermodynamic models to dynamic simulation by comparing the results from dynamic simulation with real data from refinery for both initial and final states. The initial state results are obtained from the design case and the final stage results are obtained from the actual operating case. Three models of equation of state, Generic-Redlich-Kwong(GRK), Soave-Redlich-Kwong(SRK) and Peng-Robinson(PR) are used and compared to select the best thermodynamics model that fits the column behavior.

For this column, n-butane is selected as a key component for both distillate and bottom product because of its sensitivity to the column operation. Furthermore, propane is selected to represent a light component and n-hexane is selected to represent a heavy component.

#### 7.1 Test the accuracy of the Dynamic Simulation program

To test the accuracy of the dynamic simulation program, the existing steady state program PRO II is selected to compare the results with the steady state result that obtained from the dynamic simulation program. For both programs, three thermodynamic models(GRK, SRK and PR) are applied to

calculate the behavior of the Debutanizer column. The column compose of 25 plates(not included condenser and reboiler) and 6 components. The data required for this column which consists of characteristic of column and feed data are shown in Table 7-1.

The results are shown in Tables 7-2 to 7-5.

**Table 7-1 Characteristic of column and feed data**

Characteristic of column								
Total number of plates (NT)			=	25				
Number of tray in stripping section (NS)			=	9				
Weir height in stripping section, inch (WHS)			=	3.44				
Weir height in rectifying section, inch (WHR)			=	3.44				
Column diameter in stripping section, inch (WHS)			=	72.0				
Column diameter in rectifying section, inch (WHR)			=	72.0				
Weir length in stripping section, inch (WLS)			=	51.1				
Weir length in rectifying section, inch (WLR)			=	51.1				
Volumetric holdup in column base, ft <sup>3</sup> (MVB)			=	130.0				
Volumetric holdup in reflux drum, ft <sup>3</sup> (MVD)			=	7.87				
Feed Data								
Phase	Temp ( F )	Feed Flowrate (ibmole/hr)	Propane X1	Isobutane X2	N-Butane X3	Isopentane X4	N-Propane X5	N-Hexane X6
Liquid	233.6	1452.5	0.0685	0.02792	0.2062	0.14865	0.2287	0.32
Vapor	233.6	2.18	0.013531	0.075961	0.27746	0.19462	0.18776	0.12889

**Table 7-2 Simulation results from Dynamic program, Steady state program and Real data**

Composition	Real data	Dynamic simulation			PRO II		
		GRK	SRK	PR	GRK	SRK	PR
1. Distillate product							
Propane	0.26590	0.282624	0.242986	0.234288	0.278733	0.248204	0.250281
N-butane	0.55860	0.536330	0.580351	0.588967	0.528551	0.562918	0.566272
2. Bottom product							
N-butane	0.00520	0.058674	0.004910	0.003959	0.006674	0.004765	0.004629
N-hexane	0.65800	0.411983	0.629849	0.645465	0.502430	0.636956	0.646457

**Table 7-3 Percent deviation between PRO II and Real data**

Composition	% Deviation		
	GRK	SRK	PR
1. Distillate product			
Propane	4.83	6.65	5.87
N-butane	5.38	0.77	1.37
2. Bottom product			
N-butane	28.346	8.36	10.98
N-hexane	23.64	3.2	1.75

**Table 7-4 Percent deviation between Dynamic simulation and Real data**

Composition	% Deviation		
	GRK	SRK	PR
1. Distillate product			
Propane	6.29	8.61	11.88
N-butane	4.00	3.89	5.435
2. Bottom product			
N-butane	37.39	4.27	1.90
N-hexane	1028.3	5.57	2.38

**Table 7-5 Percent deviation between Dynamic simulation and PRO II**

Composition	% Deviation		
	GRK	SRK	PR
1. Distillate product			
Propane	1.38	2.14	6.8
N-butane	1.45	3.00	3.85
2. Bottom product			
N-butane	88.62	2.95	16.92
N-hexane	21.95	1.12	0.15

Table 7-3 shows percent deviation between steady state program PRO II and real data. For distillate product the results show that percent deviation between PRO II and real data are less than 10 percent for every thermodynamic models (GRK, SRK and PR). For bottom product, SRK and PR models agree with real data but GRK model deviated from real data more than 20 %, especially in heavy component (n-hexane).



The results from dynamic simulation program agree with the results from PRO II, as illustrated in table 7-3, that every thermodynamic models (GRK, SRK and PR) agree with real data for distillate product. But for bottom product, SRK and PR models agree with real data but GRK model deviate from real data more than 30 %, especially in heavy component (n-hexane).

From these results, it can be concluded that both PRO II and dynamic program deviate from the real data by themselves and the predicted result from PRO II does not closely agree with real data than dynamic simulation program for every components. However the deviation for both PRO II and dynamic simulation are in the reasonable acceptable range. Percent deviation between dynamic simulation and PRO II are shown in table 7-5.

The difference deviation of GRK, SRK and PR result from the different original formular of GRK, SRK and PR thermodynamic models in the following equation,

For GRK model

$$P = \frac{RT}{v-b} - \frac{a}{v[v+b]T^{1/2}}$$

$$a = a_c = 0.42748 \frac{R^2 T_c^{3/2}}{P_c}$$

$$b = b_c = 0.08664 \frac{RT_c}{P_c}$$

For SRK model

$$P = \frac{RT}{v-b} - \frac{a}{v[v+b]}$$

$$a = a_c \left[ 1 + (0.480 + 1.57\omega - 0.176\omega^2) \left( 1 - t_r^{1/2} \right) \right]^2$$

$$a_c = 0.42748 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.08664 \frac{RT_c}{P_c}$$

For PR model

$$P = \frac{RT}{v-b} - \frac{a}{v[v+b] + b[v-b]}$$

$$a = a_c \left[ 1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5}) \right]^2$$

$$a_c = 0.45724 \frac{R^2 T_c^2}{P_c}$$

$$b = b_c = 0.07780 \frac{RT_c}{P_c}$$

It can be seen from the formula that GRK equation contained only two critical constant,  $T_c$  and  $P_c$ , thus they alone are insufficient to generalize thermodynamic behavior. However, generalization is substantially improved by incorporating a third constant like SRK and PR equation. A very effective third constant is the acentric factor introduced by Pitzer et al. The acentric factor accounts the differences in molecular shape and greatly improves ability to predict vapor pressure and other liquid phase thermodynamic. Moreover the result for the bottom composition agree with the conclusion of Peng and Robinson that further development of PR model is likely to improve prediction of liquid density and phase equilibrium in the critical region, however use of such equation appears to be limited to relatively small molecules. The result also agree with West and Erber (1973) that the SRK correlation appears to be particularly well suited for predicting K-value and enthalpy for natural gas system.

## 7.2 Application to an oil refinery

In order to select the best thermodynamic models for dynamic simulation of distillation column, the Debutanizer column of The Bangchak Petroleum Public Company is selected as column case study. The results for both initial state and final state of dynamic simulation model are compared with the real data from the Debutanizer column. The initial state results are obtained from dynamic program by using the design data. The final state results are obtained from dynamic program by using the different actual operating data as different case study. For every case study, the initial state is calculated from using the feed data for design case in Table 7-6.

**Table 7-6 Feed data for design case**

Phase	Temp ( F)	Feed Flowrate (lbmole/hr)	Propane X1	Isobutane X2	N-butane X3	Isopentane X4	N-pentane X5	N-hexane X6
Liquid	233.60	1263.11	0.03873	0.03772	0.16720	0.20764	0.22923	0.31947
Vapor	233.60	1.900	0.13531	0.07596	0.27746	0.19462	0.18776	0.12889

### 7.2.1 Case study 1

In this case, the feed flowrate and feed composition are changed from the design case as shown in table 7-7. The dynamic simulation program is used to calculate the behavior of the column for both initial and final states. Simulation results are shown in table 7-8 and Figure 7-1 to 7-4.

Table 7-7 Feed data for case study 1

FEED DATA								
Phase	Temp F	Feed Flowrate lbmole/hr	Propane x1	Isobutane x2	N-Butane x3	Isopentane x4	N-Pentane x5	N-Hexane x6
Liquid	233.60	1187.3	0.038730	0.04772	0.15720	0.20764	0.22923	0.31947
Vapor	233.60	1.780	0.013531	0.075961	0.27746	0.19462	0.18776	0.12889

Table 7-8 Percent deviation of initial state and final state from real data

Component	% Deviation					
	Initial state			Final state		
	GRK	SRK	PR	GRK	SRK	PR
1. Distillate product						
Propane	22.80	0.24	3.00	560.70	0.10	22.69
N-butane	13.71	0.20	1.86	597.25	6.53	21.92
2. Bottom product						
N-butane	856.17	17.79	19.28	460.04	5.30	6.810
N-hexane	32.69	2.79	1.24	33.36	7.39	12.71



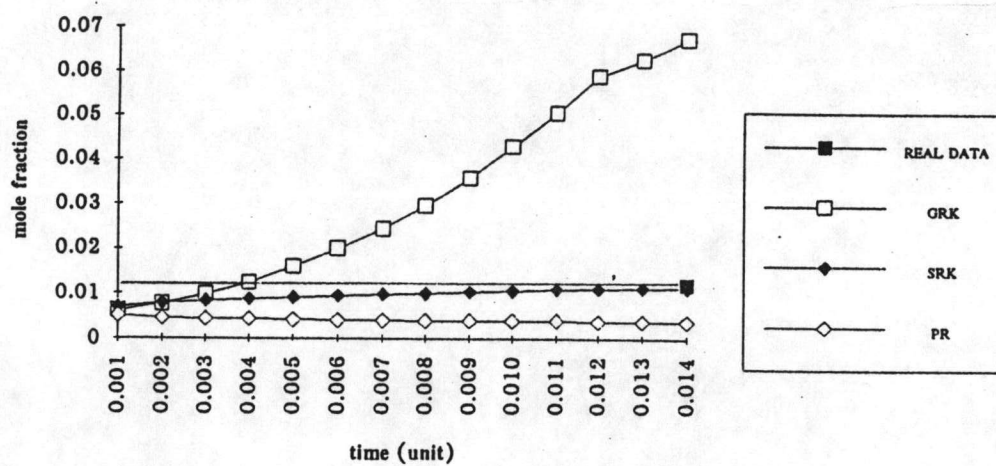


Figure 7-1 Bottom product composition (N-butane) of case 1

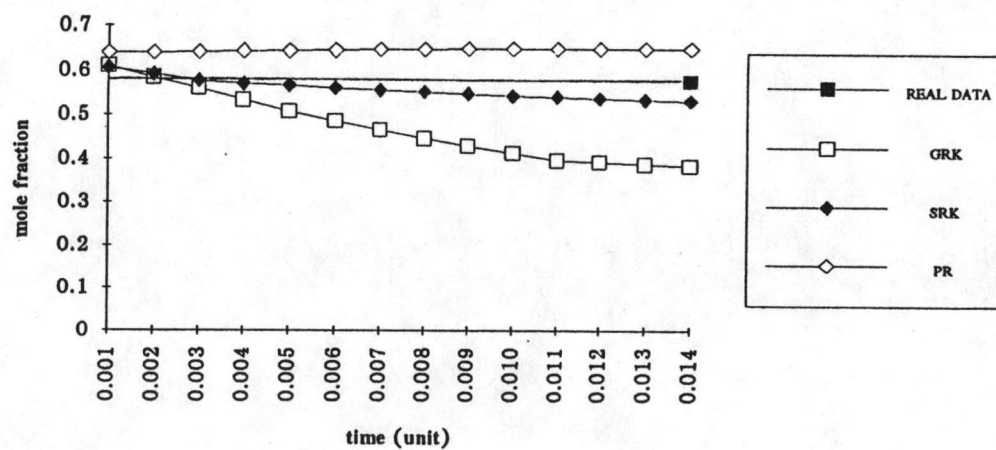


Figure 7-2 Bottom product composition (N-hexane) of case 1

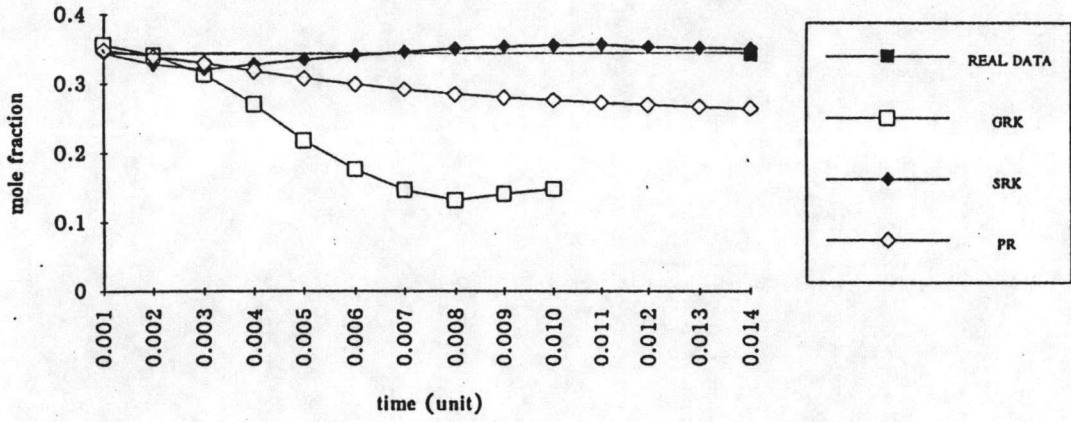


Figure 7-3 Distillate product composition (propane) of case 1

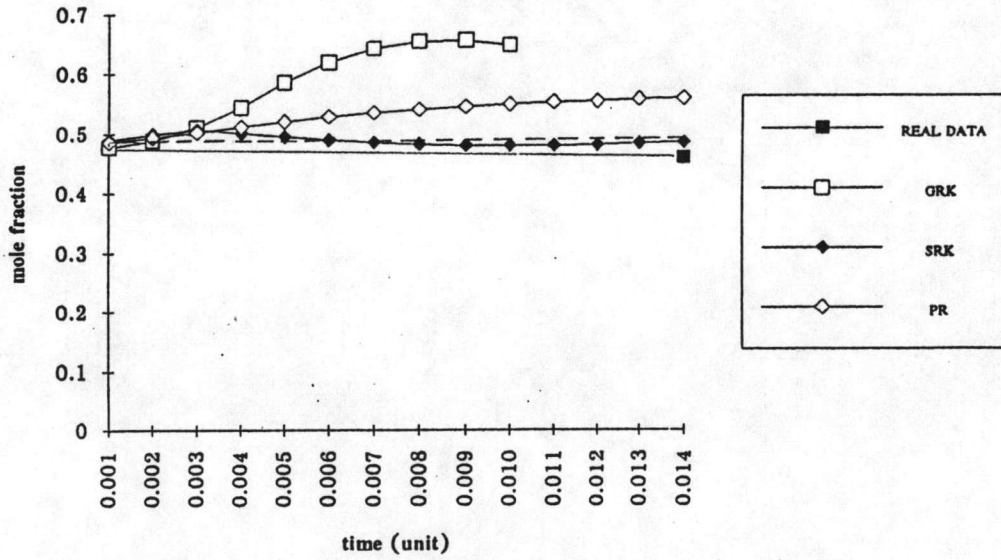


Figure 7-4 Distillate product composition (N-butane) of case 1

Table 7-8 shows that the result from initial state for GRK, SRK and PR are less deviated from real data than final state. This results expresses that the dynamic simulation program accumulate deviation from various time that program calculate for dynamic behavior. However, the deviation of final state from real data for some thermodynamic models are in the reasonable range for acceptance as shown in Figure 7-1 to 7-4.

Figure 7-1 and 7-2 show the bottom composition of n-butane and n-hexane for GRK, SRK and PR models and the real data from the refinery. For comparison between a different thermodynamic models, the results show that SRK and PR models are closer agree with the real data for a heavy component (n-hexane) than GRK model. For a light component (n-butane), we found that only SRK are closely agree with real data.

Figure 7-3 and 7-4 show the distillate composition of propane and n-butane for GRK, SRK and PR models and the real data from the refinery. The figure shown that only SRK model agrees with the real data for both propane and n-butane. We found that the results from PR model are less deviated from the real data than GRK model.

These results concede with the conclusion of Edmister(1968) and Henley and Seader(1976) that the GRK is not good to predict liquid phase thermodynamic properties and it failed to predict vapor pressure for a wide range of molecular shape. Also the result agrees with Van Ness and Abbot (1982) that both GRK and SRK equation of state are able to produce qualitative description of VLE, however the SRK is superior. As described the important of the third critical constant in the previous paragraph, the result for the bottom composition agrees with the conclusion of Peng and Robinson that further development of PR model is likely to improve prediction of liquid density and phase equilibrium in the critical region, however use of such equation appears to be limited to relatively small molecules. The result also agrees with West and Erber (1973) that the SRK correlation appears to be particularly well suited for predicting K-value and enthalpy for natural gas system.

### 7.2.2 Case study 2

In this case, the feed flowrate and feed composition are changed from the design case as shown in table 7-9. The dynamic simulation program is used to calculate the behavior of the column for both initial state and final state.

**Table 7-9 Feed data for case study 2**

FEED DATA								
Phase	Temp F	Feed Flowrate lbmole/hr	Propane x1	Isobutane x2	N-Butane x3	Isopentane x4	N-Pentane x5	N-Hexane x6
Liquid	233.60	1136.79	0.037710	0.05874	0.14730	0.20754	0.20924	0.33850
Vapor	233.60	1.850	0.013531	0.075961	0.27746	0.19462	0.18776	0.12889

Simulation results are shown in table 7-10 and Figure 7-5 to Figure 7-8.

**Table 7-10 Percent deviation of initial state and final state from real data**

Component	% Deviation					
	Initial state			Final state		
	GRK	SRK	PR	GRK	SRK	PR
1. Distillate product						
Propane	22.80	0.24	3.00	-	0.57	17.81
N-butane	13.71	0.20	1.86	97.60	7.40	16.72
2. Bottom product						
N-butane	856.17	17.79	19.28	325.63	2.94	53.18
N-hexane	32.69	2.79	1.24	30.60	8.10	3.98



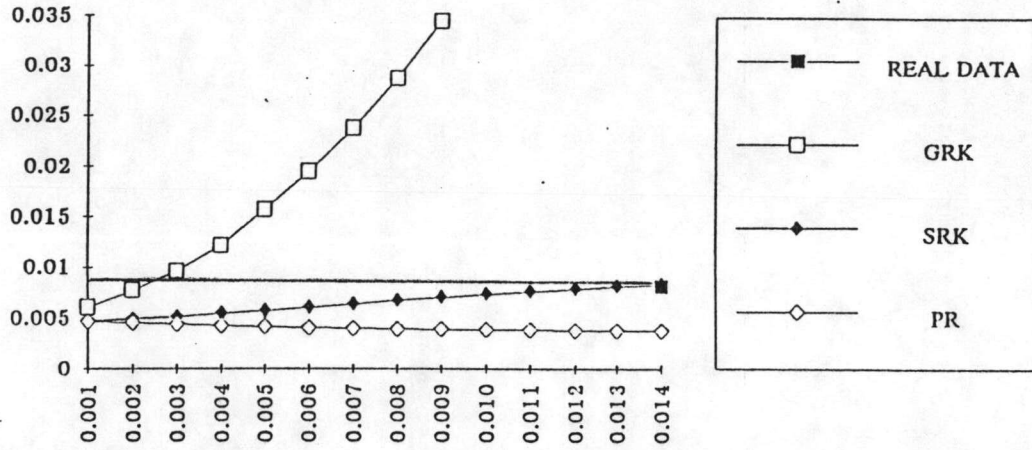


Figure 7-5 Bottom product composition (N-butane) of case 2

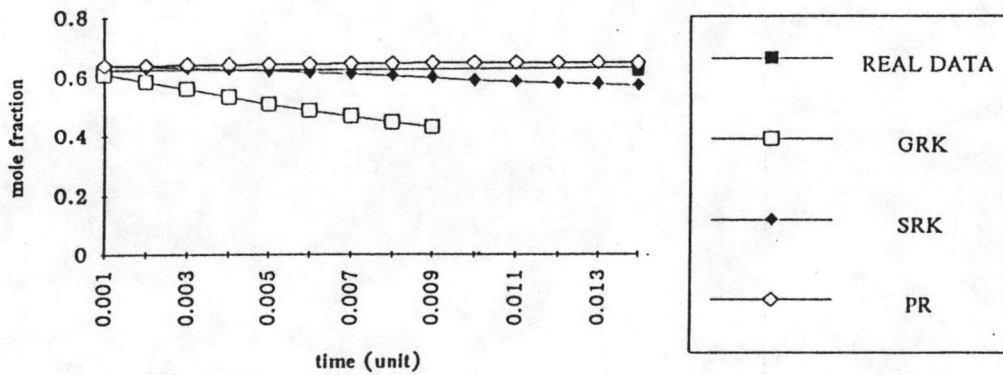


Figure 7-6 Bottom product composition (N-hexane) of case 2

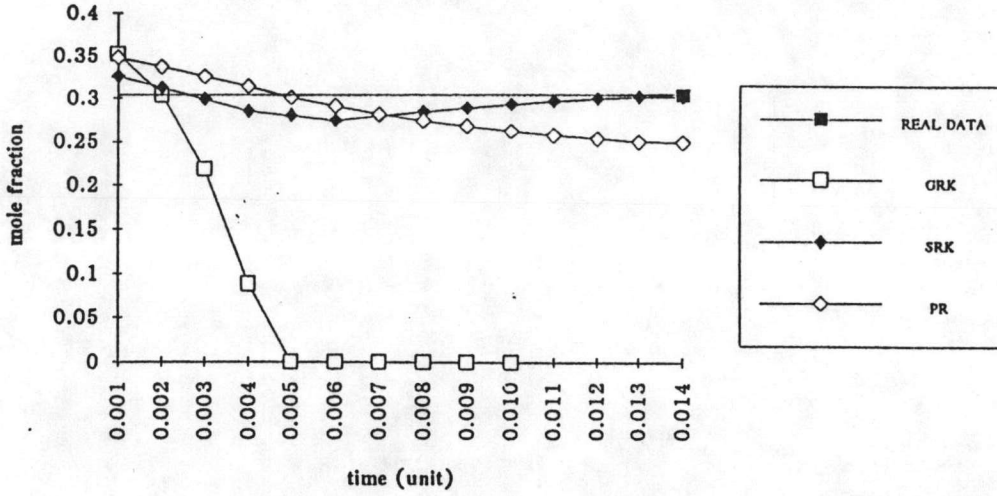


Figure 7-7 Distillate product composition (propane) of case 2

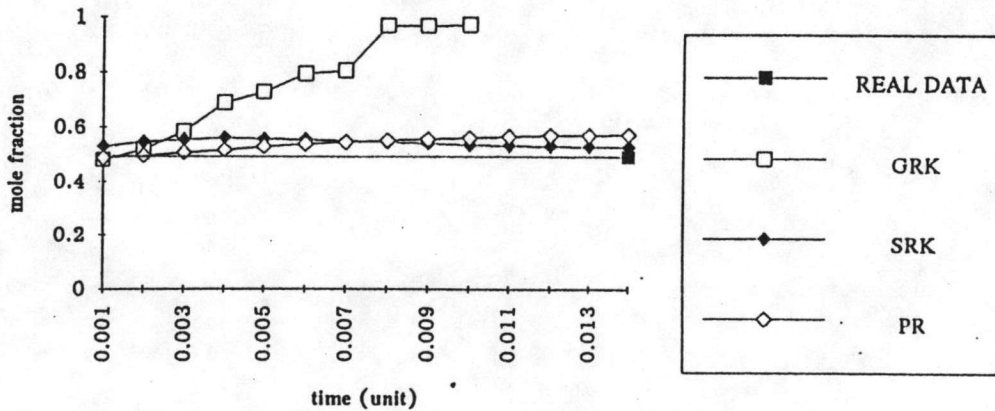


Figure 7-8 Distillate product composition (N-butane) of case 2

Table 7-10 shows that the result from initial state for GRK, SRK and PR less deviated from real data than final state. This results agree with case study 1 that the dynamic simulation program accumulates deviation from various time that program calculates for dynamic behavior. However, the deviation of final state from real data for some thermodynamic models are in the reasonable range for acceptance as shown in Figure 7-5 to 7-8.

Again, the results of the calculation are compared among the GRK, SRK, PR and a real data from the refinery as shown by considering the composition's response in bottom and top stages. In Figure 7-5 and 7-6 the dynamic response of the bottom stage composition of n-butane and n-hexane show that both SRK and PR models are closely agree with real data for n-hexane. Furthermore, the results show that GRK model is very deviated from the real data for both n-butane and n-hexane.

Figure 7-6 and 7-8 show the distillate composition of propane and n-butane for GRK, SRK and PR models and the real data from the refinery. Once again, the obtained data shows that only SRK model agrees with the real data from the distillation column for both propane and n-butane. For the PR model, the results of the distillate are small deviated from the real data in reasonable range for acceptance.

Like case study 1, the results agree with the conclusion of Edmister (1968) and Henley and Seader (1976) that the GRK is not good to predict liquid phase thermodynamic properties and it is failure to predict vapor pressure for a wide range of molecular shape. Also the results agree with Van Ness and Abbot (1982) that both GRK and SRK equation of state are able to produce qualitative description of VLE, however the SRK is closely superior. Furthermore, the results for bottom composition agree with the conclusion of Peng and Robinson that further development of PR model is likely to improve prediction of liquid density and phase equilibrium in the critical region, however use of such equation appears to be limited to relatively small molecules.

### 7.2.3 Case study 3

In this case, the feed flowrate and feed composition are changed from the design case as shown in table 7-11. The dynamic simulation program is used to calculate the behavior of the column for both initial state and final state.

**Table 7-11 Feed data for case study 3**

FEED DATA								
Phase	Temp F	Feed Flowrate lbmole/hr	Propane x1	Isobutane x2	N-Butane x3	Isopentane x4	N-Pentane x5	N-Hexane x6
Liquid	233.60	1452.5	0.068500	0.027920	0.20620	0.14865	0.22870	0.3200
Vapor	233.60	2.180	0.013531	0.075961	0.27746	0.19462	0.18776	0.12889

Simulation results are shown in table 7-12 and Figure 7-9 to Figure 7-12.

**Table 7-12 % deviation of initial state and final state from real data**

Component	% Deviation					
	Initial state			Final state		
	GRK	SRK	PR	GRK	SRK	PR
1. Distillate product						
Propane	22.80	0.24	3.00	2.52	8.61	11.88
N-butane	13.71	0.20	1.86	-	3.93	5.47
2. Bottom product						
N-butane	856.17	17.79	19.28	1028.34	5.58	23.86
N-hexane	32.69	2.79	1.24	37.38	4.28	1.30



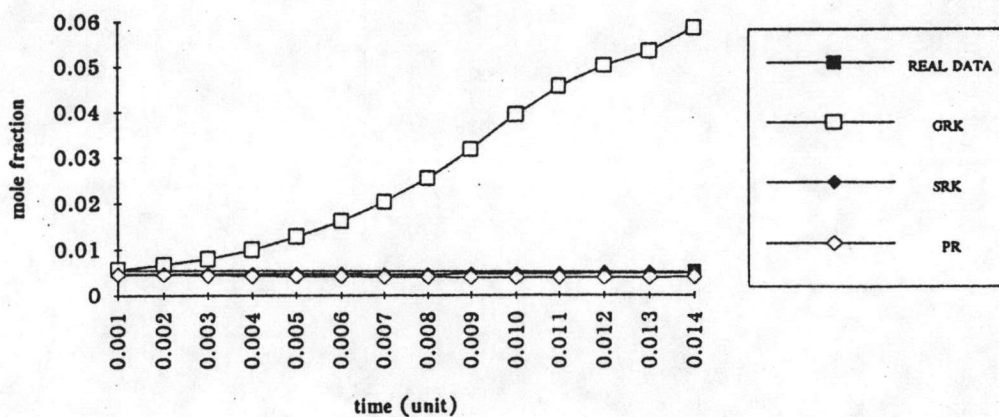


Figure 7-9 Bottom product composition (N-butane) of case 3

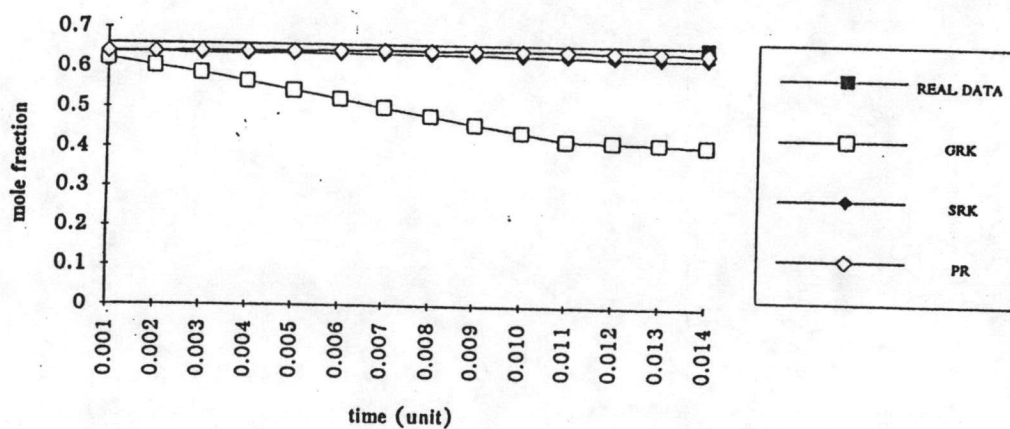


Figure 7-10 Bottom product composition (N-hexane) of case 3

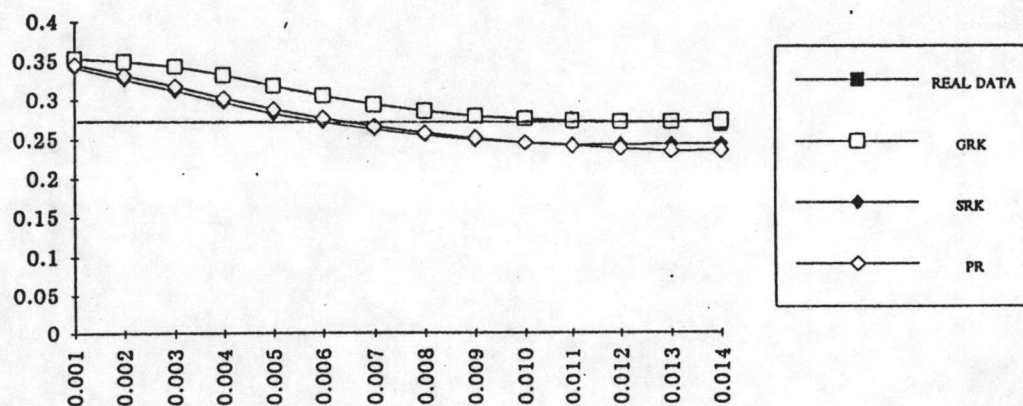


Figure 7-11 Distillate product composition (propane) of case 3

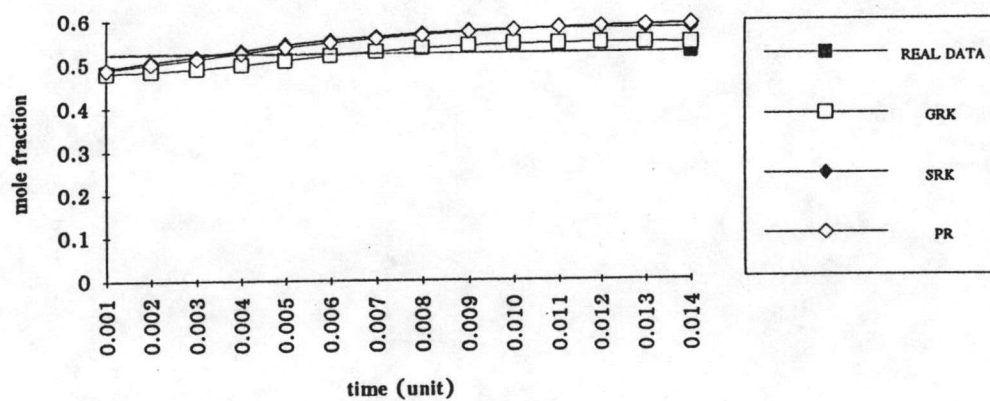


Figure 7-12 Distillate product composition (N-butane) of case 3

Table 7-13 shows that the result from initial state for GRK, SRK and PR are less deviated from real data than final state. Again, this results agree with case study 1 and 2 that the dynamic simulation program accumulates deviation from various time that program calculates for dynamic behavior. However, the deviation of final state from real data for some thermodynamic models are in the reasonable range for acceptance as shown in Figure 7-9 to Figure 7-12

In the same way as case study 1 and 2, Figure 7-9 and 7-10 show the bottom composition of n-butane and n-hexane for GRK, SRK and PR models and the real data from the refinery. From these figures, it is seen that SRK and PR models are closely agree with the real data for a heavy component (n-hexane) than GRK model. For a light component (n-butane), we found that both SRK and PR are closely agree with real data.

Figure 7-11 and 7-12 show the distillate composition of propane and n-butane for GRK, SRK and PR models and the real data from the refinery. The figures show that SRK model agree with the real data for both propane and n-butane.

In the same way as case study 1 and 2, the results agree with the conclusion of Edmister(1968) and Henley and Seader(1976) that the GRK is not good to predict liquid phase thermodynamic properties and it is failure to predict vapor pressure for a wide range of molecular shape. Also the results agree with Van Ness and Abbot(1982) that both GRK and SRK equation of state are able to produce qualitative description of VLE, however the SRK is closely superior. Furthermore, the results for bottom composition agree with the conclusion of Peng and Robinson that further development of PR model is likely to improve prediction of liquid density and phase equilibrium in the critical region, however use of such equation appears to be limited to relatively small molecules.

### 7.3 Summary

From the results in case 1, 2 and 3, it is shown that only SRK model closely agree with a real data for both propane and n-butane in the distillation composition and the result from PR model are less deviated from the real data than GRK model. These results agree with the conclusion of Edmister (1968) and Henley and Seader(1976) that the GRK is not good to predict liquid phase thermodynamic properties and it is failure to predict vapor pressure for a wide range of molecular shape. Also the results agree with Van Ness and Abbot (1982) that both GRK and SRK equation of state are able to produce qualitative description of VLE, however the SRK is closely superior. These events occurred because GRK equation contained only to critical constant,  $T_c$  and  $P_c$ , that they alone are insufficient to generalize thermodynamic behavior. However, generalization is substantially improved by incorporating into the equation a third constant like SRK and PR equation. A very effective third constant is the acentric factor introduced by Pitzer et al. The acentric factor accounts the differences in molecular shape and greatly improve ability to predict vapor pressure and other liquid phase thermodynamic.

The results for bottom composition show that both SRK and PR model are closely agree with the real data for a liquid heavy component, n-hexane. The result agree with the conclusion of Peng and Robinson that further development of PR model is likely to improve prediction of liquid density and phase equilibrium in the critical region, however use of such equation appears to be limited to relatively small molecules. The result also agree with West and Erber (1973) that the SRK correlation appears to be particularly well suited for predicting K-value and enthalpy for natural gas system.